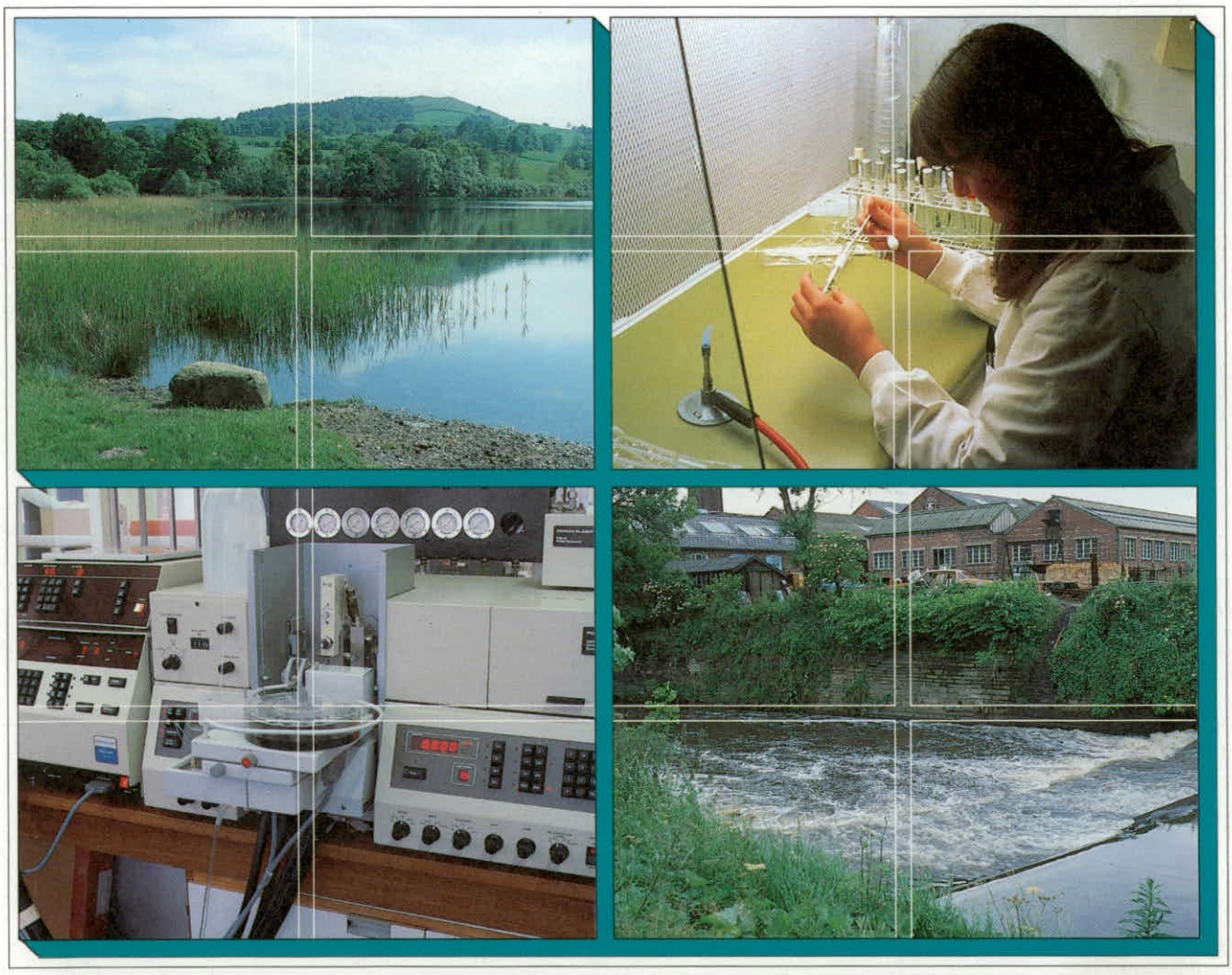
ADB

Institute of Freshwater Ecology

The interaction between pesticides and particles in rivers Final Report

W.A. House PhD CChem FRSC
I.S. Farr BSc
Z. Ou
J.S. Welton PhD CBiol MIBiol
D.R. Orr



Natural Environment Research Council

INSTITUTE OF FRESHWATER ECOLOGY
River Laboratory, East Stoke, Wareham, Dorset BH20 6BB

Tel: 0929 462314
Fax: 0929 462180

The Interaction between Pesticides and Particles in Rivers

W.A. House PhD C.Chem FRSC
I.S. Farr BSc
Z. Ou
J.S. Welton PhD CBiol MIBiol
D.R. Orr

Project leader:	W A House
Report start date:	1 November 1989
Report end date:	31 March 1992
Report to:	Department of the Environment Romney House, 43 Marsham Street London SW1P 3PY
Contract No:	PECD/7/7/329
IFE Report Ref:	RL/T04053h1/5
TFS Project No:	T04053h1

This is an unpublished report and should not be cited without permission, which should be sought through the Director of the Institute of Freshwater Ecology in the first instance.

The Institute of Freshwater Ecology is part of the Terrestrial and Freshwater Sciences Directorate of the Natural Environment Research Council.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

GLOSSARY OF SYMBOLS

$A_\lambda^{1\,cm}$ light absorbance in 1 cm cell at wavelength λ
A_i area of unit, ha
A_v area to volume ratio of container, cm^{-1}, Equation 6.2

C confirmed by mass spectrometry
C concentration of colloid in ng dm^{-3} (Equation 5.1)
C_e equilibrium concentration of pesticide, µg dm^{-3}
C_E concentration of pesticide in the external solution of the dialysis experiments
C_G concentration of pesticide in equilibrium with the soil
C_i, C_o concentration of pesticide in the inflow (i) and outflow (o) of a section of river, Equation 6.6
C_I concentration of pesticide in the internal solution of the dialysis experiments
C_s concentration of suspended solids, ng dm^{-3}

DCM dichromethane

ECD electron-capture-detector
EL eluate
ET_i evapotranspiration in unit i, dm^3 ha^{-1} d^{-1}

GC gas chromatography
GF/F glass microfibre filters, §6.1.2
GLC gas-liquid chromatography

K_a adsorption constant, in cm, Equation 6.1
K_A distribution coefficient normalised with respect to the specific surface area of the sediment, m
K_d distribution coefficient, Equation 4.1
K_D Kurdena-Danish extraction unit
K_{dc} distribution coefficient normalised with respect to colloids, §5.3
K_f field distribution coefficient, §4.4
K_{oc} distribution coefficient normalised with respect to organic carbon, §4.4
K_{om} distribution coefficient normalised with respect to organic matter, §4.4 and Equation 7.2
K_{omf} field distribution coefficient normalised with respect to organic matter, §4.4
K_{ow} octanol-water distribution coefficient

MS mass spectrometry
MSD mass-spectrometer detector

n_a adsorption amount, µg g^{-1} or µmol kg^{-1}
NA not analysed
NC not confirmed by mass spectrometry
ND not detected
NPD nitrogen-phosphorus thermionic detector

OM organic matter content (% by mass)

P probability factor in t-test
P_i rainfall in unit i, $dm^3\ ha^{-1}\ d^{-1}$
PTFE fluorinated ethylene propylene

q flow-rate, $dm^3\ s^{-1}$

R_1 surface run-off
R_2 sub-surface run-off
R_3 groundwater run-off or input
R_4 point source input
RRT relative retention time
RT retention time of peak in GLC

SD standard deviation

S_i run-off in unit area, $dm^3\ ha^{-1}\ d^{-1}$
SS suspended solids

Tr trace

%SS percentage of pesticide associated with the suspended solids, Equation 6.8

δ percentage loss of pesticide to container surface, Equation 6.2
ΔC_h difference in herbicide concentration in colloid experiments ng dm^{-3}, Equation 5.2
Σ specific surface area, $m^2\ g^{-1}$

1. SUMMARY

The interaction between pesticides in water and sediments or suspended particulate matter is complex because it depends on both the nature of the pesticide eg polar character, solubility in water, lipophilic properties, and the composition of the sediment eg mineralogy, particle size, concentration and composition of organic matter.

In this work, three groups of pesticides have been chosen for specific study: the synthetic pyrethroids including permethrin, the organochlorines including lindane and the triazine herbicides including simazine. The occurrence of these groups of compounds at several river sites in England and Wales is measured together with the distribution of some of the compounds between the water and sediment. The results are in reasonable agreement with the theoretical expectations for lindane, DDE, dieldrin and permethrin but not for simazine which is found at a greater concentration in the sediment than expected. The results indicate the presence of several pesticides in river waters and sediments with the pyrethroids, permethrin and deltamethrin, found in some sediments. The impact of sediment bound lindane, permethrin and simazine on benthic invertebrates is uncertain although, as discussed for permethrin, the predicted equilibrium concentration of pesticide in the interstitial water may provide the best indicator for the evaluation of the toxicity of the sediment.

Experiments designed to examine the association between simazine or permethrin and colloids (particles less than 0.2 μm in size) derived from river sediments, indicates that the association is relatively weak for simazine but very strong for permethrin. The enhanced mobility of colloids, compared with other particulate matter, means that this result has important implications for the prediction of the translocation of permethrin in rivers.

The adsorption of pesticides on suspended solids during a rainstorm is studied at one of the sites. The majority of the lindane, atrazine and simazine is shown to be in the soluble and colloid fractions and most of the DDT, DDE and TDE is associated with the suspended solids. Some general conclusions regarding the contribution of suspended solids to the overall transport of the pesticides are offered together with appropriate predictive relationships.

Adsorption measurements for simazine on two sediments at 5 and 25°C enable comparisons with distributions observed in the field samples. A large disparity exists between the two results indicating the differences in the kinetics of the adsorption and desorption processes. The results from the pesticide release experiments at 25°C in the dark using contaminated sediments show that DDE, TDE, dieldrin, permethrin and deltamethrin are not detectable released whereas lindane and simazine are released and degraded during the two week incubation.

2. INTRODUCTION

The interaction between pesticides in freshwater and particles, either in the sediment or suspended in the water, is important in the assessment of their translocation and impact on fauna and flora in the environment. The pesticides may enter the river as a solute in the aqueous phase and subsequently partition between the water and particulate components in the river sediment or they may enter in association with suspended solids and colloids via surface or sub-surface run-off from agricultural land or discrete sewage discharges.

Although considerable effort is now being addressed by the water industry to gather information about the concentration of certain pesticides dissolved in water at strategic river sites, very little information is currently available about the concentration of pesticides in river sediments, suspended particulates or colloids. The partition and concentration of all pesticides onto particulate materials means that these matrices are important in the relative accumulation or release of the compounds and thus exert a key role in determining the concentration of pesticides in general in interstitial waters and the fauna and flora associated with the sediment. The differences between soils and sediments, *viz* particle size/aggregation, organic matter content and composition, redox condition, water composition and saturation, in many instances severely restricts the application of results obtained with soils to river or lake sediments.

The general nature of the topic, as evident from the title of the project, and because of the multitude of pesticides in current usage, meant that it was essential at the outset to focus resources on particular groups of pesticides and concentrate on those interactions between pesticides and solids which are expected to be of most significance. Part of the study involved developing new techniques for analysing sediments and suspended matter for pesticides. The initial field survey provided information on the occurrence of the selected pesticides and revealed some anomalies in the distribution of simazine between water and sediments which warranted further laboratory studies. The implications of the association of pesticides with sediments on their toxicity to invertebrates was also considered. Other work focused on the association of the chosen pesticides with suspended solids during storm conditions and laboratory studies of the association of permethrin and simazine with sediment colloids. The release of pesticides from contaminated sediments was studied in some detail.

The main objectives of the work and the success in meeting these objectives are summarised as follows.

2.1 Survey of sediments and suspended particles

The first stage of the study was the measurement of the concentration of selected compounds at chosen river sites. The pyrethroids were chosen because of their increasing use in the U.K., the lipophilic character of the molecules and reports of their occurrence in rivers. The other pesticides chosen included a group of organochlorine compounds which have been widely used in the past but are less so today. These include α-BHC, lindane, heptachlor, dieldrin, DDT, DDE, TDE and endrin. Of this group, lindane is still widely used and was studied in more detail. A third group of pesticides, the triazines, was also studied because

they have physical and chemical properties which differ considerably from many of the compounds in the other two groups ie the pyrethroids and organochlorines, both in terms of their water solubility and sorption behaviour.

River sediment samples from several sites were analysed for the pesticides. These sites included several from rivers in East Anglia. The results of the development of analytical methods are given in §3 and the results of the sediment survey in §4. It was only possible to examine the suspended solids from one of the sites; the details of the development of the analytical procedures together with the results of the analysis of suspended solids are given in §6.

2.2 Evaluation of the chemical or physical properties of the particles and pesticides which determine the sorption behaviour

The interaction between particles and pesticides depends on the physical and chemical properties of both the pesticide and of the solid material. In field conditions, the heterogeneity of the sediment or suspended solids is very great and even with modern techniques is impossible to determine in any detail. Hence estimates of the interaction based on partition or distribution coefficients normalised on the mass of the whole sediment or some component of the sediment are sought. In this work, field distribution coefficients based on the field survey results have been evaluated (§4) and compared with predicted results from empirical relationships between the octanol-water partition coefficient of the pesticide and the distribution coefficient of the pesticide with the organic matter in the sediment. Detailed studies have also been made of the specific interaction of simazine at 5 and 25°C with two different sediments (§7) and between permethrin and simazine and sediment colloids at 25°C (§5).

2.3 Experimental determination of the release of selected pesticides from particles by physical, chemical and biological processes

The selective concentration of the pesticides on sediments and suspended solids, particularly after long-term or episodic exposure, may lead to circumstances of prolonged leaching of the pesticides from the solid matrix and so threaten the recovery of the ecosystem. In these circumstances, the reversibility of the sorption interaction may be crucial in determining the release rate, biodegradation and abiotic degradation.

The results in §8 include the evaluation of the degradation and release of selected pesticides from contaminated river sediments. The relatively simple incubation experiments with natural sediments illustrate basic differences between the groups of pesticides, both in terms of their degradation and release into water.

2.4 Formulation of a process-based quantitative model of the behaviour of selected pesticides in aquatic systems

A knowledge of the interaction between pesticides and sediments, suspended solids and colloids is of strategic importance to the determination of the impact of pesticides on aquatic systems, their transport to estuaries and coastal waters and their effects on water quality. Although mathematical models can be formulated, §6, the validation of these models is particularly difficult in natural systems involving trace components of relatively lipophilic organic substances. However, it is possible to make an estimate of the contribution of colloids and suspended matter to the transport of pesticides from the information gained in §4, 5, 7. In this way it is feasible to identify those pesticides which are likely to be associated with suspended solids or colloids to a sufficient degree to significantly contribute eg > 20% of the load, to the mass transport from a catchment.

With information on the load of suspended solids, it is thus possible to make some crude estimate of the total pesticide load transported downstream including those pesticides associated with suspended solids.

3. ANALYTICAL METHODS

This section briefly describes the main analytical methods used in the project. Additional techniques employed for more specialized procedures are described in the appropriate sections. These include the methods used for the analysis of suspended solids (§6), pesticide release experiments in §8 and the experiments concerned with the interaction of simazine and permethrin with sediment colloids (§5).

The techniques divide into two broad classes corresponding to the analysis of river sediments and river waters. The methods for the extraction and isolation of the organochlorine pesticides, including lindane, are similar to those for the synthetic pyrethroid insecticides. Separate methods have been developed for the analysis of the herbicide simazine.

3.1 Materials

All the pesticides were used as supplied (Promochem Ltd, St Albans) and were specified to the following purities expressed as mass per cent: α-BHC, 99.5; γ-BHC (lindane, 99.7%; p,p′-DDT, 99.8%; p-p′-DDE, 99.8%; p-p′-TDE, 99.3%; dieldrin, 99.5%; endrin, 99.0%; cis-permethrin, 99.1%; trans-permethrin, 99.8%; cypermethrin, 95.7%; fenvalerate, 90.0% and deltamethrin, 99.0%. Deltamethrin is the single isomer, (S)-α-cyano-3-phenoxybenzyl (1R,3R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate. The configuration of the substituent at the C3 atom of the cyclopropane ring is given as *cis* or *trans* relative to the position of the ester group with respect to the plane of the cyclopropane ring. The *cis* and *trans* isomers of permethrin correspond to the 3-phenoxybenzyl-(1RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate stereoisomer. Cypermethrin and fenvalerate were only available as racemic mixtures which separated on GLC as 4 and 2 components respectively. All solvents were pesticide analysis grade (BDH, Poole).

All glassware was chromic acid cleaned, rinsed with distilled water, acetone and hexane prior to use.

3.2 Procedure for the analysis of waters for organochlorine and pyrethroid pesticides

One litre of river water was placed in a 1 litre pyrex bottle with a PTFE lined screw-cap. 50 ml of hexane was added and the mixture shaken for 10 minutes before transferring it to a 1 litre separating funnel with a PTFE stop-cock. After separating, the hexane layer was drained off into a 250 ml conical flask. If a stable emulsion formed during the shaking this was broken using magnesium sulphate. The aqueous layer was shaken again with 20 ml of hexane for 5 minutes and returned to the separating funnel before draining the hexane layer into the collection flask. The empty separating funnel was then extracted with 10 ml of hexane. Dried Na_2SO_4 (heated to 110°C for a minimum of 4 hours) was added to the collection flask and shaken. This was left overnight at room temperature.

The dried extract was then placed in a Kuderna-Danish flask. The collection flask containing Na_2SO_4 was washed twice with 10 ml volumes of hexane and transferred to the Kuderna-Danish flask. The total extract was then evaporated in a steam bath using the Kuderna-Danish apparatus to give a final known volume of 2 ± 0.1 ml. The extracts were stored in 4 ml PTFE screw-capped vials at 6°C before analysis by GLC.

All samples were analysed in a batch containing a control sample of pesticide-free single distilled water. This sample will be referred to as the blank sample.

3.2.1 Solvent Extraction: Assessment of the extraction efficiency for organochlorine and pyrethroid pesticides

The validity of the method for the analysis of lindane, α-BHC, heptachlor, DDT, DDE, TDE, dieldrin, aldrin, *cis* and *trans* isomers of permethrin, cypermethrin and fenvalerate was determined in replicate by adding a known amount of a multistandard pesticide mixture to 1 litre samples of distilled water. The final aqueous concentrations were nominally 0.2 μg dm^{-3} (or ppb) in each pesticide. The compounds: lindane, α-BHC, heptachlor, DDT, *cis*-permethrin and fenvalerate were not detected in the blank. Trace levels of other compounds were detected at concentrations equivalent to <0.01 μg dm^{-3}. These trace levels can be accounted for through the carry-over from the multipesticide analysis during the GLC analysis. The trace level of this contribution was always assessed during the chromatography by including a solvent sample after the standard calibration and prior to the analysis of the samples.

The extraction efficiency of the method, expressed in terms of the percentage recovery of the original pesticides, is shown in figure 3.1. Satisfactory recoveries were obtained for all the compounds tested.

3.3 Procedure for the analysis of waters for simazine

This method follows the Standard Operating Procedure, SOP: 5/19.11.91 (IFE, River Laboratory) using a solid-phase extraction (SPE) system.

In summary, a Bond-Elut adsorption column containing octyl (C8) bonded-phase silica as the adsorbent (Analytichem International Code P606303) was used. The C8 column was fitted to a Vac-Elut (Analytichem International mode AI 6000) assembled and washed with 2-3 ml of HPLC grade MeOH. The column was then conditioned with ~ 15 ml HPLC grade water taking care not to allow the column to dry-out. The sample was then passed through the column at a rate of 30-40 ml min^{-1}. The column was then dried for *ca* 20 minutes by the passage of air. The pesticides were eluted with about 2.5 ml HPLC grade methanol into preweighed 4 ml screw capped vials at a rate of approximately 1 ml min^{-1}. The extract was then weighed to enable the volume to be calculated.

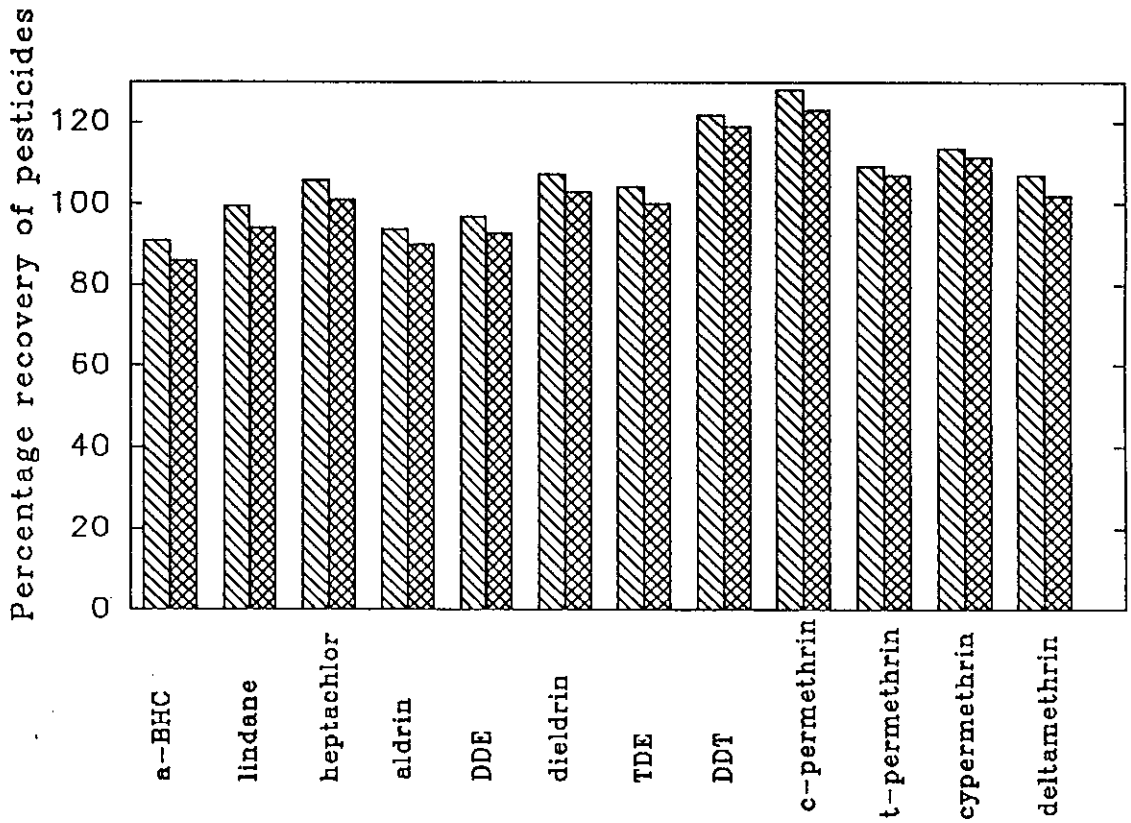


Figure 3.1 **Total recovery of organochlorine and synthetic pyrethroids from 1 litre water samples spiked to a concentration of 0.2 ppb in each compound.**

The solvent extraction procedure described in §3.2.1 was used.

3.3.1 Solid Phase Extraction: Assessment of the extraction efficiency for simazine

Simazine was added to three 1 litre samples of pesticide-free distilled water to give an aqueous concentration of 0.05 mg dm^{-3} (0.05 ppm). Together with a blank sample, the solutions were extracted as above to yield a recovery of simazine of 91 ± 14% with no simazine detected in the blank sample.

3.4 Procedure for the analysis of river sediments for organochlorine and pyrethroid pesticides

The sediments were dried using an Edwards 4K Modulo freeze-drying machine. The dried samples were sieved, first through a stainless-steel sieve of 1 mm mesh and then through a

0.5 mm mesh brass sieve. A 50 g quantity of dried sediment was transferred to the extraction flasks (500 ml Quickfit (B24//29) conical flasks). After the sediment had settled, the residues in the bottles and funnels were washed into the extraction flasks with a series of 15 to 20 ml aliquots of acetone to a total volume of approximately 150 ml per flask. The flasks were then shaken for 1 hour on an automatic shaker (STUART Flask Shaker SF1, setting 6). The solids were allowed to settle for at least 1.5 hours and then the acetone was decanted through pre-washed No.4 porosity sintered glass filters (chromic acid cleaned, acetone and hexane rinsed) set in Quickfit Buchner flasks. The extract was then transferred, with 2 ml acetone washes, to a 250 ml round-bottomed (RB) flask.

The acetone extract was reduced to a low volume (*ca* 10 ml) by rotary evaporation (Jobling Rotary Evaporator, type 349/2) at 45°C. The remaining sediments in the extraction flasks were rinsed with 50 ml acetone. The solids were allowed to settle before the acetone layer was decanted through the respective filters. Residue on the sintered filter was leached with 5 ml acetone and all leachate and rinse solutions were transferred to the respective RB flask.

The extraction was then repeated with a further 150 ml acetone and 50 ml rinse. Extensive further extractions yielded less than 10% additional permethrin from sediments. Residues in the RB flasks were taken to dryness by rotary evaporation, then redissolved in 10 ml of a solution of 5% acetone in hexane and dried over anhydrous sodium sulphate ready for further clean-up.

3.4.1 Procedure for the clean-up of the sample extract

The extracts of the sediments were usually highly coloured and unsuitable for direct use in gas-liquid chromatography (GLC). To prevent contamination of the injection port, column and detector and to allow detection of trace pesticide peaks, further separation of determinands from the background organics was required.

A two stage clean-up procedure using a Florisil adsorbent was developed. The procedure was as follows:

(a) Columns Bond-Elut, Analytichem International Part No. FL944006 Code 0690) were mounted in a Vac-Elut solid phase extraction (SPE) unit (Analytichem International model AI6000) and conditioned with 10 ml dry hexane followed by 10 ml 5% acetone/hexane.

(b) The extract in the RB flask (dissolved in 5% acetone/hexane) was loaded on to the column and the non-adsorbed solutes drawn through under reduced pressure (< 5kPa). The eluate was collected in a 100 ml beaker. The RB flask was washed with a further six (5 ml) aliquots of 5% acetone/hexane and the washings transferred to the adsorbent column.

(c) Many of the coloured components in the extract were retained on the SPE column. Permethrin, together with other pyrethroids and several organo-chlorine insecticides were eluted directly. GLC of the eluate with electron capture detection, (ECD), revealed a high-level of background interference, particularly in the region of the chromatogram where organo-chlorine pesticides elute.

(d) A second stage clean-up using Florisil activated at 160°C has been found to reduce interference to an acceptable level.

Glass columns (5 ml i.d., 120 mm in length, fitted with taps) were filled with dry hexane. A wad of glass wool (washed with acetone then hexane) was inserted followed by a 5 mm layer of granular $NaSO_4$ dried at 160°C. Florisil (100-200 mesh) activated at 160°C for more than 12 hours was added whilst hot and allowed to settle, with tapping, to give a bed depth of 100 mm. Finally 10 mm of dry $NaSO_4$ was added to protect the Florisil from atmospheric moisture.

(e) 40 ml dry hexane was passed through the column and discarded before the sample was loaded.

(f) The eluate from the first (Bondelut) column was returned to the respective RB flask and taken to dryness on the rotary evaporator taking care to remove condensing solvent.

(g) The sample residue was dissolved in dried hexane (10 ml) and applied to the Florisil column. Remaining residues were washed from the flask with two (5 ml) aliquots of hexane. The 20 ml hexane eluate from the column (column wash) contains much of the interfering background organic solutes. It has been found that permethrin and some organochlorine pesticides would require 40 ml or more hexane for elution.

(h) The pesticides were eluted with a 20 ml 5% acetone/hexane mixture. The column was then eluted with a further 20 ml 5% acetone/hexane. All eluate fractions were retained separately in 20 ml vials for later analysis. The sample volume was checked before GLC analysis.

3.4.2 Analysis of a reference sediment

Preliminary studies indicated that the method was able to detect the pyrethroid and organochlorine pesticides listed above in a range of sediments of complex composition but showed poor recoveries of two other compounds which were tested viz aldrin and heptachlor. As a result of these initial trials, a river sediment was selected for analysis to determine the background concentration of the insecticides. This was found necessary because all the sediments examined in preliminary studies contained one or more of the compounds of interest. The performance of the analytical procedure was evaluated by the addition of a multi-pesticide standard mixture to the sediment at two different concentrations followed by analysis using the method described above.

The sediment was obtained from a batch of material collected from the R. Stour (NGR SO 822715) on 12th September 1989. The organic matter in the sediment was measured by combustion of the sediment at a temperature of 550°C (Dean 1974; Vollenweider 1969). Five sub-samples (1 g) were taken for analysis. The organic content of the sediment was found to be 0.71% by mass with a coefficient of variability of 3.9%. This indicates that the sediment was sufficiently homogeneous for sub-sampling. The specific surface area of the sediment was determined as 0.94 $m^2 g^{-1}$ by nitrogen gas adsorption at 77.5 K using the B.E.T. method.

Table 3.1 **Results of the analysis of the reference sediment for organochlorine and synthetic pyrethroid pesticides. These include α-BHC, lindane, DDT, DDE, TDE, dieldrin, endrin, permethrin, cypermethrin and deltamethrin.**

Insecticide	* Concentration $\mu g\ kg^{-1}$ (dry wt)	Confirmation by MS	Monitoring ions m/z values
α-BHC	<0.1	NC	181, 219
Dieldrin	1.96 (0.25)	C	79, 263, 277
cis-Permethrin	11.05 (2.25)	C	163, 183
trans-Permethrin	4.01 (0.33)	C	163, 183
Cypermethrin	<1.0	NC	163, 181
Fenvalerate	1.50 (0.2)	NC	125, 152, 167

Key: MS - mass-spectrometry
NC - not confirmed by mass-spectrometry
C - confirmed by mass-spectrometry
* - values in brackets are the standard deviations

Duplicate samples of sediment were analysed and the results of the triplicate GLC analysis of the first eluate showed the presence of three insecticides as shown in table 3.1. Although the chromatograms are complex, it was possible to achieve the resolution of the pesticide peaks and reasonable base-line determinations for the integrations. The identity of the compounds was confirmed by mass-spectroscopy using the retention times in combination with the indicator ions as shown in the table. The relative retention times calculated with respect to aldrin for α-BHC, cypermethrin and fenvalerate were within 0.004 of the values calculated from the calibration chromatograms but the presence of these insecticides in the extract could not be confirmed by mass-spectroscopy even after the eluate was concentrated by a factor of approximately 13 times. For cypermethrin and fenvalerate, at a concentration in the sediment of ~ 1 $\mu g\ kg^{-1}$, the additional concentration step led to a final injection of ~ 60 pg which is well within the detection range of the mass-spectrometer operated in single-ion mode with a scan rate of 1.2 cycles per second. The ratio of the *cis/trans* isomers of permethrin calculated from the integration of the corresponding ECD peaks and the phenoxyltropylium (m/z = 183) ion peaks were in good agreement ie 2.76 and 2.86 respectively, demonstrating the slower biological degradation of the *cis*-isomer compared with the *trans*-isomer. Although the *trans*-isomer is the major component in the commercial products, the *cis*-isomer is more resistant to biodegradation in comparison to the *trans*-isomer. None of the other insecticides were detected by GLC analysis using either detector.

3.4.3 Assessment of the extraction efficiency and performance of the solvent extraction and isolation of organochlorine or synthetic pyrethroid insecticides

The efficiency of the extraction and isolation procedure was evaluated by adding known quantities of the multi-pesticide standard dissolved in 50 ml of acetone to 50 g of freeze-dried dry sediment, mixing and evaporating to dryness with a stream of nitrogen gas. The two concentrations used for the test were nominally 2 and 20 $\mu g\ kg^{-1}$ and were chosen to fall within the range of concentration found in the sediments studied previously. The results of the analysis of the first and second eluates from the final isolation stage are shown in tables 3.2 and 3.3 together with the calculation of the percentage recovery of each of the pesticides in the first and total eluate. An account of the initial concentration of the pesticides in the sediment was included in the calculation of the recoveries using the data shown in table 3.1 and included those compounds detected by the ECD but not later confirmed by the mass-spectrometer detector. This procedure allowed for the possible interference of co-eluting compounds in the integration of the chromatograms derived from the sediments spiked with the pesticide standard.

As shown, the overall percentage recoveries of the individual pesticides is reasonable with the lowest value of 19% obtained for γ-BHC at a concentration in the sediment of 2 $\mu g\ kg^{-1}$. The analysis of the blanks ie the extracts obtained using the above analytical method but without the sediment present in the extraction stage, indicated relatively minor interferences (see table 3.3). Substantially better recoveries were obtained for the organochlorine insecticides at the higher spike concentration of 20 $\mu g\ kg^{-1}$ eg with γ-BHC a recovery of 67% was achieved. Recoveries of between 30 and 40% for DDE and DDT were determined with little difference between the two spike concentrations. Other compounds such as endrin, TDE and deltamethrin also exhibited similar recoveries at both spike concentrations. All the pyrethroids were recovered efficiently but with some differences between the two levels of spiking. The pyrethroids cypermethrin, fenvalerate and deltamethrin required a second elution to achieve satisfactory recoveries ie a final eluate of 50 ml. For the pyrethroids the percentage of the total recovery in the second eluate increased with increasing retention time of the pesticide on the GLC column ie according to the reference number shown in table 3.2 and followed a linear trend with the logarithm of the octanol-water partition coefficient. The regression coefficient of the 10 points, including the *cis* and *trans* isomers of permethrin was determined as 0.92.

The results in table 3.2 and 3.3 also show that the variation in the replicate concentrations obtained from the ECD detector are greater for the pyrethroids than for the organochlorine pesticides. This is because of the lower sensitivity of the detector to the pyrethroids ie lower response factor, and also the broadening of the chromatography peaks associated with the longer retention times on the GLC column.

Table 3.2 **Evaluation of the extraction and isolation efficiency of organochlorine and synthetic pyrethroid pesticides from a sediment: results of the analysis of the reference sediment after the addition of the multi-pesticide standard of nominal concentration of 20 µg kg^{-1} (dry weight)**

Pesticide	Ref. No.	Total concentration in sediment /µg kg^{-1}	Concentration calculated from first eluate /µg kg^{-1}	Percentage recovery	Concentration calculated from total eluate /µg kg^{-1}	Final recovery	
						Percentage recovery	Coefficient of variation %
α-BHC	1	20.10	15.3	76	15.5	77	0.6
γ-BHC	2	20.68	13.8	67	13.9	67	0.9
DDE	3	20.00	7.6	38	7.9	39	0.6
Dieldrin	4	22.37	18.1	81	18.3	82	1.4
Endrin	5	20.12	15.1	75	15.2	76	1.4
TDE	6	20.00	10.0	50	10.4	52	1.2
DDT	7	23.04	9.0	39	9.1	39	5.3
cis-Permethrin	8	31.48	22.0	70	23.0	73	2.9
trans-Permethrin	9	28.06	26.4	94	27.2	97	1.4
Cypermethrin	10	30.79	16.3	53	21.0	68	6.6
Fenvalerate	11	22.92	10.9	48	15.4	67	18.0
Deltamethrin	12	20.00	12.8	64	19.4	97	16.0

Table 3.3 **Evaluation of the extraction and isolation efficiency of organochlorine and synthetic pyrethroid pesticides from a sediment: results of the analysis of the reference sediment after the addition of the multi-pesticide standard of nominal concentration of 2 µg kg^{-1} (dry weight)**

Pesticide	Total concentration in sediment /µg kg^{-1}	Concentration calculated from first eluate /µg kg^{-1}	Percentage recovery	Concentration calculated from total eluate /µg kg^{-1}	Concentration in blank /µg kg^{-1}	Final recovery	
						Percentage recovery	Coefficient of variation %
α-BHC	2.06	1.0	50	1.0	<0.1	50	0.9
γ-BHC	2.07	0.4	18	0.4	<0.1	19	4.3
DDE	2.00	0.5	26	0.5	ND	27	5.2
Dieldrin	4.37	1.7	38	1.7	ND	38	2.4
Endrin	2.01	1.4	69	1.4	ND	71	3.2
TDE	2.00	1.0	51	1.1	ND	56	1.8
DDT	2.30	0.7	29	0.7	ND	30	2.4
cis-Permethrin	13.44	6.1	45	6.7	ND	50	2.7
trans-Permethrin	7.32	5.7	78	5.9	1.1	81	5.5
Cypermethrin	6.60	6.0	91	6.3	ND	96	10.6
Fenvalerate	3.66	2.4	65	3.1	ND	85	9.7
Deltamethrin	2.00	1.4	70	2.1	ND	104	3.3

3.5 Procedure for the analysis of river sediments for simazine

The method of extraction and isolation is the same as that described for the synthetic pyrethroids and organochlorine pesticides (§3.4) except that the final elution from the Florisil (magnesium silicate adsorbent) involves a third elution of 10% acetone is hexane.

3.5.1 Assessment of the extraction efficiency and performance of the solvent extraction and isolation of simazine

The sediment used for the tests was collected from the R. Stour near Stourport in Worcestershire on 12.9.88 (NGR SO 822715). This sediment was freeze-dried and then sieved through a 0.5 mm brass sieve, well-mixed and stored at room temperature until use.

A quantity of 50 g of dry sediment was placed in each of three 500 ml conical flasks. A fourth flask received no sediment and was designated as a blank. Two of the flasks containing sediment were spiked with simazine in 2.5 ml of acetone to achieve concentrations of 50 µg kg^{-1} and 100 µg kg^{-1} (dry weight) of simazine in the sediment. The same quantity of acetone was added to each of the other flasks but without any simazine addition. The flask containing sediment without simazine addition was designated as a sediment blank.

The flasks were shaken vigorously to distribute the solvent spike uniformly throughout the sediment. They were allowed to stand with occasional shaking to permit the penetration of the simazine into the sediment matrix. After two hours, the flasks were tilted and the acetone removed using a gentle stream of air with periodic rotation of the flasks to redistribute the contents. When the flasks were dry, they were capped and allowed to stand overnight. The subsequent extractions were performed in the flasks used for spiking.

Initial trials on the recoveries from the second stage of the clean-up using a Florisil column activated to 160°C and conditioned with dry hexane, indicated that the majority of simazine eluted in the second 20 ml volume of eluate (5% acetone in hexane). The results obtained using a clean adsorption column and one pre-loaded with an extract in 10 ml hexane from a sediment containing a high percentage of organic matter are shown in figure 3.2. The sample of 200 µg of simazine dissolved in 10 ml of hexane was loaded onto the adsorption column. This was followed by a 20 ml wash of dried hexane and then subsequent volumes of 5% acetone in hexane eluates. No simazine could be detected in the column wash and only a small proportion in the first 5% acetone in hexane eluate (1EL). In view of these results the following elution method was used:

1. 20 ml of hexane wash
2. 20 ml of 5% acetone in hexane eluate; 1EL
3. 20 ml of 5% acetone in hexane eluate; 2EL
4. 20 ml of 10% acetone in hexane eluate; 3EL

The solvent polarity was increased in the third eluate to ensure complete removal of simazine from the column. The results from the analysis using the above method gave a distribution of simazine of 0% in the wash, 5.6% in 1EL, 86.0% in 2EL and 8.7% in 3EL with a total recovery of 100.3%.

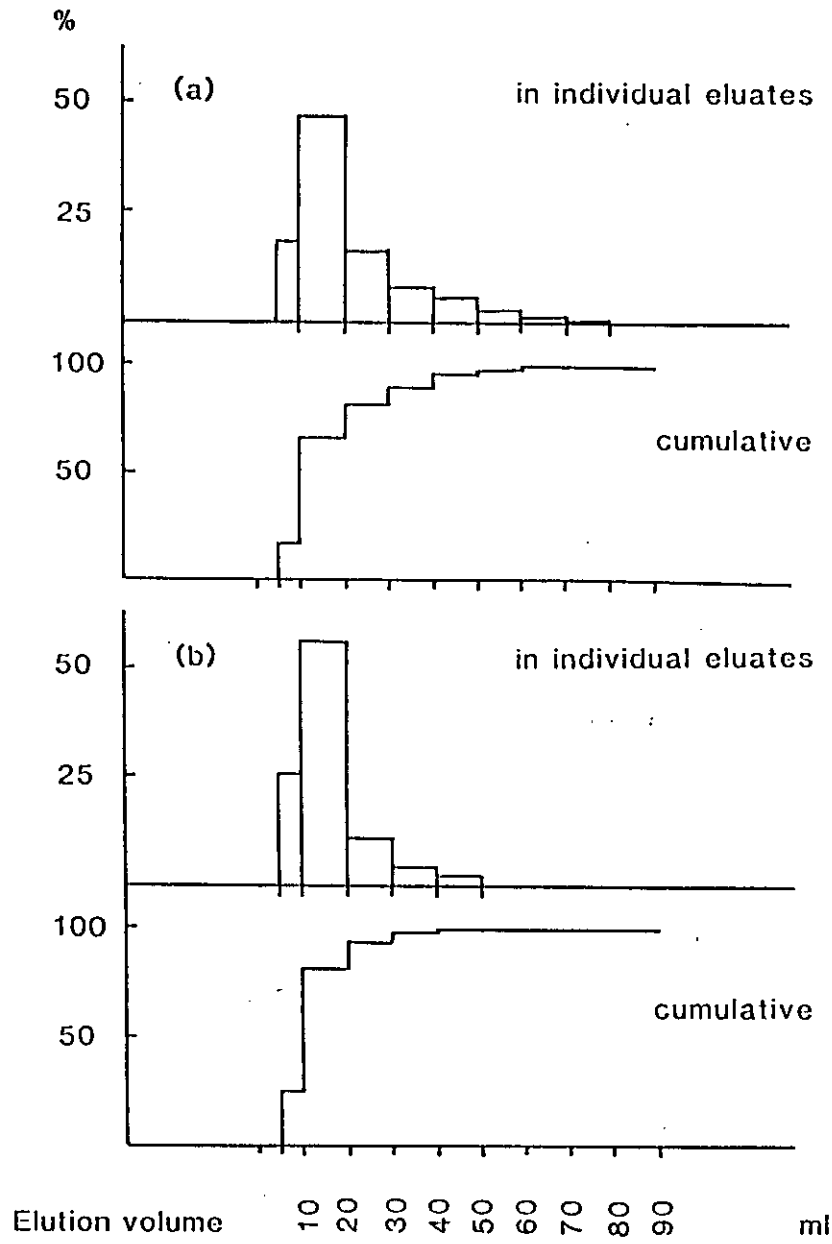


Figure 3.2 **Percentage recovery of simazine from Florisil columns eluted with 5% acetone in hexane (a) clean column (b) column pre-loaded with sediment extract.**

Following the initial trials with the final clean-up stage, the extractions of the 4 sediment samples was completed using the procedure described previously with the modifications of the final elution from the second clean-up stage described above. The eluates were adjusted to 20 ml with 5% acetone in hexane and 10 ml samples were then reduced to a volume of 1 ml using a stream of dry nitrogen gas.

The extracts were analysed using GLC/MSD with the method described and quantification using both the m/z = 201 and 186 ions with the machine operated in selected-ion-monitoring (SIM) mode. The calibration of the detector was found to be linear over the range 0.2-5 µg ml^{-1} (1 µl injection) of simazine in the DCM extract. A single external standard of 0.4 µg ml^{-1} in DCM was used for calibration of the detector. The results of the analysis are shown in table 3.4 and figure 3.3. Simazine could not be detected in the sediment blank eluates but traces were detected in the first and third eluates (1EL and 3EL) from the solvent blank. In both cases detection of the target ion for simazine (m/z = 201 amu) at the expected retention time was confirmed by the presence of the m/z = 186 amu ion. No simazine was detected in the second eluate. Correction for the concentration found in the blank sample only reduces the recovery in the high concentration spike by 1% and the low level spike by 2.5%.

Table 3.4 **Results of the assessment of the extraction efficiency and isolation of simazine from a sediment spiked at low (40 µg kg^{-1}) and high (100 µg kg^{-1}) levels.**

Eluate	Amount recovered /µg		% of total spike		% of recovered spike	
	Ion (m/z) 201	186	201	186	201	186
	LOW CONCENTRATION SPIKE - 40 µg kg^{-1} (dry weight)					
Wash	0	0	0	0	0	0
1EL	0.23	0.21	11.5	10.5	16.3	14.2
2EL	1.12	1.19	56.0	59.5	78.8	80.4
3EL	0.07	0.08	3.5	4.0	4.9	5.4
Total	1.42	1.48	71.0	74.0	100	100
	HIGH CONCENTRATION SPIKE - 100 µg kg^{-1} (dry weight)					
Wash	Tr	0	0	0	0	0
1EL	1.26	1.28	25.2	25.6	35.0	34.8
2EL	2.29	2.31	45.8	46.2	63.6	62.8
3EL	0.05	0.09	1.0	1.7	1.4	2.4
Total	3.60	3.68	72.0	73.5	100	100

Key: Tr - Trace
1EL, 2EL, 3EL: First, second and third eluates from Florisil column (details in text)

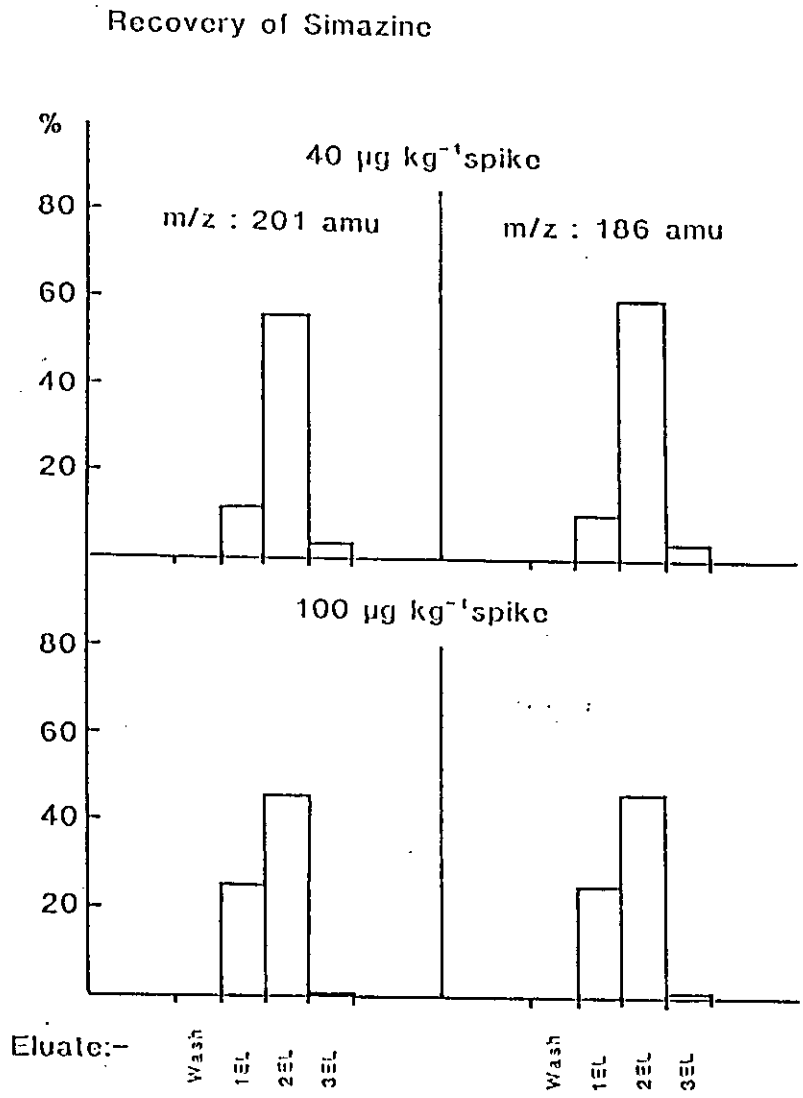


Figure 3.3 Recovery of simazine from the spiked sediment at two concentrations of spike material.

The results shown in table 3.4 and figure 3.3 illustrate the reasonable recoveries *ca* 70%, obtained for the river sediment extractions and clean-up procedure. Although the majority of the simazine is in the second eluate, it is necessary to analyse both other fractions. Table 3.4 also shows that similar results are obtained using the 201 (molecular and base ion) and 186 ions.

3.6 Gas chromatography with electron capture, nitrogen-phosphorus-thermionic and quadrupole mass-spectrometer detection

The extracts of the pesticides from the water and sediment samples were analysed by gas-chromatography using either: (a) Perkin-Elmer 8700 instrument with a split-splitless injector, an electron-capture-detector (ECD) and a 30 m, 0.25 mm diameter fused silica capillary with 5% phenyl-methyl silicone stationary phase; (b) a Perkin-Elmer 8700 instrument with a programmable temperature vaporiser (PTV) injector, a nitrogen-phosphorus thermionic detector (NPD) and a 30 m, 0.255 mm diameter fused silica capillary column with a DB-1301 liquid phase; (c) a Hewlett-Packard 5890 series II GC/MS incorporating a quadupole mass-selective-detector with a split-splitless injector and a 25 m, 0.20 mm diameter fused silica capillary column with a 5% phenyl-methyl-silicon stationary phase (0.33 µm film thickness).

3.6.1 Analysis of the synthetic pyrethroids and organochlorine pesticides using ECD

The configuration and conditions are as follows:

Configuration:

Injector	-	Split/splitless
Column	-	DB5 Jones Chromatography
Detector	-	ECD (Electron Capture Detector)

Oven conditions:

Oven temperature (°C)	50	170	240	280
Isothermal time (min)	2.0	0.0	7	2
Ramp rate (°C min^{-1})	30.0	10.0	2.0	

Injector conditions:

Temperature 310°C
Splitless for 30 seconds

Detector condition:

Temperature 350°C

Gases:

Makeup:	N_2	
Carrier:	He	
Septum purge		≈ 5 ml min^{-1}
Flow rate		≈ 50 ml min^{-1}

Recognition of a peak as a particular compound is on the basis of the match of retention time relative to an internal standard retention time (relative retention time, RRT) compared to a standard calibration run. RRTs have been found to be stable to within ± 0.001 during a single day, but to drift 0.002 over several days. Prior to every sample analysis RRT values were calibrated with an injection of a mixed pesticide standard. Several calibrations were

performed each day. Calibration was done using a multi-pesticide standard prepared in hexane to give nominal concentrations in each of the compounds as 0.05 mg dm^{-3} ie 0.1 ng injected. The linearity of the detector response was determined using a fixed injection of 2 µl of standards of 0.2, 0.05 and 0.92 mg dm^{-3}. Linear calibrations were obtained for all the compounds in this study.

3.6.2 Analysis of simazine using NPD

Configuration:

Injector	-	PTV	(Programmable Temperature Vaporizer)
Column	-	DB1301	Jones Chromatography
Detector	-	NPD	(Nitrogen Specific Detector)

Oven conditions:	Initial temperature	140°C for 1 minute
	First ramp	20°C per minute
	Isothermal	240°C for 7 minutes

Injector conditions:	Initial temperature	100°C for 1 minute in split mode
	Vaporization temperature	280°C for 5 minutes in splitless mode for 1 minute
	Final temperature	150°C

Gases:	Makeup:	N_2
	Carrier:	He
	Septum purge:	~ 5 ml min^{-1}
	Flow rate:	~ 50 ml min^{-1}

3.6.3 Analysis of the synthetic pyrethroids and organochlorine pesticides using MSD

Configuration:

Injector	-	Split/splitless
Column	-	HP5
Detector	-	Quadrupole mass-spectrometer
Interface temperature	-	320°C

Oven conditions:

Oven temperatures (°C)	50	170	240	280
Isothermal time (min)	2	0	0	8
Ramp rate (°C min^{-1})	30	5	2	

Injector conditions:

Temperature 285°C

Gases:

Carrier:	He at a flow rate of 15 ml min^{-1}
Septum purge:	He; 5 ml min^{-1}

Ion Groups

Pesticide	Target ion (amu)	Quantifier ion (1) (amu)	Quantifier ion (2) (amu)
αBHC	181	219	290
simazine	201	186	-
lindane	181	219	290
dichlorobiphenyl	222	152	-
heptachlor	100	272	372
aldrin	263	66	365
DDE/Dieldrin	246	176	79/263
endrin	263	243	381
TDE	235	165	320
DDT	235	165	354
phosalone	182	121	-
permethrin	183	163	-
cypermethrin	163	181	-
fenvalerate	167	125	-
deltamethrin	181	253	-

3.6.4 Analysis of simazine and atrazine using MSD

Configuration

Injector	-	Split/splitless
Column	-	HP1
Detector	-	Quadrupole mass-spectrometer
Interface temperature	-	260°C

Oven conditions

Oven temperature (°C)	40	205	240
Isothermal time (min)	3	7	2
Ramp rate (°C min^{-1})	40	40	

Injector conditions

Temperature 230°C

Gases

Carrier:	He at a flow rate 15 ml min^{-1}
Septum purge:	He; 5 ml min^{-1}

Ion Groups

Pesticide	Target ion	Qualifier ion (1)	Qualifier ion (2)
Simazine	201	186	173
Atrazine	200	215	217

4. THE OCCURRENCE OF SYNTHETIC PYRETHROID, SELECTED ORGANOCHLORINE AND TRIAZINE PESTICIDES IN RIVER SEDIMENTS AND WATERS

The analysis of sediments for pesticides is very time consuming requiring specialist techniques and complex chromatographic analysis. This limited the number of samples that could be examined in any detail. Rather than take multiple samples from a single site or examine the distribution of pesticides in the river bed at one site, it was decided to take surface sediment samples from several sites over the country. The sites were chosen on the basis of: (a) reported use of pesticides within the catchment of the stream or river; (b) observed changes in invertebrate communities in which pesticide usage had been implicated and (c) known discharged of pesticide from sewage works upstream of the sampling location.

Table 4.1 Location of the river sites studied together with the organic matter content and total pesticide concentration in the sediment at some of the sites. The standard deviations of duplicates are shown in brackets.

Sample code	Site designation	National grid reference	Date of sampling	Organic matter content % wt	Total pesticide concentration /µg kg^{-1} (dry wt)
A	Wicken Fen Lode	TL 555701	13.6.90	23.3 (0.8)	2.2
B	Reach Fen Lode	TL 548691	13.6.90	20.8 (0.6)	29.9
C	Bere Stream (sand)	SY 858923	20.3.90	1.6 (7.8)	3.5
D	Bere Stream (organic)	SY 858923	20.3.90	11.4 (2.5)	11.3
E	Rosemaund (1)	SO 555478	12.7.90	8.2 (0.1)	123.2
F	Rosemaund (2)	SO 555478	12.7.90	11.4 (0.2)	133.4
G	Rosemaund (3)	SO 555478	12.7.90	9.2 (0.2)	87.0
H	R. Stour (Worcestershire)	SO 822715	12.9.88	0.89 (0.04)	17.8
I	R. Stour (Worcestershire)	SO 822715	13.9.89	0.71 (0.03)	18.7
J	Great Ouse, Brampton	TL 221698	31.10.90	-	-
K	Great Ouse, Godmanchester	TL 244707	24.10.90	-	-
L	Swavesy, drainage system	TL 360695	26.10.90	-	-
M	Wicken Fen Lode	TL 555701	26.10.90	-	-
N	Reach Fen Lode	TL 548691	26.10.90	-	-

4.1 Location of the field sites

The river sites chosen for sampling are listed in table 4.1. Samples A, B, J, K, L, M and N are from sites situated in East Anglia and were primarily chosen because of the intensive agriculture in the area. Both Wicken fen lode and Reach lode are in the Ely-Ouse system and are drainage channels on the River Cam in Cambridgeshire. The samples C and D were from a chalk stream, the Bere Stream, a tributary to the River Piddle in Dorset. The sampling sites were adjacent, with sample C from a sand bank and D from a darker "organic-rich" sediment which had accumulated in a marginal area. This stream was chosen because of a recorded change in the invertebrate community in recent years. It is the only site at which samples from different areas of the river bed were taken.

Samples E, F and G were taken from a field drainage ditch on a mixed farm situated in Herefordshire. The catchment has been described in some detail by Matthiessen (1988). This catchment is being used for modelling the transport of pesticides and offers the advantage that records of the use of pesticides on the farm are available.

Samples H and I were obtained in September 1988 and 1989 respectively from the River Stour near Stourport in Worcestershire. This was the only site chosen in a predominantly industrial area with a known discharge of permethrin from local manufacturing industry in which permethrin was used as a moth-proofing agent.

Surface sediments were collected from the top 3-6 cm using a drag net method. Each drag was about 1 metre in length, running radially or parallel ensuring that the drags did not cross. The drags were about 25 cm in width. If necessary the sediments were transferred on site through a 5 mm screen into wide-necked glass jars with tops lined with aluminium foil. The sediments were transported back to the laboratory, further sieved through 1 mm mesh brass sieves as necessary, stored overnight in the dark at 4°C and then frozen and freeze-dried until the weight loss was <0.1% in ≅ 48 h. The sediments were then sieved through a 0.5 mm mesh brass sieve, thoroughly mixed and then stored as necessary in the dark at 4°C under a nitrogen gas atmosphere.

The amount of organic matter in the sediments was estimated by combustion at 550°C using duplicate 5 g subsamples of sediment following the method discussed by Vollenweider (1969) and Dean (1974). Separate experiments were also done to test the performance of the combustion method using a 1:1 (by mass) mixture of calcium carbonate and quartz. The results showed that the maximum loss of carbon dioxide from the calcium carbonate amounted to < 2% by mass of the calcium carbonate. The results for each of the samples are shown in table 4.1. The two samples, E and H, have been characterised in more detail to determine their mineralogy and specific surface area for detailed adsorption-desorption studies.

The water samples were collected at the same time as the sediment samples in 1 litre pyrex bottles fitted with PTFE screw caps. The bottles were not pre-rinsed with river water prior to sampling to avoid any adsorption of pesticides onto the inner glass surface. The samples were stored in the dark at 4°C and analysed as soon as possible after collection.

4.2 Results of the analysis of the water samples

The results of the analysis are shown in table 4.2. The standard deviations quoted are for the duplicate analysis of each extract except for sample G which was not replicated and sample H which was processed in triplicate ie 3 separate litre samples, with the GLC analysis done in duplicate. Those compounds that also occurred in the sediment samples are marked with an asterisk. Samples F and G also contained simazine.

Table 4.2 Concentration of organochlorine and pyrethroid pesticides in river waters/ng dm^{-3}. Values in brackets are standard deviations appropriate to GLC analysis. C indicates confirmation by MSD.

Name	A	B	C/D	E	G	H^1	H^2	H^3
α-BHC	1(0)	1(0)	-	<1	<1	*11(0.2)	7(0.2)	9(0.3)
γ-BHC	*2(0.1)C	*5(0.1)C	-	*2(0.5)	*12	*41(3)	38(0.2)C	34(7)C
DDE	-	-	-	*5(2)	-	-	*22(0.4)C	4(1)C
Dieldrin	-	-	-	-	-	*9(0.2)C	8(0.1)C	6(1)C
Endrin	-	2(2)	-	-	-	-	-	-
TDE	-	-	2(0.1)	-	-	-	2(1)	-
DDT	-	-	-	*<1	-	14(1)C	259(6)C	-
c-per′	40(1)C	16(2)	*17(12)C	-	-	*468(48)C	323(2)C	191(23)C
t-per′	-	-	-	-	-	*67(7)C	39(17)C	82(34)C
cyp′	11(6)	-	-	-	-	10(6)	24(10)	29(18)
fen′	-	-	-	<10	-	-	-	-
simazine	NA	NA	NA	-	1300	NA	NA	NA
total	54	24	19	19	13†	620	722	355

NA not analysed
† excludes simazine
* compounds also found in sediment samples

Apart from sample C/D, all the waters contained lindane at concentrations between 2 and 38 ng dm^{-3}. In most cases this was confirmed by mass-spectroscopy (EI) using the indicator ions, m/z, 181 and 219. α-BHC was found in the same samples but at concentrations near the limits of detection of the method. Heptachlor and deltamethrin were not detected in any of the samples and fenvalerate, which was detected in sample E, was also at the limits of detection using ECD and could not be detected using the MSD with ions, m/z, 181 and 253.

Endrin was only detected in sample B at a concentration near the limits of detection. DDT and its metabolites, DDE and TDE were found in some samples. In particular, sample H contained both DDT and DDE but the results of the analysis of separate 1 litre samples indicated a high variability between samples eg DDT was not detected in one sample but at concentrations of 14 and 259 ng dm^{-3} in the other two samples with a concentration in the blank determined as 2 ng dm^{-3}. The concentration of DDE determined in these samples was also very variable, ie 0, 4, 22 ng dm^{-3}, with none detected in the blank. Permethrin was detected at a number of sites with the *cis* isomer the most abundant. The highest concentrations were found at sites A and H with the results from H again showing variations between samples. This probably reflects the heterogeneity in the colloidal content in the individual samples. It is significant that better reproducibility between samples was obtained for α-BHC and γ-BHC (table 4.2) which are more soluble in water than the other pesticides studied. Technical permethrin has a *cis:trans* isomer ratio of 40:60. The results obtained for sample H indicate a ratio of between 70:30 and 89:11 in the water samples.

The majority of the water samples were not analysed for simazine. A concentration of 1300 ng dm^{-3} of simazine was detected in sample G.

4.3 Results of the analysis of the sediment samples

The results of the analysis of samples A, B and C, D are shown in table 4.3. The results for sample A indicate negligible concentrations of the pesticides, with the concentration either similar to that in the blank or close to the limits of detection of the method. Although both permethrin and cypermethrin were detected by ECD in the water sample extracts, these were not detected in the corresponding sediments. The concentrations found in sample B were significantly higher than those in sample A with traces of several organochlorine compounds including DDE and TDE. *Trans*-permethrin was also detected by GLC with MSD but could not be quantified using ECD because of the co-elution of another substance close to where the permethrin eluted. The differences in the pesticide contents of the two sediments is not obviously related to differences in the total organic matter content of the sediment (table 4.1) and is not reflected in the pesticide concentrations in the associated waters at the time of sampling.

The concentration of pesticides in sample C and D are also low with sample D having higher levels of all the pesticides. *Trans*-permethrin, although detected in the water (table 4.2), was only detected in the sandy sediment, C, and not in sample D. At this site the sediment heterogeneity measured in terms of the organic matter content does appear to be an important factor in determining the other pesticide distributions.

The results from the farm site ie samples E, F and G, are shown in table 4.4. The results indicate much higher concentrations of several pesticides in the sediments at all the sites sampled including lindane, deltamethrin, DDT and its metabolites. The sediments were similar in appearance, texture and organic content. Both DDT and DDE decrease in concentration downstream whilst the concentration of TDE was more variable. Neither DDT or its metabolites were detected in the blank sample. This is the only site at which deltamethrin has been found in the sediments. Difficulties have been experienced in

confirming the presence of low concentrations of fenvalerate and deltamethrin with the MSD in samples including the multi-pesticide standard used in the calibration. However the agreement of the RRTs for samples E, F and G and the standards obtained from the ECD are very good ie within 0.002. As shown in table 4.4, significant concentrations of dieldrin and α-BHC were also detected in some of the samples.

Table 4.3 Concentration of pesticides in the river sediments for samples A-D/μg kg^{-1}. †: quantified using MSD with m/z=163 ion. C indicates confirmation by MSD.

Name	Blank	A	B	Blank	C	D
α-BHC	0.2	-	-	-	-	0.3C
γ-BHC	-	0.2	1.2	-	0.1	0.3
DDE	-	0.4C	3.0C	-	-	2.2C
Dieldrin	1.0	1.0C	2.0C	0.7	-	-
Endrin	0.3	-	-	-	-	-
TDE	-	-	2.0C	-	-	0.9C
DDT	-	-	-	0.2	0.6	7.6C
c-permethrin	1.0	-	-	-	<1	-
t-permethrin	0.3	-	18†	-	-	-
cypermethrin	-	-	2.7	-	-	-
fenvalerate	0.3	0.6	1.0C	-	2.2	-

The results for the two samples H an I are shown in table 4.5. The standard deviations given in the table include variation in the triplicate and duplicate analysis of samples H and I respectively together with the variation in the GLC duplication. The predominant pesticides were the permethrin isomers and dieldrin probably originating from industrial activity in the area. These were also important components in the associated waters collected at the same time as sample H. The *cis:trans* isomer ratio is 58:42 for sample H and 74:26 for sample I and as for the water samples, reflects the persistence of the *cis* compared with the *trans* isomer, the latter being the major component in the technical product.

Table 4.4 **Concentration of pesticides in river sediments for samples E-G/μg kg^{-1}. Values in brackets are the standard deviations of GLC duplicates. Endrin, *trans*-permethrin and cypermethrin were not detected. C indicates confirmation by MSD.**

Name	Blank	E	F	G
α-BHC	0.12 (0)	-	1.7 (0.5)	-
γ-BHC	0.02 (0.03)	0.4 (0.1)	1.0 (0.1)	0.8 (0.1)
DDE	-	53.6 (0.9)C	30.9 (1.6)C	12.3 (0.9)C
Dieldrin	0.3 (0.1)	-	6.7 (0.2)C	6.0 (0.6)C
TDE	-	5.1 (0.3)C	28.3 (1.5)C	18.4 (1.9)C
DDT	-	62.2 (1.2)C	47.3 (4.3)C	9.4 (1.1)C
c-permethrin	0.6 (0.1)	-	-	-
fenvalerate	-	-	3.6 (0.8)	2.6 (1.3)
deltamethrin	-	1.9 (0.4)	14.0 (0.8)	37.5 (2.0)

Table 4.5 **Concentration of pesticides in river sediments for samples H and I/μg kg^{-1}. Values in brackets are the standard deviations described in the text. Endrin, TDE, DDT and deltamethrin were not detected. Sample H was not analysed for the presence of deltamethrin. C indicates confirmation by MSD.**

Name	Blank	H	Blank	I
α-BHC	0.1	<0.2	<0.1	<0.1
γ-BHC	0.1	0.1 (0.07)	<0.1	-
DDE	<0.1	0.2 (0.03)	-	-
Dieldrin	<0.2	1.0 (0.2)C	-	2.0 (0.3)C
c-permethrin	-	9.5 (1.6)C	-	11.1 (2.3)C
t-permethrin	1.0	6.8 (2.2)C	1.0	4.0 (0.3)C
cypermethrin	1.0	-	-	<1
fenvalerate	-	-	-	1.5 (0.2)

Some of the sediment samples were analysed separately for the triazines, atrazine and simazine using the methods described in §3.5 and §3.6.4. The results are collected in table 4.6.

Table 4.6 Results of the analysis of the sediment samples for atrazine and simazine

Sample/Site designation	Concentration of simazine /µg kg^{-1} (dry weight)	Concentration of atrazine /µg kg^{-1} (dry weight)
E, Rosemaund (1)	ND	NA
F, Rosemaund (2)	192	NA
G, Rosemaund (3)	188	NA
*I, R. Stour (Worcestershire)	6.2	NA
K, Great Ouse, Godmanchester	<1	ND
N, Reach Fen Lode	ND	ND
M, Wicken Fen Lode	1.8	ND
J, Great Ouse, Brampton	18.0	ND
L, Swavesy, drainage system	1.9	0.7

Key: ND: not detected in sample ie <0.5 µg kg^{-1} (dry weight)
NA: not analysed

Note: *This sample was analysed by soxhlet extraction with dichloromethane, DCM. 20 g of freeze-dried sediment was placed in a pre-extracted cellulose extraction thimble (single thickness supplied by Whatman cat. no. 1800 258) and extracted with 200 ml pesticide grade DCM for 6 h at a rate of one solvent cycle every five minutes. The resulting extract was concentrated in a Kuderna-Danish concentrator to a volume of *ca.* 10 ml and then reduced to 4 ml using a flow of dry nitrogen gas. The final extract was then analysed by gas-liquid chromatography with mass-spectrometry, GC/MS, for simazine only (§3.6.4). This method was unsatisfactory for most of the sediments because of the absence of any clean-up of the extract before GLC analysis.

The first samples analysed were from the Farm site and contained high concentrations of simazine with relatively low concentration in the water (table 4.2). This result prompted a wider survey of the occurrence of simazine and atrazine in river sediments.

All the sites in E. Anglia (see table 4.6) had concentrations <20 µg kg^{-1}. Simazine was detected at low concentrations in the Godmanchester, Wicken Lode and Swavesy sediments. The detection was only possible when the extracts were concentrated by a factor of 10 using a stream of dry nitrogen gas passed over the solvent surface. At concentrations <2.0 µg kg^{-1}, the quantification is difficult. The result from the analysis of the sediment from the Brampton site on the Great Ouse may be an overestimate because of the co-elution of an interfering 201 amu fragment in the GC analysis. A coincident confirmation ion was detected.

The results for atrazine are shown in table 4.6. Only the Swavesy sediment contained atrazine at a relatively low concentration.

4.4 Comparison of field and predicted distribution coefficients

At certain sites it is possible to calculate a field distribution coefficient, K_f, from measurements of specific pesticides in the water and sediment.

The distribution coefficient, K_d, is defined as:

$$K_d = \frac{\textit{concentration of compound, solid phase, } \mu g\ kg^{-1} \textit{ (dry wt)}}{\textit{concentration of compound, aqueous phase, } \mu g\ dm^{-3}} \qquad (4.1)$$

where the solid phase is the sediment matrix and the aqueous phase is the fresh water and ideally does not include that pesticide associated with suspended solids or colloid material (<0.2 μm in size). In practice the denominator usually refers to the 'whole' water sample or a water sample after filtration through a 0.45 μm membrane filter. As shown later, §5 and §6, this can lead to serious errors in the estimate of K_d.

The field distribution coefficient is analogous to K_d ((eqn (4.1)) with the substitution of the appropriate field measurements. This is only a crude estimate of the distribution coefficient, K_d, because of a number of assumptions implicit in the calculation viz: (a) an equilibrium exists between the freshwater and sediment at the time of sampling and (b) the concentration measured in the water represents a truly soluble fraction and excludes pesticides associated with both colloids and suspended material. In field conditions it is difficult to rigorously evaluate the uncertainties caused by these assumptions because of the dynamic nature of the system and the problems of transferring samples to laboratory for further study without destroying the natural conditions. In spite of these limitations it is worthwhile to record the values of K_f and use the organic contents of the sediment to calculate K_{omf} values where K_{omf} = 100 K_f / OM with OM values given in table 4.1. This has been done for those pesticides that were detected in both the water and sediment samples and the results are summarised in table 4.7.

γ-BHC was in five of the samples and gave log K_{omf} values between 2.5 and 3.4 and log K_f between 0.5 and 2.4. These values compare with log K_d reported by Saleh et al (1982) of between 1.8 and 3.4 and the K_{omf} values are in reasonable agreement with those predicted from the Collander relationship (Briggs 1981):

$$\log K_{om} = 0.52 \log K_{ow} + 0.62 \qquad (4.2)$$

where K_{ow} is the octanol-water coefficient, ie 2.54 obtained using log K_{ow} for lindane of 3.7 (Saleh et al. 1982).

Table 4.7 Comparison of field distribution coefficients, K_{omf} and the values calculated from the octanol-water partition coefficients, K_{ow} using the Collander relationship (Briggs 1981), eqn (4.2).

Pesticide	Field value Log K_{omf}	Predicted value Log K_{om}
Lindane	2.5 - 3.4	2.5
DDE	3.1, 5.1	3.6 - 4.2
Dieldrin	3.2	3.8
Permethrin	3.5, 4.1	3.3 - 3.8
Simazine	3.2	2.2*

* calculated from K_d and OM values determined by Talbert and Fletchall (1965), for 25 soils. The mean value was used for the prediction of log K_{om}.

The results for DDE show more variation with values of log K_{omf} of 5.1 and 3.1 for samples E and H respectively compared with calculated values from eqn (4.2) of between 3.6 and 4.2 depending on the choice of K_{ow} (Hawker and Connell 1988).

The results for dieldrin in sample H lead to values of log K_{omf} of 3.2 which compares with the calculated value of 3.8 obtained with log K_{ow}=6.2 (Briggs 1981). The log K_f value is 2.2 and is in the range of the measured values of 2.2 (Bowman et al. 1985) and 2.7 (Sharom et al. 1980).

The results for permethrin obtained for sample H together with the mean water concentrations given in table 4.2 lead to log K_d values of 1.5 and 2.0 for the *cis* and *trans* isomers and log K_{om} values of 3.50 and 4.1 respectively. These results compare with a log K_d=2.59 for a 40:60 *cis-trans* mixture (Sharom and Solomon 1981) and a value of 2.30 given by Hill (1989). Equation (4.1) predicts a result of between 3.3 and 3.8 depending on the choice of log K_{ow}. The values chosen here were 6.2 from Muir et al (1985) and 5.23 from Lockhart et al (1983). The agreement of the calculated log K_{om} results and the values determined here ie 3.5 and 4.1, is no doubt fortuitous.

The result for simazine does indicate a serious difference between the field and predicted values of the distribution coefficients. The predicted value was taken from results of a survey of 25 soils and is higher than the value calculated by Brown & Flagg (1981) from the regression equation:

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006 \qquad (4.3)$$

of log K_{om} = 1.79 with $K_{om} \cong 1.7\ K_{oc}$

4.5 Conclusion

Several pesticides have been found in different river sediments and in their associated water. In most instances the concentration of organochlorine compounds is low with the notable exception of samples E-G from the Rosemaund Farm in Herefordshire.

Pyrethroids have been measured in many of the sediments and some waters. These include permethrin in samples from the Bere Stream in Dorset (Sample C/D) and R. Stour in Worcestershire (Samples H and I), deltamethrin used on hops at the Rosemaund Farm ((E-G) and *cis*-permethrin in water samples A, B, C/D and H. Because of the lipophilic character of the pyrethroids, they are likely to be strongly adsorbed to suspended matter and may interact with colloid components in river water and sediments.

The results of the survey of atrazine and simazine, although limited in scope, do indicate that concentrations as high as those found in the Rosemaund Farm sediment vis ~ 200 μg kg^{-1} (dry weight) are not widely occurring, at least in the Great Ouse system. However, the values found are not unimportant because of the implications regarding the equilibrium concentrations in the associated water. For a sediment with a concentration of simazine of ~ 2 μg kg^{-1} and K_d ~ 5 dm^3 kg^{-1}, an equilibrium interstitial water concentration of dissolved simazine of ~ 0.4 μg dm^{-3} is expected. No measurements have been made of interstitial water concentrations.

No published information is available concerning the concentration of pesticides in river sediments. A project "Strategic ecosystem studies of large slow flowing lowland rivers" performed for DoE and later the National Rivers Authority, NRA, by the Institute of Freshwater Ecology involved some survey work of river waters and sediments in November 1988, June 1989, November 1989 and June 1990. The results of the analysis of the water samples from the Great Ouse and associated water bodies are broadly in line with the results obtained by the NRA for the organochlorine pesticides. No comparable data are available for the pyrethroids but the results obtained by IFE indicate high values of some pyrethroids in river water viz cypermethrin at a concentration of 0.52 μg dm^{-3} was found on the Great Ouse at Godmanchester in the November 1989 survey. *Cis* and *trans* permethrin occurred at many sites at concentrations <0.1 μg dm^{-3} with in general lower concentrations of cypermethrin and fenvalerate.

The concentrations of the pesticides found in the sediments were much higher than in the associated water. Lindane occurred at most of the sites at concentrations <5 μg kg^{-1} (dry weight) as did dieldrin (0.1 - 13 μg kg^{-1}) and TDE (1 - 16 μg kg^{-1}). The pyrethroids, *cis* and *trans* permethrin, also occurred at most of the sites with concentrations as high as 118 μg kg^{-1} at St Neots on the Great Ouse. In most cases the *cis* isomer predominated over the *trans* isomer. There is obviously a need for further research on the pyrethroids in sediments, particularly in view of the trend towards the increasing use of pyrethroids. The results obtained here at the Bere Stream (Dorset) and R. Stour, Worcestershire indicate this may not be localised to E. Anglia.

5. INTERACTION OF SEDIMENT COLLOIDS WITH SIMAZINE AND PERMETHRIN

The filtration of water samples through 0.45 µm membrane filters, although removing the coarser particles, does permit colloids and fine particulate material into the filtrate. Hence in any analysis of the filtrate for pesticides, the final results reflect not only the dissolved component but also the pesticide associated with fine particulates and colloids. In some instances, depending on the chemical properties of the pesticide and the colloid, the association may be substantial and lead to a significant contribution to the transport of the pesticide, both in rivers and from the unsaturated zone to groundwaters.

Several studies reported in the literature have provided evidence for the interaction of hydrophobic organic compounds and colloidal macromolecules in water (Gschwend & Wu 1985; Hassett & Milicic 1985 and Kile *et al.* 1990). Sometimes this has been investigated in terms of the enhanced solubility of the organic compound in waters containing humic and fulvic acids. This approach has arisen from the common procedure of filtering freshwater samples through 0.45 µm membranes to separate the particulate bound and soluble components of the analyt. However, the colloid component ie <0.2 µm in diameter, also pass through with the filtrate and so any pesticides associated with the colloids are included as the "soluble" fraction thus leading to conditions of so-called "enhanced solubility". The observed enhancement has been accounted for by a partition between dissolved organic matter (DOM) or organic colloids and the solute. The strength of the interaction is thought to be closely related to the molecular size and composition of the DOM and to the intrinsic water solubility of the solute (Kile *et al.* 1990).

The importance of colloids in determining the speciation and long-term environmental and health impact of hydrophobic compounds in aquatic systems has only recently been recognized (Senesi & Chen 1990). A substantial fraction of pollutant found in the aqueous phase may interact strongly with colloids and significantly affect the rate of volatilization, transfer to sediments, biological uptake and bioaccumulation or chemical degradation. Unfortunately, little information is available concerning the specific interaction of the pesticides, lindane, simazine and permethrin with sediment colloids or DOM in general. No reports have been found which quantify the interaction of permethrin with either well characterized colloids or natural colloids. There is only one report of the interaction between the triazine herbicides and colloids. Means & Wijayaratne (1982) determined K_{oc} values for atrazine of between 1690 and 13,600 for various estuarine colloids. Their results indicate that natural colloids have the potential to be important substrates in the transport of hydrophobic contaminants in aquatic systems.

The work reported here examines the interaction of simazine and permethrin with a sediment colloid. The investigation is an initial attempt to quantify the interaction of the pesticides with colloids.

5.1 Apparatus and methods

It was not possible to amend the automated adsorption cell, §7, to accommodate ultrafiltration membranes with a molecular weight cut-off of 1000. Although this offered the best solution to the characterization of the interaction over a concentration range of both herbicide and colloid, the further development of the system would have taken some time.

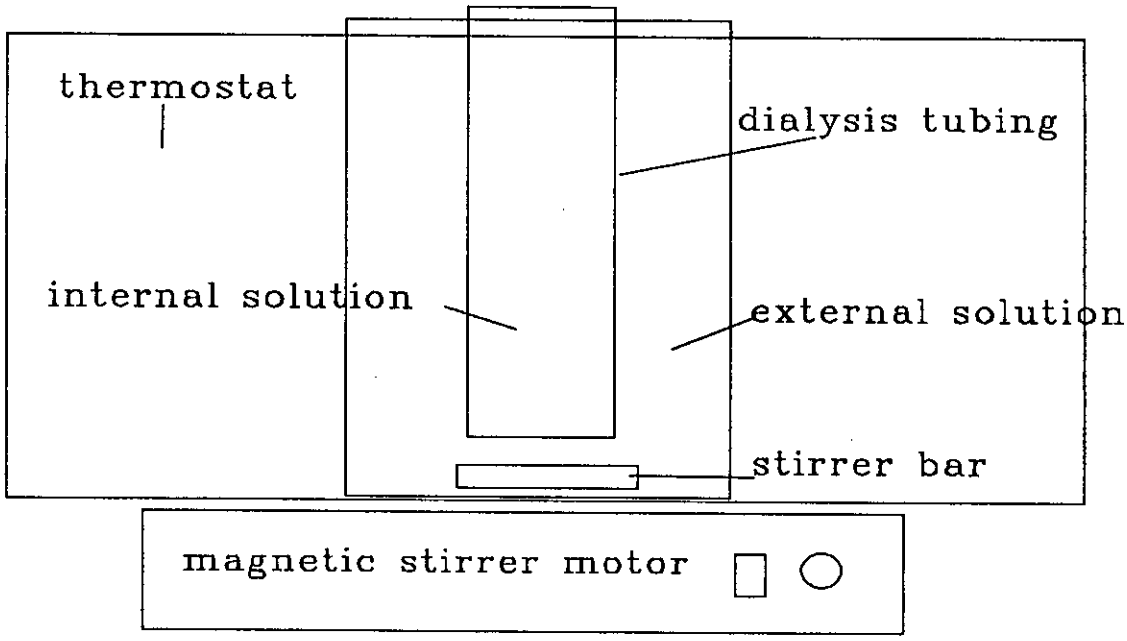


Figure 5.1 Apparatus used for the determination of the interaction of pesticides with colloids associated with river sediments

Another method involves dialysis using the apparatus shown in figure 5.1. The whole assembly is contained in a water thermostat at 25°C. The cellulose dialysis tubing was from SIGMA (product number D-7884) with a molecular weight cut-off of 1200. This permitted the free-passage of the herbicide but restricted the passage of the colloid material.

The experiments involved tests of the attainment of equilibrium and experiments with the colloids isolated from the sediments that were used in adsorption experiments, §7. The colloid was placed in the outer container, termed the external solution (see figure 5.1), and the dialysis tubing was filled with pesticide free distilled water. The dialysis tubing was thoroughly washed before use over a period of 2 days.

The analysis for simazine was done by passing 10 ml of solution through a preconditioned C8 solid-phase-extraction column using the method described previously, §3, with a modification involving a solvent change of the final extract to reconstitute in 0.5 ml of DCM before analysis by GC/MS using the 201 amu target ion for quantification. This procedure enabled duplicates or triplicates to be analysed together with a control blank. The relatively small volumes available for analysis of the internal solution limited the detection to approximately 0.5 μg dm^{-3}. This could be improved using the specific nitrogen detector, NPD, but more ideally by using a larger volume of solution for the analysis.

The analysis for permethrin was by the same extraction procedure as for simazine but with chromatographic analysis by GLC with detection by ECD as described in §3.

5.2 Attainment of equilibrium

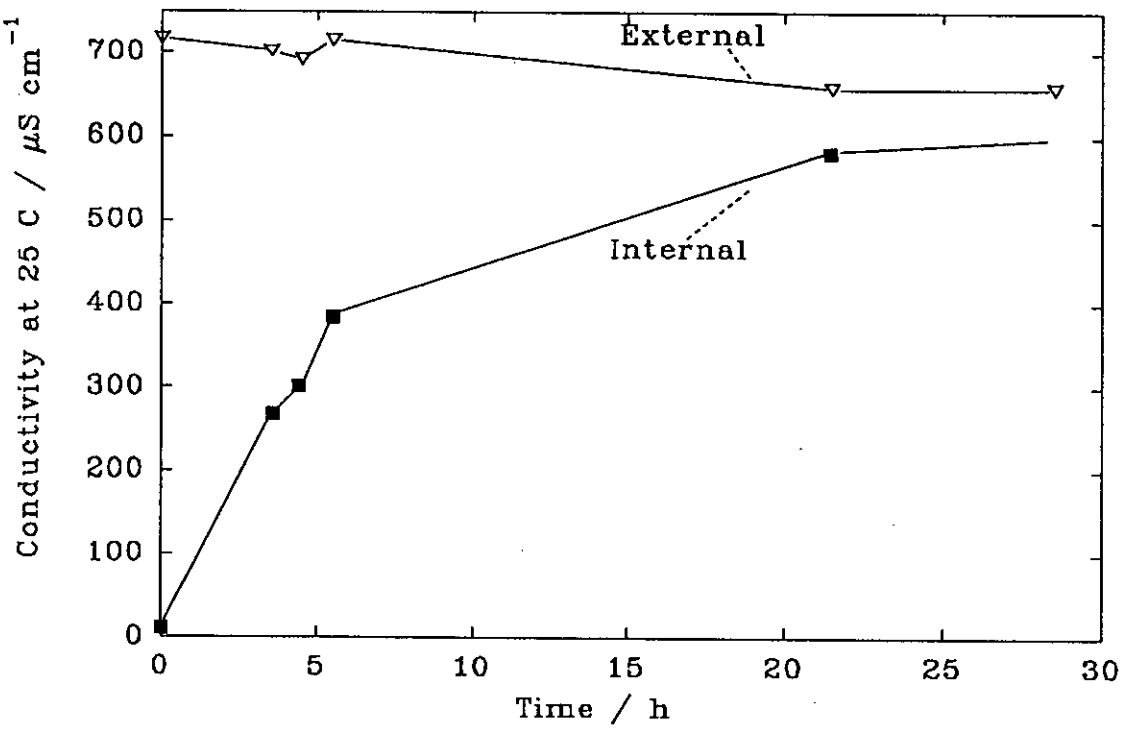


Figure 5.2 **Attainment of equilibrium in the dialysis experiments. Key: 'External' refers to the solution outside the dialysis tubing and 'Internal' to the solution inside the dialysis tubing.**

The supernatant from the adsorption experiments with sediment B, §7, ie previously filtered through 0.2 µm cellulose nitrate filter and containing simazine at a concentration of ≈ 35 µg dm^{-3}, was placed in a 190 ml pyrex bottle. The dialysis tubing was filled with 30 ml of pesticide-free distilled water and placed in the pyrex bottle. The bottle was immersed in a thermostat at 25 ± 0.2°C and the external solution stirred using a magnetic follower. The top of the flask was sealed. Measurements of the electrical conductivity of the internal and external solutions were made over a period of approximately 30 h. The results, shown in figure 5.2, indicate that equilibrium across the membrane had occurred in this period. The differences in conductivity were attributed to the presence of polyanions in the colloid fraction.

5.3 Results of the measurement of the interaction of simazine with sediment colloids

The colloids were prepared from the sediments by placing 20 g of the sediment into 1 litre of 10 mM $KHCO_3$ in a glass bottle with PTFE screw cap and shaking overnight at 25°C. The suspension was then filtered through a GF/F microfibre pad, followed by a 0.2 µm Sartorius 11307 membrane filter. The absorbance of the final filtrate was measured at wavelengths of 460, 660, 400 and 340 nm to permit some estimation of the humic/fulvic acid contents.

A "humic" fraction of sediment B (see §7) was isolated by a procedure described by Marchesi *et al.* (1991a). This involved the treatment of 250 g of sediment with 500 ml 0.1 M NaOH for 24 h, filtration of the supernatant and subsequent acidification with concentrated HCl to a final pH of 1.5. The isolated humic fraction was dissolved in 0.1 M NaOH, precipitated with HCl, washed with distilled water and centrifuged for 10 min (g_{av} 4600). This procedure was repeated before the sample was freeze-dried. The isolated material was used to measure the absorbance at 340 nm in 10 mM $KHCO_3$ solutions over a concentration range of the humic fraction of 1-50 mg dm^{-3}. The calibration line was used to estimate the concentration of the humic fraction in the internal and external solution in the dialysis experiments. In addition, the adsorptive properties of the isolate could in the future be compared with the properties of the sediment colloid prior to fractionation.

The measured concentrations of simazine in the internal and external solutions obtained after an equilibrium period of approximately 3 days are shown in table 5.1. The details of the two sediments, A and B, have been given in §7, and are those sediments used in the adsorption studies. The results for both colloids ie isolated from sediments A and B, show no significant (t-test, 5% probability level) difference between the concentrations of simazine in the internal and external solutions and support the conclusion that the measurement of simazine in the filtrate in the adsorption experiments is valid ie the fraction of simazine associating with the colloid is negligible and below the level of uncertainty in the analytical method. The humic fraction at the end of the dialysis was estimated from the absorbance measurement at 340 nm to be ≈ 40 mg dm^{-3}.

The standard deviations shown in table 5.1 permit an estimation of the range of K_{dc} (partition coefficient normalized with respect to colloids) for the colloid that can be determined by this dialysis method. The percentage of simazine adsorbed to the colloid expressed in terms of the total amount of simazine in the apparatus ie dissolved plus adsorbed may be expressed:

$$\textit{Percentage adsorbed, } \%n_a = \frac{100\ C\ K_{dc}\ 10^{-6}}{1 + C\ K_{dc}\ 10^{-6}} \qquad (5.1)$$

where C is the concentration of the colloid in mg dm^{-3} and K_{dc} ($dm^3\ kg^{-1}$) is the partition coefficient for the colloid. Equation 5.1 is illustrated in figure 5.3 for various values of C including 30 mg dm^{-3} determined for the experiments with sediment B.

Table 5.1 **Results of the dialysis experiments with simazine at 25°C. The values in brackets are standard deviations of duplicate samples unless otherwise stated. The value of P is the probability that it is incorrect to assert that the two means are different.**

Experiment Number	Sediment Code	Concentration /µg dm^{-3}		P
		Internal	External	
17	A	36.1 (2.5)*	36.4 (2.1)	0.914
19	A	27.1 (1.6)	27.8 (1.4)	0.568
20	B	31.5 (0.8)	31.5 (0)	0.423
21	B	1.85 (0.56)*	1.43 (0.50)*	0.384

Note * triplicate samples: none of the means for the internal and external concentrations were significantly different at the 5% probability level.

The difference in the herbicide concentration between the internal and external solutions ΔC_h, is:

$$\Delta C_h = C_e\ K_{dc}\ C \times 10^{-3} \qquad (5.2)$$

where C_e is the equilibrium concentration of herbicide (µg dm^{-3}). Equating ΔC_h with the mean standard deviations for the two concentrations of simazine (table 5.1), leads to minimum values of K_{dc} that can be determined by this method of approximately 1900 for C_e = 30 µg dm^{-3} and 8800 for C_e = 2 µg dm^{-3}, both calculated with C = 30 mg dm^{-3}. This assumes that the saturation concentration for adsorption is >30 µg dm^{-3} which is reasonable and supported by the linear isotherm data for atrazine on colloidal matter of Means & Wijayaratne (1982) which extended to herbicide concentrations of 400 µg dm^{-3}. It is therefore unlikely that the colloids are saturated at the much lower concentrations studied here.

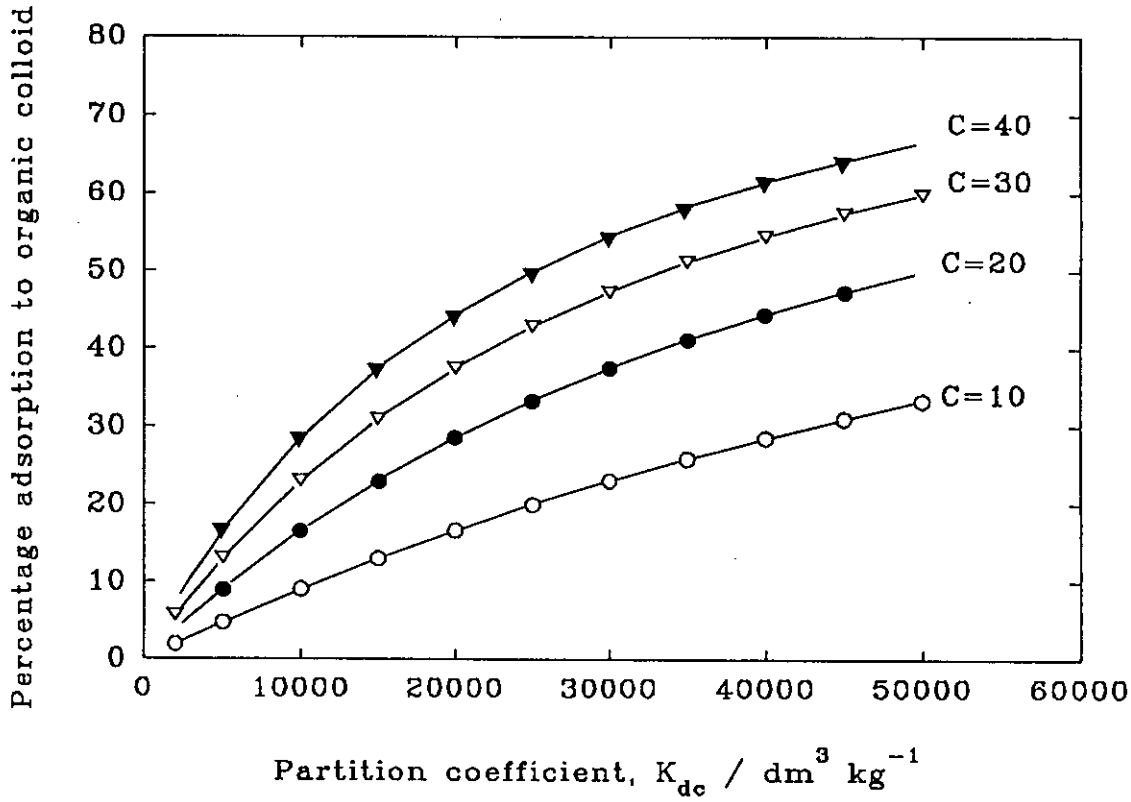


Figure 5.3 **Theoretical relationship illustrating the dependence of the adsorption on the values of the distribution coefficient for the colloid fraction.**

The concentration of the colloids, C, is given in units of mg dm^{-3}.

5.4 Results of the measurements of the interaction of permethrin with the sediment colloids

The colloids were prepared from sediment B in the manner described in §5.3. This sediment has been used in a number of investigations including the simazine adsorption experiments described in §7 and studies of the interaction of alkyl sulphates and linear alkylbenzenesulphonates detergent residues (Marchesi *et al.* 1991a; Marchesi *et al.* 1991b). No experiments were performed with sediment A. A 250 ml quantity of stock solution of *trans*-permethrin was prepared using a re-circulating system with distilled water circulation through an all glass/PTFE apparatus using a Radiometer ABU80 autoburette system operated in automatic 'fill mode'. The *trans*-permethrin was mounted on 0.4 mm (40 mesh) pre-cleaned GLC glass beads contained in a 3 ml Baker solid-phase-extraction (SPE 7328-03) column capped with PTFE frits. A stainless steel PTFE tap was inserted after the glass column to permit control of the liquid flow. The flow rate was maintained at ≈ 1.3 ml min^{-1} over a period of *ca* 40 h. The final concentration of *trans*-permethrin in the stock solution was 175.6 ± 2.2 µg dm^{-3}.

Dialysis experiments were performed using *trans*-permethrin by dilution of the stock solution in 10 mm $KHCO_3$. The same apparatus and procedures for the simazine experiments, §5.3, were employed. The results of the analysis of the internal and external solutions are given in table 5.2 together with the standard deviations obtained from the triplicate analysis of the extracts. Absorbance measurements, $A^{1\ cm}$, at λ = 340 nm of the external solution at the beginning and end of the dialysis experiments indicated a slight decrease *viz* $A^{1\ cm}_{340\ nm}$ = 0.273 at the beginning of the dialysis, decreasing to 0.249 at the end with an increase of $A^{1\ cm}_{340\ nm}$ = 0.070 in the internal solution. These measurements correspond to concentrations of 41 mg dm^{-3}, 39 mg dm^{-3} and 11 mg dm^{-3} of the humic fraction in the external solution at the start and finish of the dialysis and in the internal solution at the end respectively.

Table 5.2 **Results of the dialysis experiments with permethrin at 25°C. The values in brackets are standard deviations of the analysis of individual extracts. C_E and C_I are the concentrations of permethrin found in the external and internal solutions respectively.**

Sediment Code	Concentration /μg dm^{-3}		C_E/D_I
	Internal	External	
B	26.60 (1.29)	58.84 (1.11)	2.21
B	16.39 (1.14)	36.11 (1.42)	2.20

The differences in the concentration of permethrin in the external and internal solutions shown in table 5.2, reflect the association of permethrin with the sediment colloid in the external solution. It is seen that the ratio of the concentrations in the external and internal solutions is constant.

The partition coefficient describing the interaction with the colloidal material, K_{dc}, may be defined:

$$K_{dc} = \frac{\textit{concentration of pesticide associated with colloid, ng } g^{-1}}{\textit{concentration of dissolved pesticide, ng } ml^{-1}} \qquad (5.3)$$

in units of ml g^{-1} or dm^3 kg^{-1}.

$$K_{dc} = \frac{(C_E - C_I)}{C\ C_I}.10^6\ (dm^3\ kg^{-1}) \qquad (5.4)$$

where C is the concentration of the colloid in mg dm^{-3}, C_E is the concentration of permethrin in the external solution (ng ml^{-1}) and C_I is the concentration in the internal solution (ng ml^{-1}).

The concentration, C_I, is assumed to be the concentration of the dissolved or 'free' pesticide not associated with colloids.

Equation 5.4 may be written:

$$K_{dc} = \frac{10^6}{C} [(C_E / C_I) - 1] \qquad (5.5)$$

so that the ratio C_E / C_I should be constant and directly proportional to the colloid partition coefficient, K_{dc}. The calculation of K_{dc} (equation 5.5) requires a value of C, the concentration of the adsorbent in the aqueous phase. As a first approximation, it is assumed here that C may be equated to the concentration of the humic fraction of the colloid as determined from the absorbance measurements. Further research is necessary to validate this assumption and to characterize the colloid components. However, with C ≈ 40 mg dm^{-3}, calculated using an extinction coefficient, ε, = 6.32 dm^3 g^{-1} cm^{-1}, the partition coefficient, K_{dc}, may be calculated from the C_E / C_I ratio given in table 5.2. This yields a value of K_{dc} ≈ 30,000 dm^3 kg^{-1} (ie log K_{dc} = 4.48) indicating that a high percentage of the permethrin is adsorbed to the colloid fraction for the concentration range 10 - 40 mg dm^{-3} illustrated in figure 5.3.

5.5 Conclusion

The results, illustrated in figure 5.3, show that colloids may contribute significantly to transport of pesticides, particularly those compounds with moderately high values of K_{dc}. The results of the dialysis experiments, although preliminary in nature, do indicate the K_{dc} for simazine for the sediments studied are less that 2000 and therefore colloids are likely to make only a small contribution to the total transport. Questions still remain concerning the stability of simazine associated with colloid material, the reversibility of the interaction and variability of K_{dc} with colloids from different origins. The latter necessitates the further development of specialized equipment and techniques not available at present.

In contrast, the results for permethrin indicate a substantial adsorption to colloid materials in sediment B. The derived K_{dc} ≈ 30,000 dm^3 kg^{-1} is likely to be an underestimate because of the occurrence of some organic components in the internal solution in the dialysis experiments. The results suggest that for interstitial water containing > 30 mg dm^{-3} of the humic acid fraction, the majority of the permethrin is not truly dissolved but adsorbed to colloid components (< 0.2 μm in diameter).

More detailed research is needed to investigate this further and should include the application of automated techniques developed for measuring the adsorption of trace components of pesticides to suspended solids (§7). Among the improvements suggested are:

(a) Development of an automated system based on the equipment used for adsorption measurements with suspended solids (§7); this will permit a range of colloids at different concentrations and origin to be studied over a range of pesticide concentrations.

(b) Development of simple techniques to characterize sediment colloids from different origins and relate these characteristics to their adsorptive properties.

(c) Evaluation of the stability of pesticides associated with colloids.

(d) Measurement of the release of pesticides adsorbed to colloids and their fate after coagulation in salt waters eg in the intertidal reaches of rivers, in estuaries and in near-coastal waters.

6. ANALYSIS OF PESTICIDES ASSOCIATED WITH SUSPENDED SOLIDS

The field survey work (§4) concentrated on the measurement of selected pesticides in "whole" water samples and surface sediments. It is also important to evaluate the transport of pesticides with suspended solids. Unfortunately little research has been published on pesticides associated with suspended solids and it was therefore necessary to perform detailed checks of the methodology before field samples could be examined. The feasibility of using small volumes *ca* 1 litre, with separation of suspended solids by filtration was investigated. The development of such methods would enable pesticide concentrations in water and suspended solids to be monitored separately during major storm run-off eg during a river spate. Results were also compared with those obtained using a continuous-flow-centrifugation procedure to separate the suspended solids from a large volume of water.

The separation of the sediment or suspended solids from the associated solution is a crucial step in the determination of the distribution of the pesticide, particularly when it is desirable to measure the amount of the compound in solution as well as sorbed to the sediment by an independent analysis. The separation may involve a combination of filtration and centrifugation steps but in any event it is impossible to achieve this completely. Hence some knowledge of sorption from the aqueous solution to the container walls or filtration membrane is essential.

The purpose of this work is to evaluate (a) the adsorption affinity of selected pesticides, including lindane, simazine and permethrin, to glass and PTFE bottles and (b) the relative adsorption affinity of the same pesticides to membrane filters used for the separation of suspended solids from solution or sediments from their associated solutions in sorption studies. In these situations it is impracticable to extract the container walls or membrane filters with organic solvents because of the possibility of extraction of pesticides from suspended solids adhering to the surfaces.

6.1 Methods

The following pesticides were included in the development work: ∝-BHC, lindane, *p,p'*-DDE, *p,p'*-TDE, dieldrin, endrin, *cis*-permethrin, *trans*-permethrin, cypermethrin, fenvalerate, deltamethrin, atrazine and simazine.

6.1.1 Sorption to glass and PTFE surfaces

100 ml Duran wide-necked borosilicate glass bottles and 100 ml PTFE (fluorinated ethylene propylene bodies with screw tops of Tefzel, ethylenetetrafluoroethylene) were used in these experiments. The area of the internal surface of the bottles was estimated has 153.08 cm^2 and 155.35 cm^2 for the glass and PTFE bottles respectively.

An aliquot of 0.5 ml of the multi-pesticide standard in 5% acetone in hexane was added to each of four glass and four PTFE bottles and the solvent evaporated using dry nitrogen gas. 100 ml of 10 mM potassium hydrogen carbonate, prepared from pesticide free distilled water, was added to each of the bottles (pH = 8.3) and shaken in the dark at 25°C. The nominal

concentration of each pesticide was 0.25 μg dm^{-3} (ppb). A control blank sample containing 100 ml of 10 mM potassium hydrogen carbonate was included for each type of bottle; these were treated in the same way as those samples containing pesticides. After this first stage, *ca* 66 hours, the contents of two glass and two PTFE bottles together with the controls were analysed using the solid-phase-extraction (SPE) method described below. The empty bottles were not rinsed with distilled water but carefully drained and allowed to dry at room temperature before extraction with 10 ml of dichloromenthane, DCM, for *ca* 48 hours. After transferring the extract to a collection tube, the bottles were further rinsed with three 3 ml aliquots of DCM.

A second stage involved transferring the contents of the two remaining glass and PTFE bottles to identical empty bottles. These were shaken at 25°C for *ca* 2 days before the contents and empty bottles were analysed for pesticides as described above. The final eluates from the solution and bottle extraction were evaporated to dryness using a gentle stream of dry nitrogen and reconstituted in 500 μl of 5% acetone in hexane for GLC analysis.

6.1.2 Sorption to Filters

The following membrane filters were compared:

Filter 1: 0.2 μm cellulose nitrate, CN1 (Sartorius SM 11307).

Filter 2: 0.2 μm cellulose nitrate as above but boiled for 5 minutes in 400 ml of distilled water and freeze dried overnight; this treatment reduces the amount of wetting agent on the filter (referred to as CN2).

Filter 3: 0.2 μm Anopore inorganic membranes (Whatman, 20021S50).

Filter 4: GF/F glass microfibre pad, nominally 0.7 μm pore size: the filter was pretreated to remove organic carbon by heating to 550 °C overnight.

Filter 5: 0.4 μm Nuclepore filter, NP.

The pesticides were prepared in 10 mM potassium hydrogen carbonate solution contained in 100 ml glass bottles as described above. A control blank containing no pesticides was included as well as an additional sample of pesticide solution for the assessment of the recovery without filtration. The samples were shaken for 2 days at 25°C before separation. Prior to filtration, the filters were washed by the passage of 100 ml of distilled water and the washings discarded. After filtration the bottles were rinsed with two 10 ml aliquots of the filtrate and the excess solution removed from the filters by aspiration for a further two minutes. The glass bottles were extracted with DCM and treated as described in (a) above. The filtrate was analysed by the SPE method described below, followed by a solvent exchange to 5% acetone in hexane and analysis by GLC. The filters were frozen and then freeze-dried overnight. The volume of water evaporated from the filters was determined from the weight change on drying to enable the appropriate corrections to be applied for the pesticide in solution on the wet filters.

The filters were extracted overnight at 25°C in a 10 ml reaction vial using 10 ml of DCM. After separating the extract from the filter, the filter and reaction vial were washed with three aliquots of 3 ml of DCM, the washings added to the extract and evaporated for a solvent change with 500 μl of 5% acetone in hexane.

6.1.3 Water Analysis

All aqueous solutions were analyzed by the method described in §3.3 using a solid-phase-extraction (SPE) technique with 3 ml bonded silica C8 columns (Analytichem International). The procedure involved methanol conditioning, washing with HPLC grade water and after extraction and drying, elution with 2 ml of HPLC grade methanol.

6.1.4 Chromatography Analysis

The organochlorine and pyrethroid pesticides were analysed using the method described in §3.6.1. The instrument was calibrated using a 0.05 μg ml^{-1} multi-pesticide standard solution prepared in 5% acetone in hexane with 0.5 μg ml^{-1} internal standard of phosalone.

The triazines were analysed by GC/MS in selective-ion mode with the target ions of 215 and 186 amu for atrazine and simazine respectively using the method described in §3.6.4. Calibration for the triazines was done using external standards of concentration 0.02, 0.05, 0.08 and 0.20 μg ml^{-1}. With the separate analysis of simazine and atrazine ie monitoring a single ion for each analysis, the linearity of the response was good over this range of concentration.

Table 6.1 Comparison of the mean percentage recoveries from aqueous solutions in glass bottles in experiments with and without filtration. The standard deviations are shown in brackets.

Pesticide	Samples unfiltered	Samples filtered
α-BHC	30.5 (19.3)	51.9 (7.9)
lindane	52.2 (11.4)	64.5 (4.8)
DDE	70.0 (12.2)	72.0 (11.4)
dieldrin	73.2 (7.9)	65.0 (6.9)
endrin	84.5 (3.5)	78.5 (6.5)
TDE	62.3 (3.1)	60.2 (11.2)
DDT	73.7 (12.0)	64.9 (14.8)
cis-permethrin	95.9 (21.0)	72.1 (12.5)
trans-permethrin	88.2 (19.5)	67.0 (27.0)
cypermethrin	47.5 (11.1)	44.7 (11.7)
fenvalerate 1	70.6 (8.1)	57.7 (13.0)
fenvalerate 2	70.3 (9.6)	58.6 (12.3)
simazine	99.3 (12.7)	*
atrazine	121.3 (13.0)	100.7 (11.4)

* not quantified because of the detection of co-eluting compounds in the control blank.

6.2 Adsorption to glass and PTFE

The recoveries of the pesticides in glass bottles, expressed as a percentage of the total addition, are shown in table 6.1. These have been calculated for the recovery sample in the filtration experiments and the first stage in the bottle adsorption experiments. The results illustrate some losses of compounds in the procedure that cannot be accounted for by the uptake on the glass. The recoveries are satisfactory ie ≥ 70%, for DDE, dieldrin, endrin, DDT, permethrin, fenvalerate, atrazine and simazine.

A comparison of the partition of the pesticides between the solution and container surface is shown in figure 6.1. For six of the compounds *viz*: α-BHC, lindane, dieldrin, endrin, atrazine and simazine, the retention to the glass and PTFE is relatively small ie < 15% of the total, with in most instances greater adsorption to PTFE than to glass. In contrast, the majority of the insecticides DDT, TDE, DDE and the pyrethroids were recovered from the container surfaces. Although some residual water was inevitably left in the bottles after separation and draining, the low concentrations of pesticide in the water meant that the error introduced in the determination of the contribution of the bottle adsorption was minimal eg the amount of water remaining on the glass was determined as 0.20 ± 0.12 g which for *cis*-permethrin corresponds to *ca* 0.01 ng compared with a total of 19 ng extracted from the vessel.

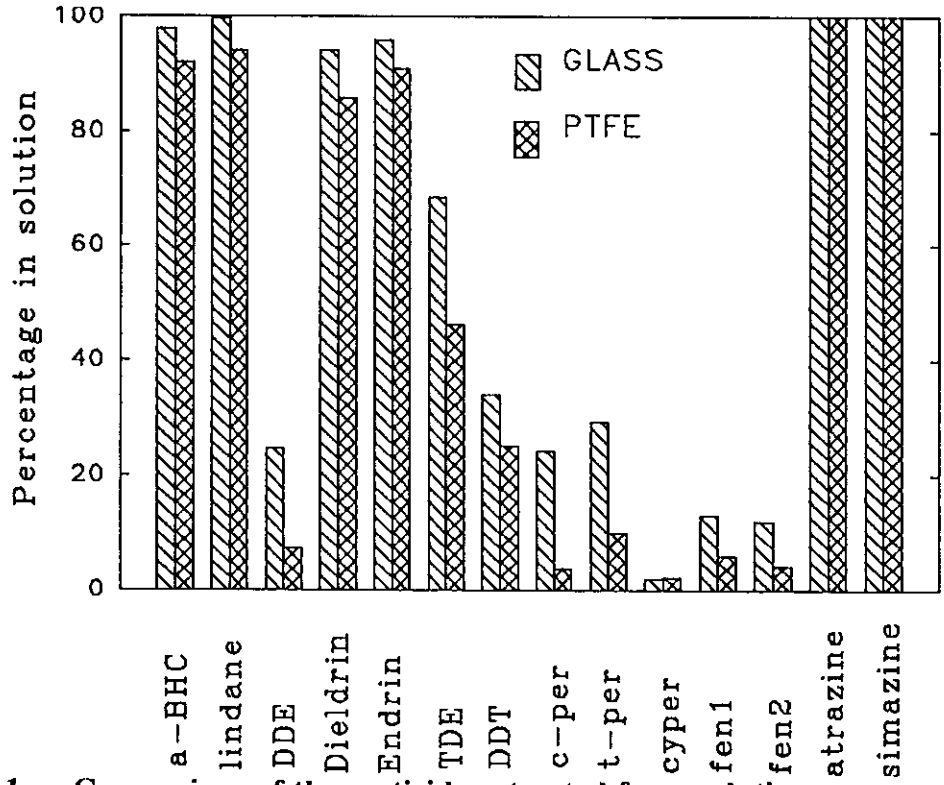


Figure 6.1 Comparison of the pesticide extracted from solution as a percentage of the total recovered in the experiments with glass and PTFE bottles.

The results of the partition of the pesticides between solution and the container surfaces were used to calculate an adsorption constant, K_a, defined as:

$$K_a = \frac{\textit{amount of pesticide per unit area of surface, ng cm}^{-2}}{\textit{concentration aqueous solution, ng cm}^{-3}} \qquad (6.1)$$

with K_a in units of cm. This equation is applicable at low concentrations of the dissolved pesticide in the region of the linear adsorption isotherm where the compounds are not expected to compete for adsorption sites.

Table 6.2 **Mean values of the distribution coefficient, K_a, calculated for glass and PTFE containers with the associated standard deviations appropriate to the range of concentrations determined in the solutions. Values for permethrin, cypermethrin and fenvalerate are mean values calculated for these compounds. Simazine and atrazine were not detected on the glass or PTFE.**

	Glass surface		PTFE surface	
Pesticide	K_a / cm	Concentration range /ng ml^{-1}	K_a / cm	Concentration range /ng ml^{-1}
α-BHC	0.014 (0.007)	0.05	0.036 (0.011)	0.01-0.04
lindane	0.005	0.04-0.12	0.048	0.04-0.07
DDE	1.35 (0.38)	0.03-0.05	5.94 (1.35)	0.005-0.02
dieldrin	0.027 (0.009)	0.17-0.19	0.093 (0.009)	0.11-0.15
endrin	0.019 (0.006)	0.19-0.21	0.059 (0.005)	0.12-0.18
TDE	0.226 (0.053)	0.09-0.11	0.887 (0.087)	0.01-0.07
DDT	0.870 (0.250)	0.04-0.07	2.028 (0.116)	0.008-0.04
permethrin	1.44 (0.30)	0.01-0.07	3.32 (1.68)	0.001-0.01
cypermethrin	43.3 (16.8)	0.002-0.007	11.61 (5.97)	0.002-0.007
fenvalerate	8.15 (2.48)	0.002-0.03	11.80 (3.99)	0.002-0.01

The distribution coefficients were calculated from the independent determinations and are listed in table 6.2. The values of the adsorption constant, K_a, show large differences between the pesticides with the largest values for the pyrethroids. Both triazines showed no adsorption to glass or PTFE. The results in table 6.2 were used to see whether there was any trend in the adsorption behaviour with a defined property of the pesticides. The most common property chosen to characterize the hydrophobic nature of the compounds is the octanol-water partition coefficient, K_{ow}. Values of Log K_{ow} for the organochlorine pesticides were taken from the review by Rao & Davidson (1980) and the values for the pyrethroids from those listed by Muir *et al.* (1985). The triazines were not included in the analysis. The regression analysis of the data for the organochlorine pesticides produced the relationships shown in figure 6.2 with similar correlation coefficients of 0.975 and 0.964 for the adsorption to glass and PTFE respectively. The correlations produced:

$$\text{Log } K_a = -3.929\ (\pm 0.298) + 0.659\ (\pm 0.068)\ \text{Log } K_{ow} \text{ for glass and}$$
$$\text{Log } K_a = -3.143\ (\pm 0.331) + 0.611\ (\pm 0.075)\ \text{Log } K_{ow} \text{ for PTFE,}$$

with the slopes for the two regression lines in agreement (t-test, 5%). The results for the pyrethroids do not follow this trend but gave higher values of K_a than might be expected from the octanol-water partition coefficients. The higher uncertainty in the K_{ow}'s for the pyrethroids, as compared with the organochlorine pesticides, precludes the evaluation of a simple relationship between K_a and K_{ow}.

There is a limited amount of information about the interaction of these groups of pesticides with glass and PTFE surfaces. The experiments reported by Sharom and Solomon (1980) involved much higher concentrations of permethrin eg 3 - 15 ng ml^{-1}. The data they reported may be used to calculate K_a values to compare with the results produced here. For PTFE, a K_a value of 0.33 cm was calculated which compares with a higher value for glass viz 0.75 cm at the lowest permethrin concentration reported (3.7 ng ml^{-1}). Although the isotherm for PTFE is linear, the results for the adsorption to glass indicate a non-linear isotherm with the adsorption constant decreasing with increasing concentration in solution. This may indicate that the glass surface is approaching saturation at these higher solute concentrations. The value for glass may be compared with the K_a of 1.44 cm found here for permethrin concentrations in the range of 0.01 to 0.07 ng ml^{-1}.

The implications of these results are important, not only for the determination of the concentration of pesticides on suspended solids, but also in any procedure involving the dissolution of hydrophobic compounds in aqueous solution. This may be illustrated by the calculation of the percentage loss of a compound to the container surface, δ, in the region where the adsorption isotherm is linear :

$$\delta = 100\ K_a\ A_v\ /\ (1 + A_v\ k_a) \qquad (6.2)$$

where A_v is the area to volume ratio of the containing vessel in cm^{-1}. As seen, the value of δ is independent of the aqueous concentration in the linear isotherm region. The relationship is illustrated in figure 6.3 for compounds with a log K_a between -3 and 1.0 and $A_v = 0.6$ (estimated for a litre glass bottle). The figure shows that for compounds with a $K_a \geq 0.19$ cm, more than 10% is expected to be associated with the container surface and not freely mobile in solution. The partition is particularly important for the pyrethroid insecticides.

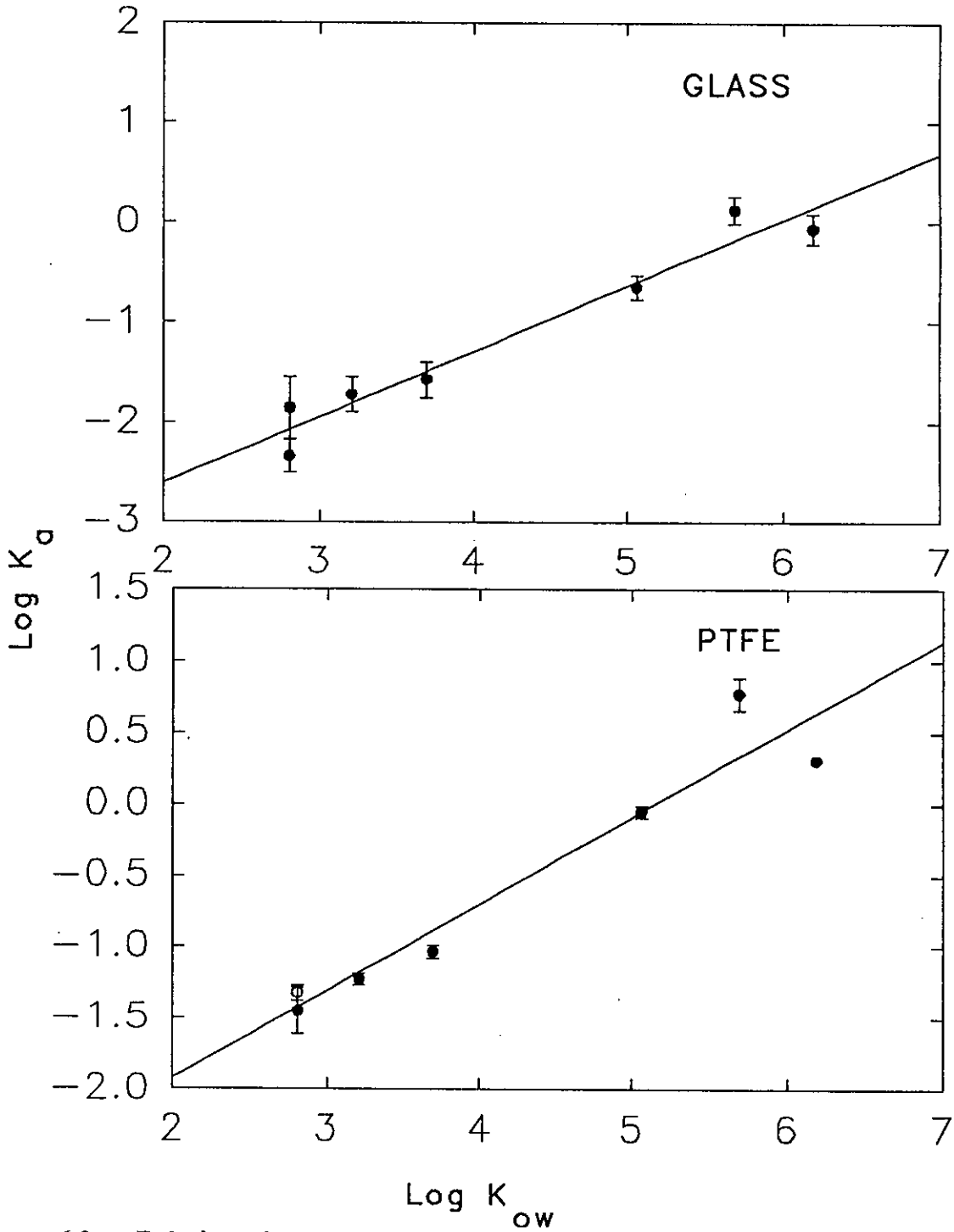


Figure 6.2 Relationship between the octanol-water partition coefficients and the adsorption constants for the organochlorine insecticides on glass and PTFE.

The values of K_a, together with the standard errors are shown in table 6.2.

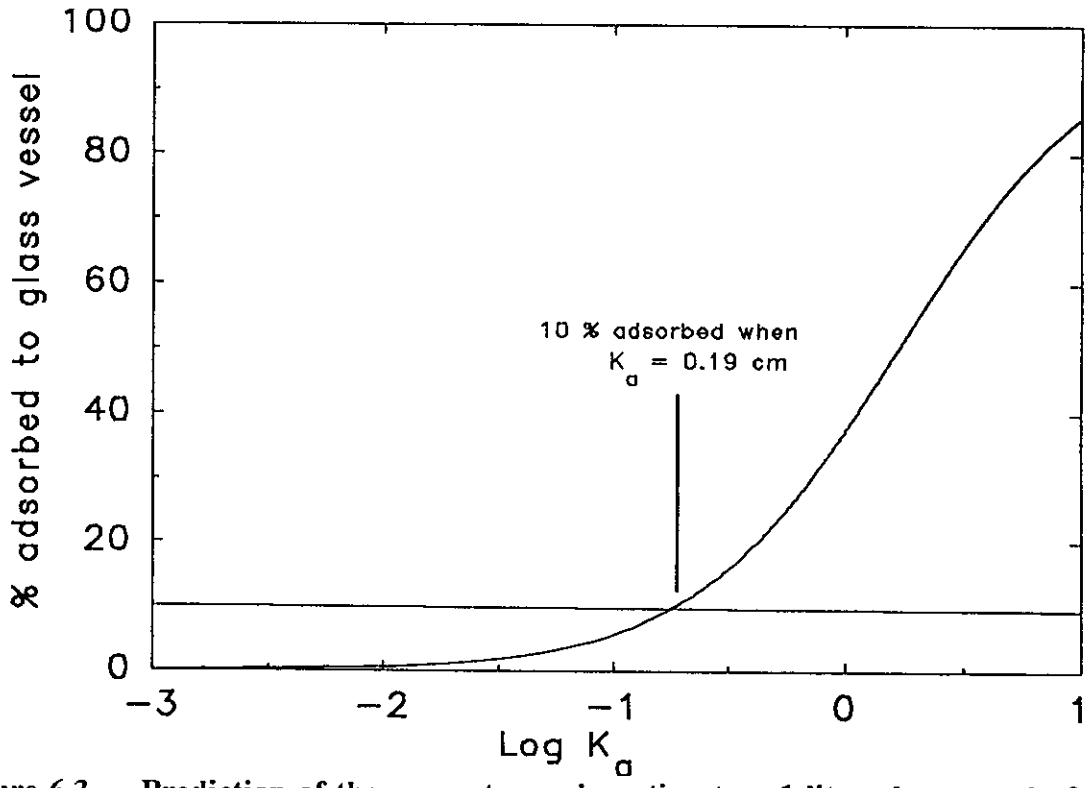


Figure 6.3 **Prediction of the percentage adsorption to a 1 litre glass vessel of area to volume ratio, A_v, = 0.6 cm^{-1} for a range of adsorption constants, K_a (in cm).**

6.3 Sorption to filters

The total recoveries of the filtered samples, as shown in table 6.1, are similar to those for the unfiltered. The results for simazine are excluded because of uncertainties in the quantitation of chromatograms from the filter extracts. Based on the sorption properties, the filters may be divided into two groups. The cellulose nitrate filters, ie 1 and 2, retained a high proportion of pesticides DDE, dieldrin, endrin, TDE, DDT and pyrethroids but little of the more water soluble compounds such as α-BHC, lindane and atrazine: this is illustrated in figure 6.4. Although there is only a little difference in the performance of the two filters, the pretreatment by boiling to reduce surfactants leads to a greater retention of most of the pesticides. The other filters retained the pesticides to a lesser extent with no appreciable adsorption of α-BHC and lindane for any of the filters and < 10% retention of dieldrin and endrin (see figure 6.4). Of these three filters, the Nuclepore retains TDE, DDT and the pyrethroids more than the other compounds. The retention by the inorganic Anopore and GF/F glass microfibre filters are similar. Some sorption of atrazine on the GF/F filter was detected and this was far greater than might be expected from the amount in the residual water. The retention of total pesticides by the filters was in the order CN2 > CN1 > NP > Anopore > GF/F with amounts of 203, 176, 80, 52 and 45 ng respectively.

The contribution of the pesticides dissolved in the residual water retained on the filters and determined by the weight change following freeze-drying, was found to be relatively small amounting to < 4% of the total extracted from the filters in most instances. The exception was DDT filtered through the GF/F filter with a calculated 8.8% contribution from the

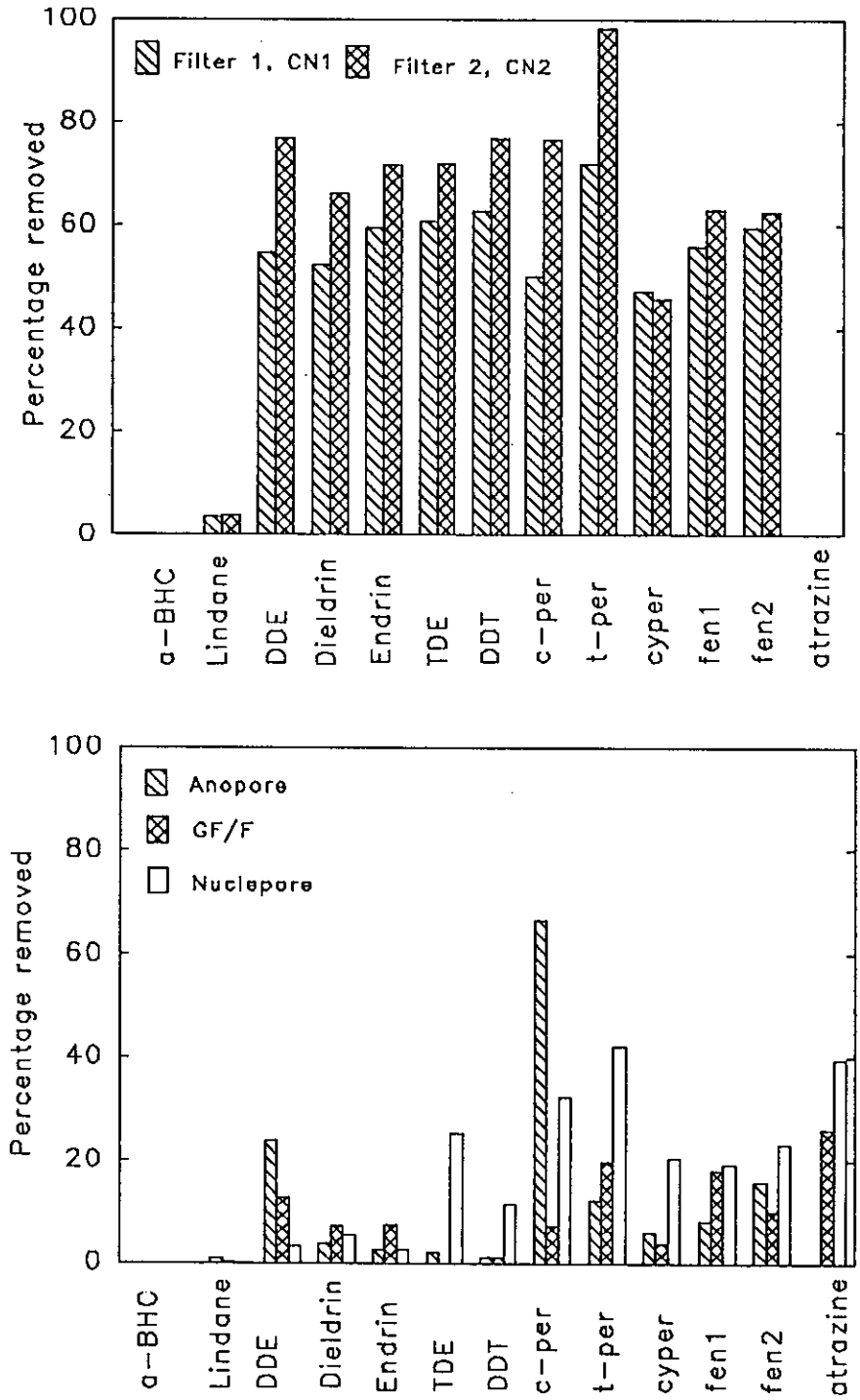


Figure 6.4 Illustration of the removal of pesticide after passage through a membrane filter expressed as a percentage of the total addition minus the amount measured on the glass. The results indicate that cellulose nitrate membranes do not retain α-BHC, lindane or atrazine whereas the inorganic filters, GF/F and Anopore, retain a smaller amount of a wide range of pesticides.

residual water. The most soluble compounds, lindane and atrazine, were not detected on the filters although a calculation indicated trace amounts ie < 0.06 ng, were expected from the residual water. Some differences in the retention of filtrate was also noted, with the GF/F filter retaining the largest volume *ca* 0.34 ml compared with the other filters, <0.18 ml with the lowest retained by the Anopore filter (0.06 g).

In an attempt to quantify these results, a value of the adsorption constant, K_a, was estimated by using the geometric area of the exposed filter. Although the actual contact area with the filter matrix is likely to be much greater, it is difficult to make a reliable estimate of this. The calculation also assumes a rapid attainment of equilibrium as the pesticides contact the filter matrix. The results, shown in table 6.3, enable comparison to be made with other filters. The geometric area of the GF/F filter was 9.6 cm^2 which was slightly lower than 12.6 cm^2 obtained for the other filters.

Table 6.3 Estimates of K_a in cm, calculated from the amount of pesticide on a filter (ng), the geometric surface area exposed to the solution (cm^2) and the concentration of pesticide in the filtrate (ng cm^{-3}). Key: - indicates that the pesticide was not detected in solution.

	Filter Number Key: CN, cellulose nitrate; NP, nuclepore.				
Pesticide	1 CN1	2 CN2	3 Anopore	4 GF/F	5 NP
α-BHC	0	0	0	0	0
lindane	0.52	0.49	0.12	0.03	0
DDE	309	121	10.3	5.6	48
dieldrin	206	2601	0.50	1.2	0.92
endrin	37	285	0.27	0.99	0.33
TDE	-	-	0.38	0	26
DDT	-	-	0.39	0	133
cis-permethrin	-	208	-	2.4	-
trans-permethrin	-	343	25	11.6	-
cypermethrin	-	-	10.9	1.8	-
fenvalerate 1	415	-	10.5	8.1	33
fenvalerate 2	226	-	21	4.1	68
atrazine	0	0	0	2.0	5.2

The results in table 6.3 show that some pesticides interact strongly with the cellulose nitrate filters to the extent that they were not detected in solution. In some instances, no pesticide could be detected on the filter eg atrazine on the cellulose nitrate and inorganic Anopore filter and α-BHC was not detected on any of the filters tested. In general the pyrethroids have a greater affinity for the filters than the organochlorine pesticides. The relationship between Log K_a and Log K_{ow}, shown in figure 6.5, is similar for the GF/F and Anopore filters with a lower slope than obtained for the Nuclepore filter. Evidently there is little difference in the retention of pesticides on the GF/F and Anopore filters.

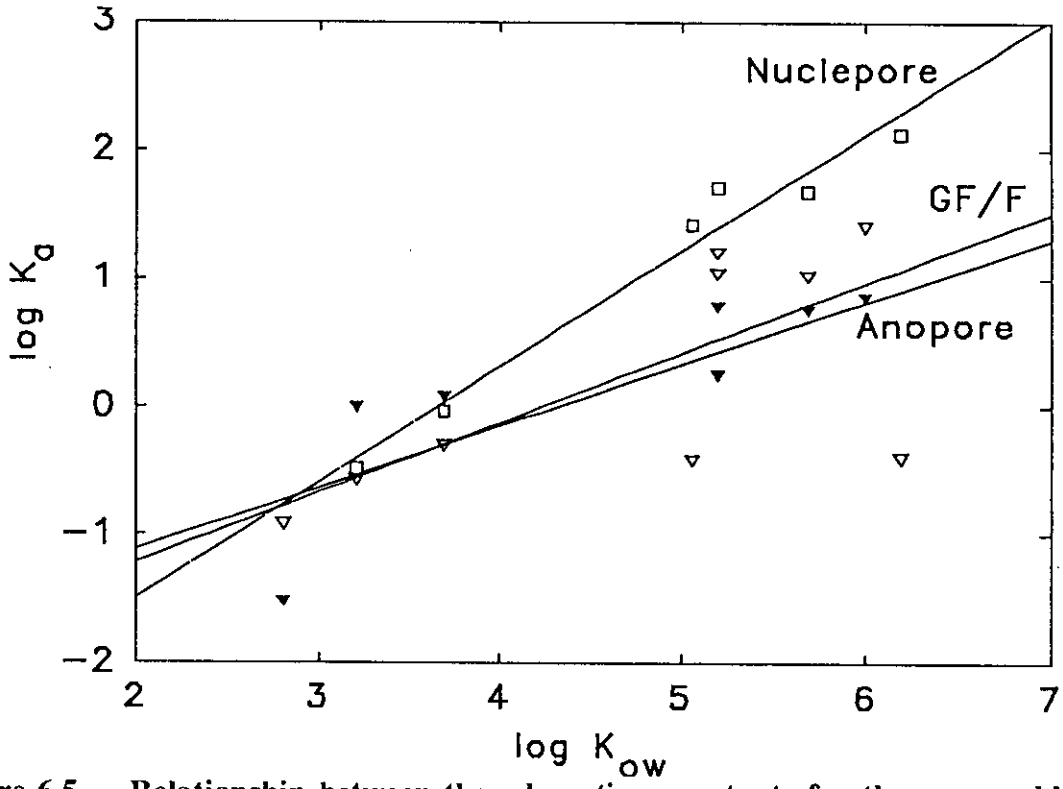


Figure 6.5 **Relationship between the adsorption constants for the organochlorine pesticides, calculated assuming a rapid equilibrium, and the octanol-water partition coefficients.**

The regression lines for the three filters are also shown.

The results above highlight some problems in handling aqueous solutions containing low concentrations of pesticides. It has been demonstrated that adsorption by containers is very important for some compounds such as the pyrethroids and organochlorines with high octanol-water partition coefficients eg for a glass surface a Log $K_{ow} > 4.9$ is expected to lead to > 10% adsorption to the container wall of a 1 litre bottle. The separation of suspended solids by filtration is possible by the careful choice of membrane filters and a detailed mass-balance taking account of the retention of the pesticides on the filter matrix.

6.4 Analysis of suspended solids collected from a field site

1 litre samples were collected from the Rosemaund Farm site (Site G, Appendix 7.1) at 1 hour intervals over a storm period of 24 hours starting at 24.00 h on 21.2.1991. These samples were stored in dark glass bottles with foil-lined Bakolite screw caps in the dark at a temperature of about 5°C until analysis. All of the samples contained appreciable suspended solids derived from soil erosion and also visible fragments of insects tentatively identified as *Sialis* spp. The sediment from this stream (sites E, F & G in table 4.4) has been found to contain appreciable concentrations of dieldrin, DDT, DDE, TDE, deltamethrin and simazine.

6.4.1 Bulk separation by centrifugation

Isolation of a bulked sample of suspended solids from 20 of the samples was undertaken by continuous-flow-centrifugation. The combined samples represent a wide range of hydrograph stages during which suspended solid sources may vary.

A refrigerated centrifuge (MSE HS.18) fitted with an MSE continuous action rotor was used to separate the suspended solids from the samples. The rotor was run at 14000 ± 1000 rpm (giving approximately 14000 g). Sample throughput was 100-150 ml min^{-1} and the centrifuge bowl temperature was less than 5°C. Sediment was collected on a polypropylene insert. The efficiency of suspended solids recovery by the centrifuge was not tested. One sample (bottle 7, visually assessed to be the most turbid of the set) was collected after a single-pass through the centrifuge. The centrifuged sample was found to contain 4.3 mg filterable suspended solids which suggested a recovery in excess of 80%. Samples were shaken thoroughly and then passed through the centrifuge in 2 l batches. Supernatant fluid was returned to the original pair of bottles, shaken and recentrifuged.

After 20 samples had been centrifuged, the accumulated sediment was resuspended in the residual water in the centrifuge bowl (220 ml), transferred to a polycarbonate centrifuge tube of known weight and centrifuged (10 min, 12000 rpm (18000 g)). The supernatant was decanted from the pellet and the tube and contents were frozen to −20°C then freeze-dried. After 4 days the tube and contents were reweighed. The weight of suspended solids recovered was 959.7 mg. The pellet was then scraped from the tube and crushed in a glass mortar. 934.3 mg were transferred to a pre-cleaned Soxhlet thimble (Whatman cellulose double thickness) and extracted for 4 hrs (72 exchanges) in a Soxhlet unit with DCM (150 ml). The extract was transferred to a Kuderna-Danish (KD) unit and evaporated to a drained volume of about 5 ml. The volume was further reduced under a stream of dry nitrogen and washings from the KD unit added. The sample was then evaporated to about 1 ml and transferred to a pre-weighed injection vial with approximately 0.5 ml of fresh DCM used to wash the residues from the evaporation vial. The sealed injection vial was reweighed to allow the calculation of the extract volume (1.60 ml). A blank control extraction was run in parallel with the suspended solids sample.

Table 6.4 Target, T, and Confirmation, C, ions used in the GC/MS analysis of the extracts from suspended solids.

Organochlorines			Pyrethroids		
	T	C		T	C
α-BHC	181	219	Permethrin	183	163
Lindane	181	219	Cypermethrin	163	181
Heptachlor	100	272	Fenvalerate	167	125
Aldrin	263	66	Deltamethrin	181	253
DDE	246	176			
Dieldrin	76	263	Triazine Herbicides		
Endrin	263	243			
TDE	253	165	Simazine	201	186
DDT	235	165	Atrazine	200	215

All samples were analysed using GC/MS in selected-ion-mode with the target and confirmation ions listed in table 6.4. The presence of a compound was recognised if target and confirmatory ion peaks were present within 0.03 mins of the Retention Time (RT) of peaks in standards. Standards at two levels were run before and after each sample series. Pesticides were quantified with reference to these external standards.

The RT of simazine and atrazine peaks in standards were variable and dependent on concentration injected. Criteria for recognition of these compounds were: peaks within ± 0.1 mins of the mean RT in standards and the presence of two confirmatory ion peaks within 0.01 mins of the target ion peak.

Quantitation with reference to external standards is on the basis of the target ion areas unless otherwise stated. Where the presence of interference in the target ion peak is suspected, for example a large excess in concentration measured using the target ion compared to the confirmatory ion peak, the value given by the confirmatory ion is reported.

The results of the analysis are shown in table 6.4. All the pesticides, apart from deltamethrin, found in the stream sediment on the previous analysis (table 4.4) were determined in the suspended solids. The GC/MS method used was found to be insensitive to the occurrence of deltamethrin but insufficient time was available to reanalyse the extracts using GLC with the electron-capture-detector.

The results show substantial concentrations of all the pesticides with reasonable agreement between the results obtained at the two levels of calibration. The target ion is the most sensitive and produces the most reliable results. Agreement with the results from the analysis using the confirmation ion is best for DDE and less so for the other compounds. However the differences do give some indication of the uncertainty in the GLC analysis.

An example of the contribution of suspended solids to the transport of pesticides is illustrated in figure 6.6 for different concentrations of suspended solids (abbreviated SS in figure 6.6). This calculation is based on an equilibrium between the dissolved pesticide and suspended solids and assumes a linear isotherm with K_d values calculated from the K_{om} (partition coefficient for organic matter) predicted by the Collander relationship (Briggs, 1981) and organic matter concentration of 40% by mass (see §6.5 for details of the modelling). This value was chosen from studies on the River Frome involving the determination of organic matter of suspended particles (separated using a 0.8 µm pore size membrane filter (Pinder *et al.* 1982). The organic matter content of suspended solids is likely to vary between locations on the same river and between rivers as well as during spates.

Table 6.5 **Results of the analysis of the suspended solids separated by centrifugation. The mass of suspended solids extracted was 934.3 mg.**

Key: SS, suspended solid; RT, deviation of the retention time from the value obtained for the standard

Pesticide	Concentration of standard /µg ml^{-1}	Target ion RT /min	Concentration in SS /µg kg^{-1}	Confirmation ion RT /min	Concentration in SS /µg kg^{-1}
DDE	0.1	0	121	-0.01	117
	0.5	0	102	-0.01	105
mean			*112*		
Dieldrin	0.1	0	79	0	126
	0.5	0	71	0	118
mean			*75*		
TDE	0.1	-0.01	42	-0.02	28
	0.5	-0.01	31	-0.02	23
mean			*37*		
DDT	0.5	0	2633	-0.01	2971
Simazine	0.2	0	41	0	-
	0.2	0	33	0	-
	2.0	0	25	0	-
	2.0	0	20	0	-
mean			*30*		
Atrazine	0.2	0	20	0	63
	2.0	0	15	0	44
mean			*18*		

The log (K_{om}) values for DDE, dieldrin and permethrin are in the range of 3.3-4.2 depending on the choice of the appropriate octanol-water distribution coefficient. For these compounds, the contribution of suspended solids in the transport is significant, particularly in spate conditions when the suspended solids concentration may reach 300-600 mg dm^{-3}. Such values have been found in rivers such as the Frome (NGR SY 869 869; Farr & Clarke, 1984) and much higher in small streams adjacent to arable land. The contribution of colloids to the transport is also likely to be significant, particularly during spates or for rivers with a high concentration of polyanionic acids such as fulvic and humic acids.

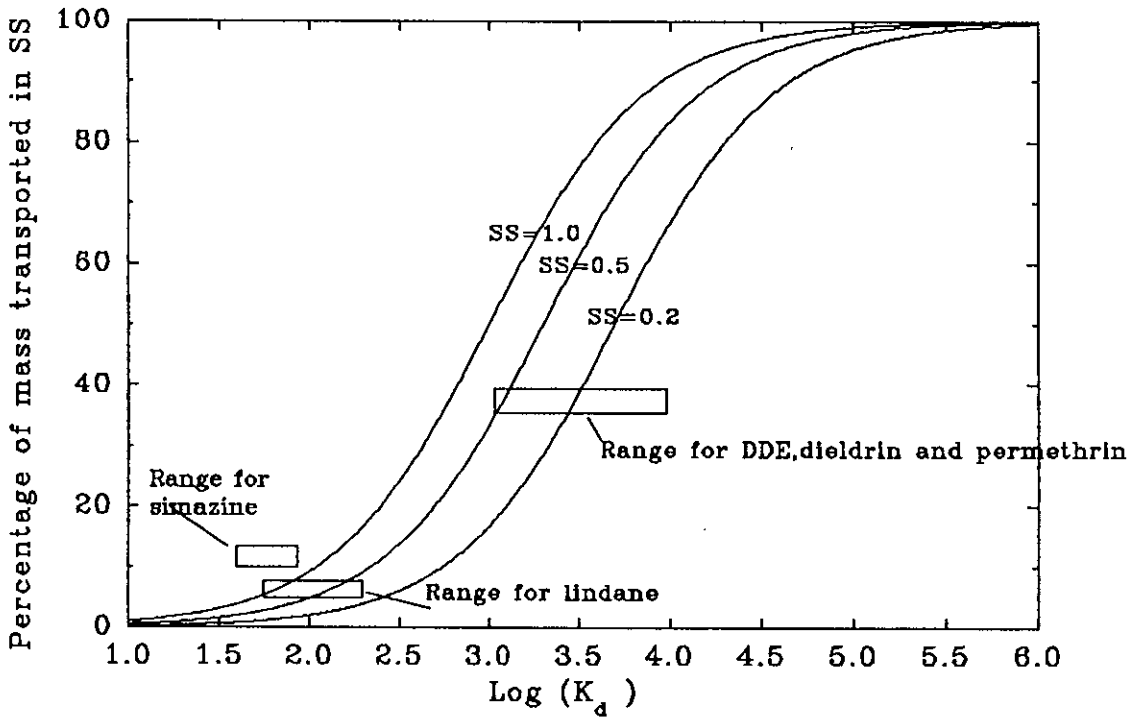


Figure 6.6 **Predicted transport of pesticides on suspended solids (SS).**

The partition coefficients are calculated from the Collander relationship (Briggs 1981) for suspended solids with an organic matter content of 40%. The range of values for the coefficients reflect the uncertainty in the octanol-water partition coefficients. Note: suspended solids (SS) are in units of g dm^{-3}.

The contribution of suspended solids to the transport of simazine is expected to be less than 10% by mass. The assumption of an equilibrium between the dissolved simazine and sorbed fraction is however still uncertain as demonstrated by the recent results of Pignatello & Huang (1991) for atrazine sorption onto field soil samples. Their results indicated that contaminated samples collected from the field can contain a large fraction of atrazine in a slowly reversible sorbed state and that this fraction increases with time of exposure to the pesticide. This implies that suspended solids derived from the erosion of contaminated soil may contain much higher concentrations of atrazine than is expected from the concentration found in the associated water. The results for simazine reported in this work support this conclusion and cast doubt on the validity of the equilibrium assumption for triazine compounds.

6.4.2 Separation by filtration using GF/F microfibre pads

The sample (1 litre) was thoroughly shaken and 100-200 ml aliquots filtered through a water rinsed, preweighed Whatman GF/F glass fibre filter pad (45 mm). The filter was clamped in a glass holder with a sintered glass support. The differential pressure was kept below 20 kPa. When filtration became very slow, the batch of liquid in the holder was allowed to complete filtration and then the pressure differential was increased for a further 5 minutes. Normally a second preweighed GF/F filter was needed to complete the separation. After completion, both filters were folded using tweezers and inserted in a preweighed amber-glass reaction vial (3 ml). The open vial was frozen to < –20°C, placed in a flask and freeze dried (18 hrs). Suspended solids weights were calculated from the final weight of vial and contents. After drying, approximately 8 ml of DCM was added and the vial crimp sealed over a PTFE faced septum. The vial was then shaken at 20°C to extract pesticide residues from the retained suspended solids. The vial was opened after 16 hrs shaking. The DCM extract containing fragments of filter and suspended solids was pipetted into a syringe attached to a stainless steel filter unit fitted with a pre-cleaned (DCM) Whatman glass fibre filter (GF/F 25 mm). The extract was filtered under slight positive pressure into a graduated tube. Residual extract was washed from the reaction vial and filter unit with a further 2 x 5 ml fresh DCM and filtered as above.

Extract and washings were evaporated to dryness under a stream of dry nitrogen, then taken up in *ca* 2 x 0.1 ml fresh DCM. The solution was transferred to an injection vial previously weighed. The injection vial was sealed and reweighed allowing calculation of the weight and volume of extract.

All aqueous water samples were analysed by solvent extraction with DCM using a similar procedure to that described previously, §3.5.1.

Two of the samples, collected during the storm, that had been retained uncentrifuged were shaken thoroughly and then mixed in a 2.5 litre glass bottle. The mixed sample was divided into two equal subsamples of 965 ml. One of these subsamples was filtered as described above and the pesticides in the particulate and aqueous phases extracted and analysed separately. The other sample was treated as a "whole" water sample and extracted without filtration. The results of the GC/MS analysis are shown in table 6.6.

Table 6.6 **Results of the analysis of the water sample after filtration, the associated suspended solids and the 'whole' water sample containing suspended solids. The weight of suspended solids was determined as 36.2 mg (dry weight). RT is the deviation of the retention time from the value obtained for the standard calibration.**

Pesticide	ion/ amu	RT /min	Filtered water concentration /ng dm^{-3}	RT /min	Suspended solids concentration /µg kg^{-1}	RT /min	Whole water sample /ng dm^{-3}
Lindane	181	−0.02	6.6	-	ND	−0.03	7.9
	219	−0.01	5.7	-	ND	−0.01	6.1
DDE	246	−0.02	5.4	−0.02	224	−0.02	14.9
	176	−0.02	14.5	−0.03	369	−0.03	18.4
Dieldrin	79	-	Tr	−0.02	93.8	−0.03	10.8
	263	-	Tr	−0.03	Tr	−0.02	10.1
TDE	235	−0.02	1.7	−0.02	53.3	−0.02	3.4
	165	-	Tr	-	ND	−0.02	2.7
DDT	235	-	ND	0.01	1587	−0.04	550
	165	-	ND	-	ND	−0.04	65
Simazine	201	−.02	337	−0.05	46	−0.02	343
	186	−.01	325	−0.05	37	−0.01	349
Atrazine	200	0	75	0.02	73	−0.02	83
	215	−0.01	79	0.02	198	0.01	84

Although the results are not directly comparable with those from the analysis of the centrifuged sample, the same pesticides are present in both suspended solid samples, and the concentrations of dieldrin, TDE and simazine are in reasonable agreement. In addition, lindane was found in both the filtered water and whole water samples at a similar concentration to that determined previously at site G ie 12 ng dm^{-3}. Lindane was also found in the sediment at site G but at a very low concentration (0.8 µg kg^{-1}), and below the limit of determination using the GC/MS.

A comparison of the amounts of pesticide in the filtered water and suspended solids with the total amount determined in the whole water sample is shown in table 6.7 and figure 6.7. Apart from dieldrin, the results of the mass balance show good agreement with the majority of the lindane, atrazine and simazine in the soluble and colloidal fractions and most of the DDT, DDE and TDE associated with the suspended solids.

Table 6.7 Mass-balance for the pesticides separated by filtration of the suspended solids. Key: Tr: trace detected but could not be quantified.

Pesticide	Amount in filtered water /ng	Amount in suspended solids /ng	Total /ng	Amount in 'whole' water sample /ng
Lindane	6.4	0	6.4	7.6
DDE	5.2	8.1	13.3	14.4
Dieldrin	Tr	3.4	3.4	10.4
TDE	1.6	1.9	3.5	3.2
DDT	Tr	57.5	57.5	62.3
Simazine	324.8	1.7	326.5	330.5
Atrazine	71.9	2.6	74.5	80.1

The results in table 6.6 may be used to determine the distribution coefficients at room temperature. The values of log K_d for DDE and TDE of 4.6 and 4.5 respectively are as expected relatively high, reflecting the lipophilic character of these compounds. It is not possible to calculate K_{om} without a knowledge of the organic matter content of the suspended solids. The K_d values for simazine and atrazine are 137 and 973 respectively and are much higher than expected from the adsorption experiments on the sediment material and other results published from soil sorption studies eg Talbert & Fletchall (1965), Williams (1968), Brown & Flagg (1981), Basile et al (1990), and Pignatello & Huang (1991) (see in table 7.4). However, the value of K_d = 137 $dm^3\ kg^{-1}$ is in reasonable agreement with that value calculated for the sediment at site G ie 145 $dm^3\ kg^{-1}$ (§4).

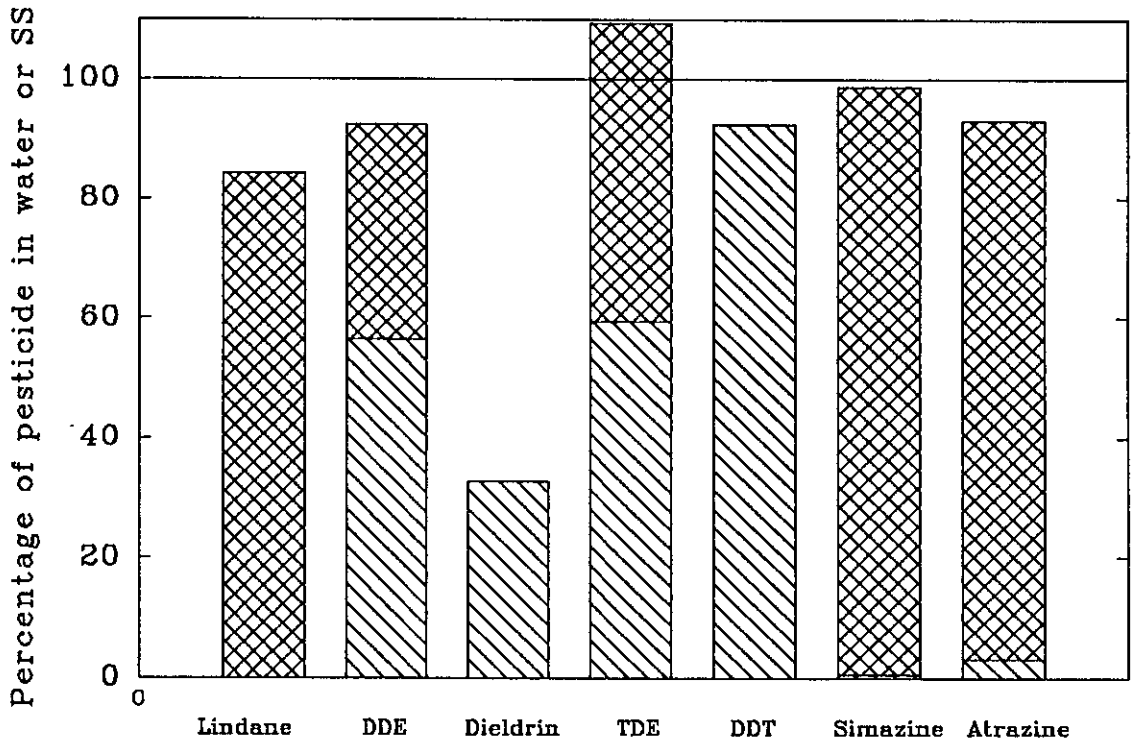


Figure 6.7 **Comparison of the percentage of pesticide found in filtered water and suspended solids measured independently. The total pesticide was determined from the analysis of a "whole" water sample.**

Key: upper, water; lower, suspended solids.

6.5 Formulation of a process-based model to describe pesticide transport

The transport of pesticides into rivers may be treated using a mass-balance approach by dividing the watershed into different units. The area in each of the n units is assumed to have approximately the same surface run-off and concentration of pesticide. The units may be related to different agricultural usage including for example, dairy farmland, woodland, arable or different types of industrial regions or urbanised areas. In these situations the mass of a pesticide input into a section of a river may be classified as (a) surface run-off, R_1; (b) subsurface run-off, R_2; (c) groundwater run-off or input, R_3; (d) point sources, R_4.

The mass of pesticide in the surface run-off may be expressed in terms of a summation of the contribution from individual units within the matrix ie:

$$R_1 = \sum_{i=1}^{n} A_i S_i C_i \qquad (6.3)$$

where A_i is the area of the unit (ha), S_i is the run-off in a unit area ($dm^3\ ha^{-1}\ d^{-1}$) and C_i is the concentration of pesticide in the run-off. Contributions to R_1 are only likely when the pesticide has been used within the defined unit. If $R_3 = 0$, then subsurface run-off may be calculated from the balance:

$$R_2 = C_G \sum_{i=1}^{n} (P_i - ET_i + S_i) A_i \qquad (6.4)$$

where P_i is the rainfall ($dm^3\ ha^{-1}\ d^{-1}$), ET_i the evapotranspiration and C_G the concentration of pesticide in equilibrium with the soil. For many lipophilic compounds, C_G will be close to zero and so R_2 is likely to contribute only a minor amount to the total balance.

The total input of the pesticide into the river is then:

$$R_t = \sum_{i=1}^{n} (C_i - C_G) A_i S_i + C_G F \sum_{i=1}^{n} A_i + R_4 \qquad (6.5)$$

where F is a constant ($= P_i - ET_i$) for all the units. After the application of pesticides to crops the difference between C_i and C_G is expected to diminish.

The mass-balance for a stretch of river may then be written in the general form:

$$0 = \int_0^t q_i C_i\, dt + R_t - \int_0^t q_o C_o\, dt + \Sigma_i f_i(t) \qquad (6.6)$$

where q_i and q_o are the inflow and outflow rates for a river section and C_i, C_o the corresponding concentrations. The processes occurring in the section may be represented in terms of a function, $f_i(t)$. These processes may either consume pesticide eg sorption onto suspended solids or sediment, sedimentation, degradation, resuspension and can be applied to any of the pesticide fractions, *viz* soluble or pesticide associated with suspended solids or colloids, as long as the interconversions between the various forms is included in $f_i(t)$.

In principle, it is difficult to estimate R_t and $\Sigma_i f_i(t)$ without extensive measurements in a characterized catchment. However, it is possible to investigate equation 6.6 in mesocosm experiments eg recirculating experimental streams (House *et al.* 1988), or manipulated channels. In this case the diffuse and point inputs can be measured and controlled enabling the calculation of the process term $\Sigma_i f_i(t)$ at any time. This may then be compared with theoretical predictions of $f_i(t)$.

Of particular interest to this project, is the proportion of the total pesticide transported in association with suspended solids. This may be estimated from equation 6.6 with R_t and $\sum_i f_i(t) = 0$ so that the transport into a river section over time, Δt, is:

$$m_i\ (\mu g\ of\ pesticide) = q_i\ C_i\ \Delta t + q_i\ n_a\ C_s\ \Delta t\ /10^6 \qquad (6.7)$$

where q_i: $dm^3\ s^{-1}$; C_i: $\mu g\ dm^{-3}$; Δt: time interval in s; n_a is the adsorption amount: $\mu g\ kg^{-1}$ (dry weight) and C_s is the concentration of suspended solids in $mg\ dm^{-3}$. The percentage of the pesticide associated with the suspended solids, %SS, is then:

$$\%SS = 100\ n_a\ C_s\ /\ (C_i \times 10^6 + n_a\ C_s) \qquad (6.8)$$

Further evaluation necessitates a knowledge of the adsorption isotherm relating n_a to C_i ie in its general form:

$$n_a = f\ (T,\ pH,\ I,\ C_i,\ OM) \qquad (6.9)$$

where I is the ionic strength and OM the dissolved organic matter. Various equations are often applied to describe the adsorption of trace organic compounds to minerals and sediments. These include the Freundlich, Langmuir, Tompkin, Volmer and Henry's law isotherms. The application of model isotherms to describing adsorption on heterogeneous surface has been reviewed by House (1983). All the isotherm equations applicable to heterogeneous surfaces reduce to the limiting Henry's law form at low adsorbate concentrations when the adsorbate - adsorbate interactions may be neglected. In this instance:

$$n_a = K_d\ C_i \qquad (6.10)$$

where n_a: $\mu g\ kg^{-1}$; C_i: $\mu g\ dm^{-3}$ and K_d is the distribution coefficient defined previously (equation 4.1) in units of $dm^3\ kg^{-1}$. Substitution of equation 6.10 into equation 6.8 leads to further simplification:

$$\%SS = 100\ K_d\ C_s\ /\ (10^6 + K_d\ C_s) \qquad (6.11)$$

so that the percentage transport on suspended solids is independent of the concentration of the pesticide in the river water and depends only on the concentration of suspended solids in the river and the affinity of the pesticides to the suspended matter ie the greater the affinity, the larger the value of the distribution coefficient, K_d. Equation 6.11 is useful in providing an estimate of the load of pesticide transported with suspended solids but the underlying assumptions implicit in the derivation must be remembered, ie:

(a) Large temperature variations (eg > 5°C) should necessitate the temperature dependence of K_d to be included in equation 6.11.

(b) The heterogeneity of the suspended solids will vary considerably during the year and also during storm events. This means that K_d will vary according to the source and composition of the suspended solids. For neutral lipophilic pesticides, this variation may be accounted, in a first approximation, by normalisation of the partition with respect to organic

matter or organic carbon content of the suspended solids eg substitution of $K_{OM} = 100\ K_d$ /OM into equation 6.11 where OM is the percentage organic matter and measurement of organic matter content of the suspended solids during different flow conditions.

(c) Equation 6.8 represents an instantaneous determination. The generalisation of equation 6.7 to determine monthly or annual loads involves integration over a time period (months or years for load evaluation) with information on the variability of q_i, E_i, C_s and K_d with time. At the moment data of q and C_s is available at a limited number of sites. C_i is measured for certain red list substances but no information on K_d (or K_d and OM) for suspended solids is available.

(d) The estimate of n_a from equation 6.10 is generally valid for trace organics which are reversible adsorbed onto the solid. However, some pesticides eg the triazines (see §7), are not always reversible adsorbed and this leads to an underestimate of n_a using the K_d from laboratory experiments in which reversible sorption occurs over short periods eg < 24 h. In this instance, the specific behaviour of individual pesticides needs to be assessed in long-term experiments.

The results obtained from equation 6.11 are illustrated in figure 6.6 for log K_d in the range of 1 to 6 and suspended solids between 200 and 1000 mg dm^{-3}. The values of K_d were calculated from the octanol-water coefficients (range of values produced in the literature) and the Collander relationship (Briggs 1981) using an organic matter content (OM) of 40%. The results for lindane and simazine show a relatively small percentage of the pesticides are associated with suspended solids ie < 10% for suspended solid concentrations < 500 mg dm^{-3}. Even using the field distribution coefficient for simazine, *ca* 137 $dm^3\ kg^{-1}$, leads to results in the range of those predicted for lindane. In contrast, the neutral and lipophilic pesticides eg DDE, dieldrin and permethrin (synthetic pyrethroids in general), indicate substantial ie > 50%, transport by suspended solids when concentration ≥ 500 mg dm^{-3}. One reason for the uncertainty of the prediction for permethrin is the differing reports of K_{ow} in the literature *viz*: log K_{ow} values of 3.49 (Coats & O'Donnell-Jeffery 1979), 6.50 (Schimmel *et al.* 1983) and 5.23 (Lockhart *et al.* 1983). There is also a need to determine K_d directly from adsorption isotherm measurements on different sediments and suspended solids to enable the validation of the Collander relationship for the synthetic pyrethroids.

7. ADSORPTION OF SIMAZINE ON RIVER SEDIMENTS

The high values of the field distribution coefficient obtained for simazine (§4) prompted further study of the adsorption behaviour on sediments. The interaction between simazine and suspended sediment was studied in detail to evaluate the distribution coefficient, the temperature dependence of adsorption and the kinetics of adsorption.

7.1 Materials

Sediment A. This sediment was obtained during the field survey from site E (Appendix 7.1) and did not contain detectable quantities of simazine. The mineral composition is shown in table 7.1. The specific surface area was determined by nitrogen adsorption as 5.34 $m^2 g^{-1}$ with a BET constant of 41. The total organic matter content was 8.2 ± 0.1% determined by combustion at 550°C. The sediment had been freeze-dried and sieved through a 0.5 mm brass sieve and stored in the dark at 5°C.

Sediment B. This was a river sediment obtained from an artificial pond (NGR 870867) through which part of a stream at the Institute of Freshwater Ecology, River Laboratory site may be directed. The sediment was collected on 20 November 1988, sieved whilst wet through a 2 mm brass sieve, dried to constant weight at 85°C and then passed successively through sieves of 2, 0.319 and 0.125 mm size. The fraction which passed through the 0.125 mm sieve was retained and used in the experiments described below. XRD analysis of the sediment revealed that the mineral composition was mainly quartz and calcite, with some feldspars and mica present. The total organic matter content was estimated from the ignition loss at 550°C to be 22.2% by weight. The specific surface area was determined by nitrogen adsorption using a multi-point BET analysis and was found to be 8.24 $m^2 g^{-1}$ with a BET c constant of 56.0. This sediment has been used in adsorption and biochemical studies on anionic surfactant interactions with sediments (Marchesi *et al.* 1991b).

Table 7.1 X-ray diffraction analysis of sediment samples E-G. Sediment E did not contain detectable amounts of simazine. The three sediments are similar in their mineralogical composition.

Site Code	Percentage composition by mass					
	Quartz	Calcite	Kaolinite	Illite	Smectite	Non-expandable clays
E	41	0	17	23	5	4
F	44	0	15	22	4	5
G	49	4	13	18	2	4

All samples ~ 10% organic matter

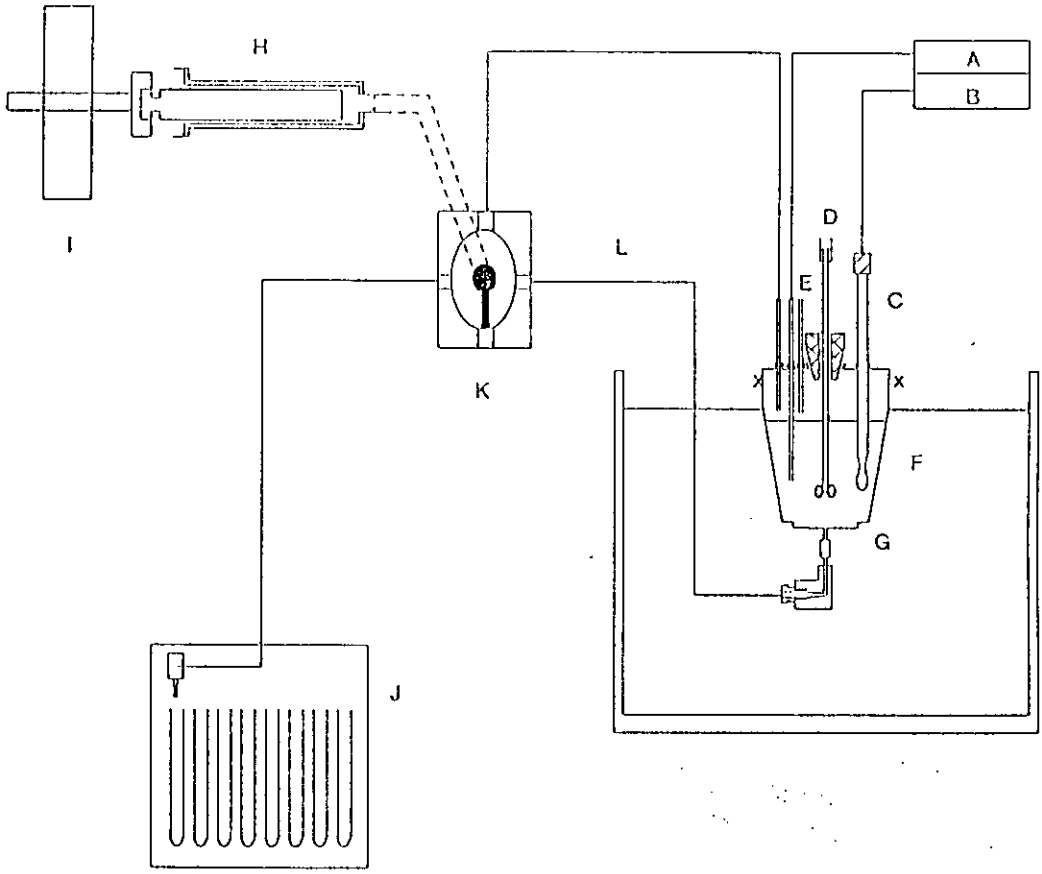


Figure 7.1 **Automated apparatus for the determination of the adsorption/desorption isotherms of pesticides on sediments and suspended solids.**

Key:

A: autoburette containing the aqueous stock solution of pesticide
B: pH meter connected to a combination glass electrode
C: combination reference and glass electrode for pH measurement
D: stirrer mechanism; paddle stirrer and motor
E: CO_2/N_2 gas supply used to control pH in the solution
F: water thermostat
G: membrane filter with support disc
H: syringe pump
I: linear actuator
J: automated sample collector
K: 4-way valve
L: small bore PTFE tubing

7.2 Apparatus for the adsorption measurements

An automated system was developed to permit the measurement of adsorption and desorption isotherms in an experiment using a single batch of sediment. The adsorption cell and associated apparatus is shown in figure 7.1. The solution in contact with the suspended adsorbent was circulated using a syringe pump through 0.2 μm cellulose nitrate filter (pre-extracted in distilled water, 100°C for 5 minutes) via valve K, operated by a stepper-motor.

This enabled the PTFE tubing and any 'dead volume' to be flushed thoroughly before a sample was directed to the fraction collector, J. The tube leading to the fraction collector was flushed with air after each sample. Approximately 200 ml of 10 mM $KHCO_3$ was weighed into the adsorption cell and allowed to come to thermal equilibrium with a CO_2/N_2 mixture to give a pH of 8.1 ± 0.1. The adsorbent was added to the cell and left for 1 hour before a sample was removed for analysis. A predetermined volume of stock solution (simazine in distilled water) was added from the autoburette and after a pre-determined time, a sample was removed for analysis. The procedure was repeated with successive additions of the stock simazine solution. The adsorption isotherm was computed from the data retrieved from the autoburette and the simazine assay data, which were introduced to the program at the end of the experiment. All operations of the syringe pump, valve, timer and autoburette were under computer control and were therefore automatic. Prior to all adsorption measurements, the system was calibrated using the above procedure with and without the membrane filter installed in the adsorption cell and in the absence of the adsorbent.

Desorption measurements can be made by replacing the stock solution with the background electrolyte, in this case 10 mM $KHCO_3$, and dilution of the adsorbate.

7.3 Preparation of the aqueous simazine stock solution

It was necessary to prepare a concentrated aqueous stock solution of simazine, preferable without the direct addition of simazine solid or an organic solvent. The dissolution of simazine in water was found to be very slow. The solubility of simazine at 25°C is not known but values at 20°C of the order of 5 mg dm^{-3} have been reported. The direct addition of simazine to water to yield a final concentration of 5 mg dm^{-3} causes problems because the solid adheres to the glass surfaces of the container and to the surface of the water. As shown in figure 7.2, the dissolution of the suspension at room temperature is slow requiring over 4 days to reach a concentration of half the published solubility limit. An alternative procedure, not involving the direct addition of the simazine solid was investigated. This involved packing a glass solid-phase-extraction column (6 ml) with solid simazine between two PTFE frits. The mass of simazine was determined, *ca* 0.17 g, before the column was placed on the inlet to a 500 ml flask. A weighed amount of distilled water was then placed in the flask and continuously recirculated through the simazine column at a rate of ≈ 5 ml min^{-1}. In these conditions the attainment of higher concentrations of simazine in a shorter time was possible (see figure 7.2) although a concentration of 5 mg dm^{-3} was not achieved even after 4 days recirculation. The simazine column was dried and reweighed to evaluate the loss of simazine.

The concentration of the 0.2 μm filtered stock solution was measured using the extraction and analysis procedure described in §3. The stock solution was stored at room temperature with checks on the concentration prior to each adsorption experiment.

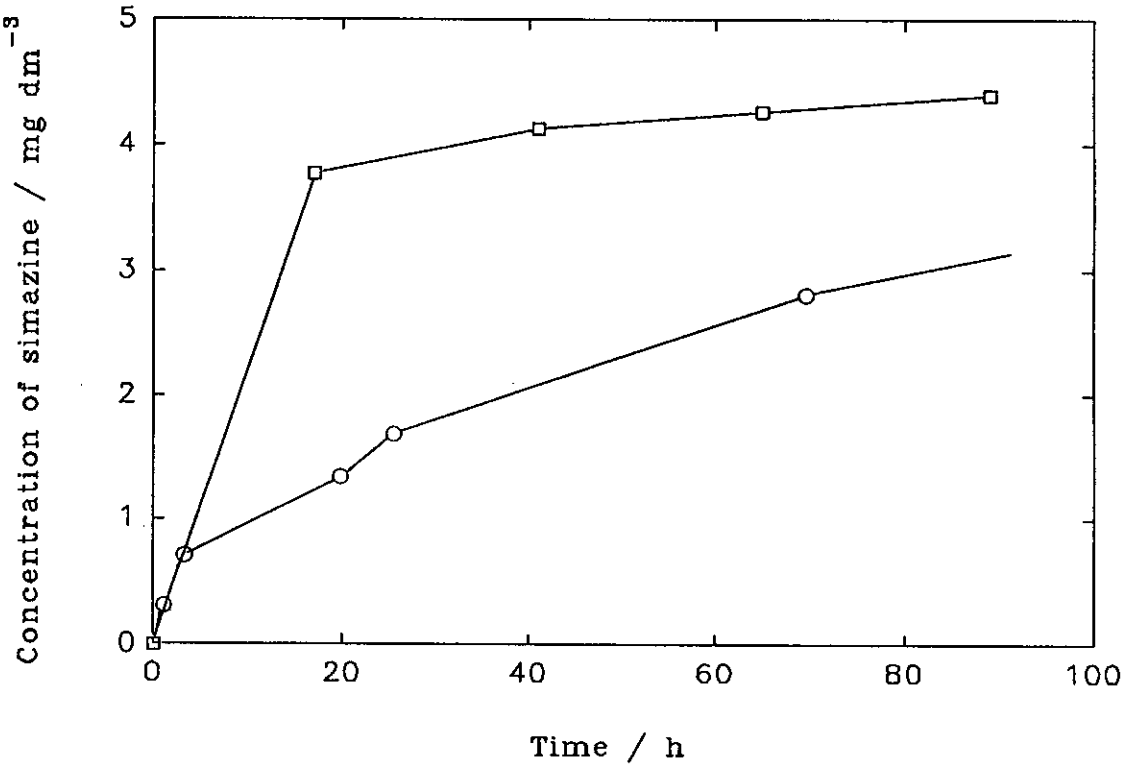


Figure 7.2 **Comparison of two methods of preparation of the simazine stock solution used in the adsorption experiments.**

The upper points correspond to the recirculation method and the lower to the results from the stirred suspension.

7.4 Control experiments using simazine

Prior to any adsorption measurements on the sediments it is necessary to perform control experiments to evaluate the adsorption behaviour of the filter pads used in the cell. This was done by determining the UV absorption at 222 nm, $A_{222}^{1\ cm}$, of simazine solutions in the concentration range of 0.01 to 0.4 mg dm^{-3} to obtain a calibration line:

$$c\ (mg\ dm^{-3}) = 0.0162 + 3.8464\ A_{222}^{1\ cm} \qquad (7.1)$$

The simazine concentrations were determined using GLC/MSD. This was then used to interpret data from the adsorption cell in experiments with and without the filter installed. The filtrate was circulated through a 1 cm quartz-cell fitted in a DU8 Beckmann spectrophotometer and returned to the adsorption apparatus.

The difference in the absorbance readings was used to calculate the amount of simazine disappearing or appearing in the cell over a concentration range of 40 to 250 μg dm^{-3}. As shown in figure 7.3, the apparent adsorption (expressed in terms of 20 g of adsorbent) is <1.0 μmol kg^{-1} with no obvious trend with increasing concentration. This result shows that adsorption measurements with 20 g of sediment are difficult below ~ 1 μmol kg^{-1} because of uncertainties in the adsorption characteristics of the filter and the errors associated with the measurement.

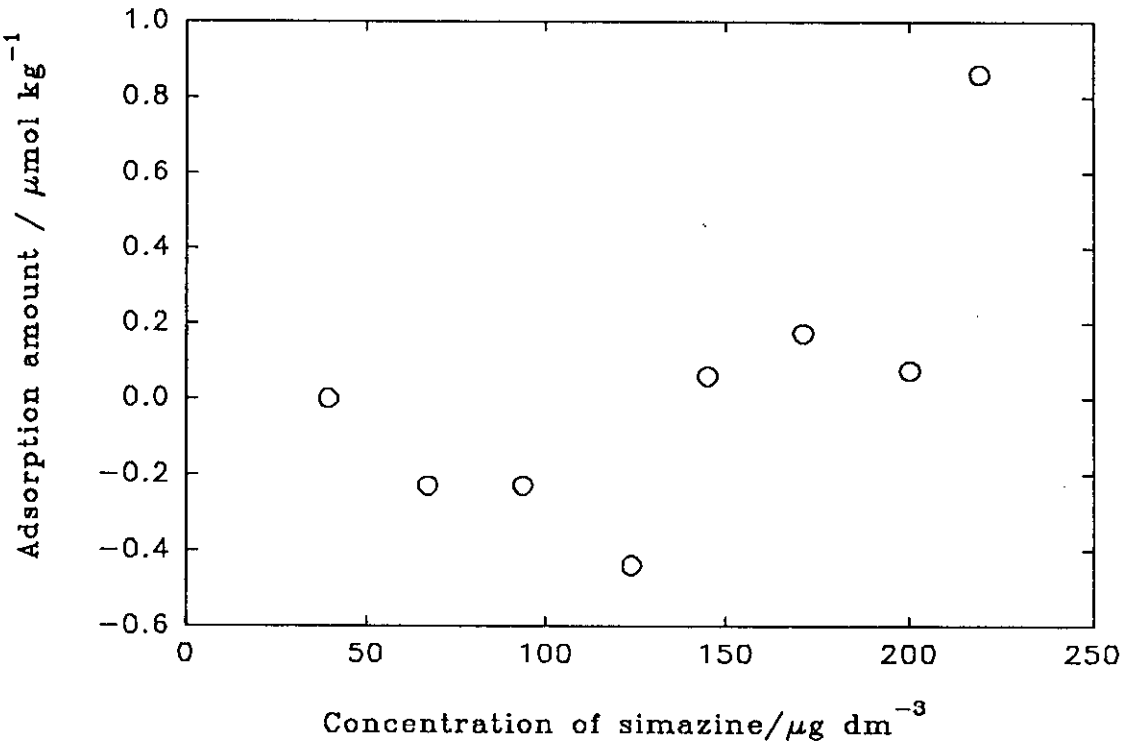


Figure 7.3 Measurements of the adsorption of the cell filter holder at 25°C; the adsorption amounts are calculated on the basis of 20 g of adsorbent.

7.5 Results of the measurement of the kinetics of adsorption

The adsorption cell was calibrated using the same method adopted for the adsorption isotherm measurement, but without the addition of a sediment. The kinetics were studied using *ca* 20 g of sediment A with the addition of a single aliquot of stock solution. Samples were then removed after 20 and 60 minutes and at subsequent intervals over a period of 30 hours. The results of the measurement of the concentration of simazine by GLC/MSD are shown in figure 7.4. The adsorption step is fast with no discernible slow stage over the 30 hours. Hence in the further work, the adsorption is measured after 1 hour equilibration.

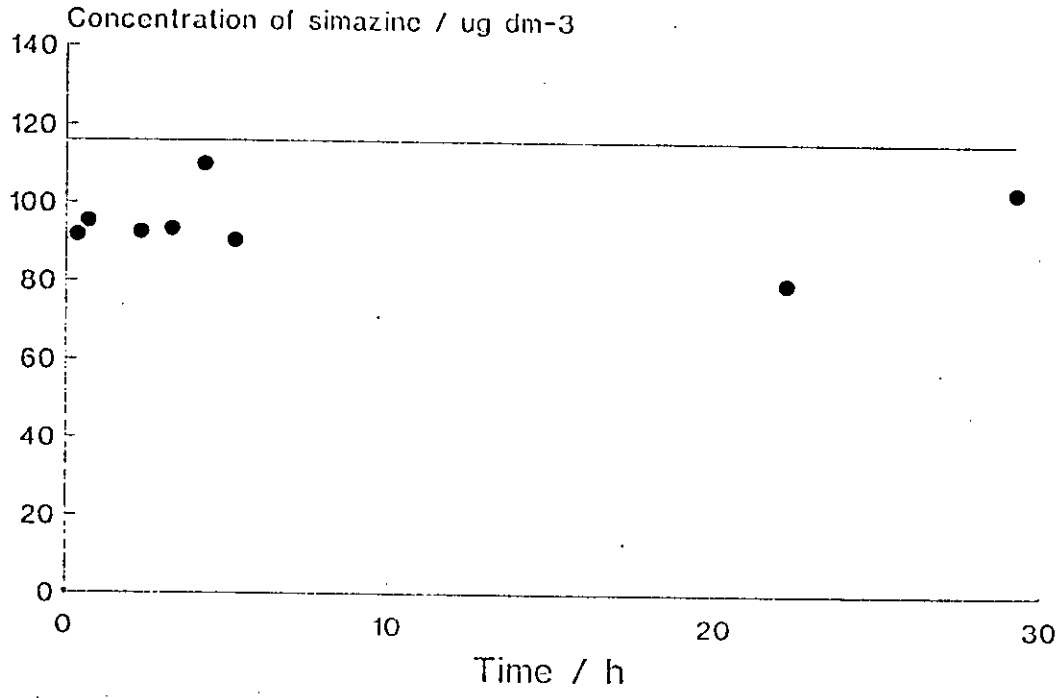


Figure 7.4 **Illustration of the kinetics of adsorption of simazine to sediment A at 25°C. The filled circles are the experimental points and the full line is the result expected without sediment in the adsorption cell.**

7.6 Adsorption isotherms at 25°C and 5°C

The isotherms at 25°C and 5°C were measured using the method described above. Each isotherm determination was accompanied by a calibration experiment with the adsorption cell containing no sediment. The pH in the solution was continuously monitored during the experiment. The CO_2/N_2 mixture controlled the pH to a value of 8.1 ± 0.1 for all the experiments and this was automatically recorded prior to each stock solution addition.

The isotherm for sediment A, measured at 25°C, is shown in figure 7.5. The concentration of simazine is within the range of environmental applications ie 0.2-1.4 μmol dm^{-3} corresponding to 40-280 μg dm^{-3} which is a considerably lower range than any previous adsorption study. A similar linear isotherm was measured at 5°C for sediment A (figure 7.6). In this instance, the isotherm exhibits a non-zero intercept attributable either to adsorption on to colloidal material (<0.2 μm in size which passes through the filter in the adsorption cell) or the adsorption amount is less than the detection limit and some degree of cooperative adsorption exists at low concentration.

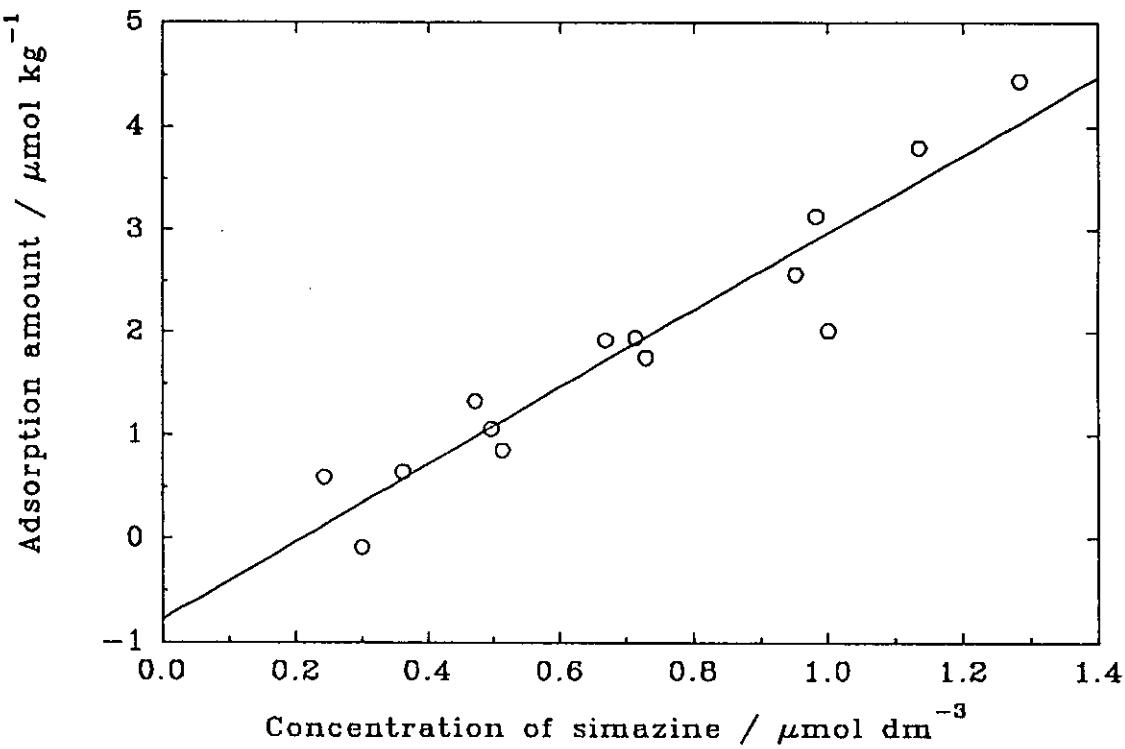


Figure 7.5 **Adsorption isotherm for simazine on sediment A measured at 25°C using the adsorption cell. The full line is the regression line from which the partition coefficient was calculated.**

The isotherms for sediment B at 5 and 25°C are shown in figure 7.7. Both isotherms are linear over the concentration range studied. There is a large increase in the adsorption with decreasing temperature not evident in the isotherms for sediment A.

A regression analysis of the isotherm data produced values of the distribution coefficient at each of the temperatures as shown in table 7.2. The corresponding log K_d values range from 0.27 to 0.98 for these temperatures and sediments. The calculation of the adsorption energy is only based on two isotherms but the large differences between sediment A and B is interesting and indicates that different mechanisms of adsorption may be operating. Both values are within the range expected of physical adsorption processes.

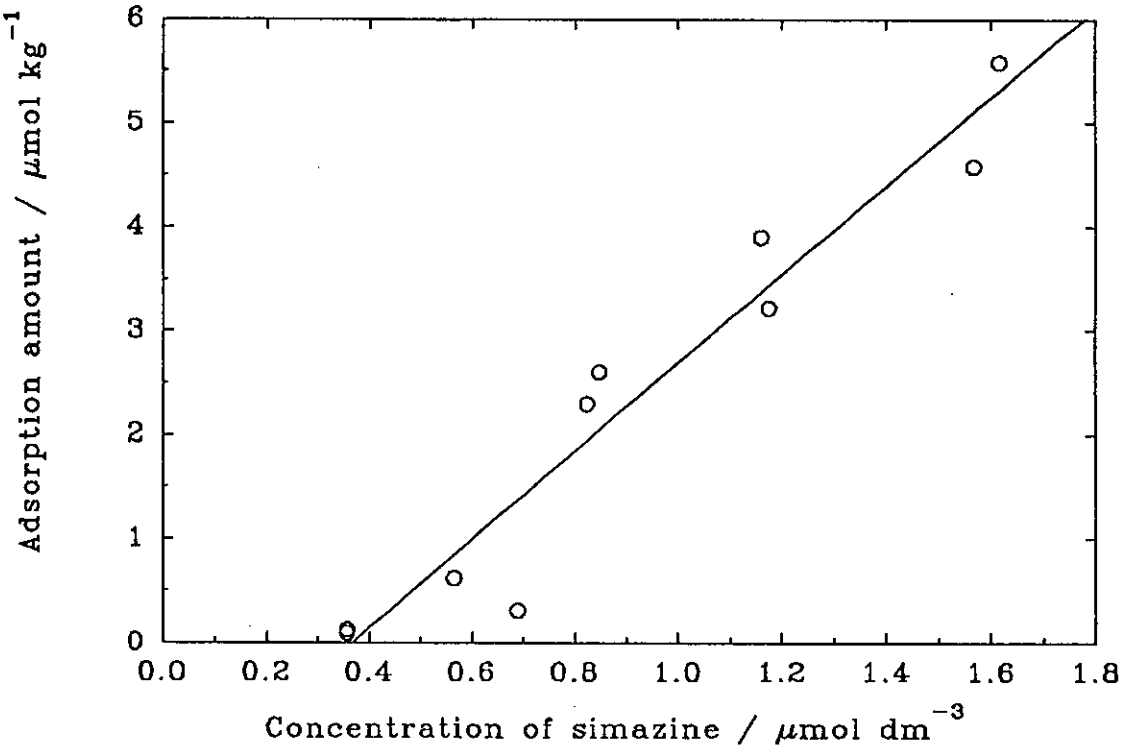


Figure 7.6 **Adsorption isotherm at 5°C for simazine on sediment A. The regression line is shown.**

Table 7.2 **Results from the measurement of the adsorption isotherms for sediments A and B. The calculated distribution coefficients, K_d, and adsorption energies for the river sediments are shown. The values in brackets are the standard deviations.**

Sediment Code	Organic matter /mass %	Distribution coefficient /dm^3 kg^{-1}		Adsorption energy /kJ mol^{-1}
		5°C	25°C	
A	8.2	4.84 (1.09)	3.76 (0.35)	8.4
B	22.2	9.56 (1.79)	1.88 (0.17)	56.2

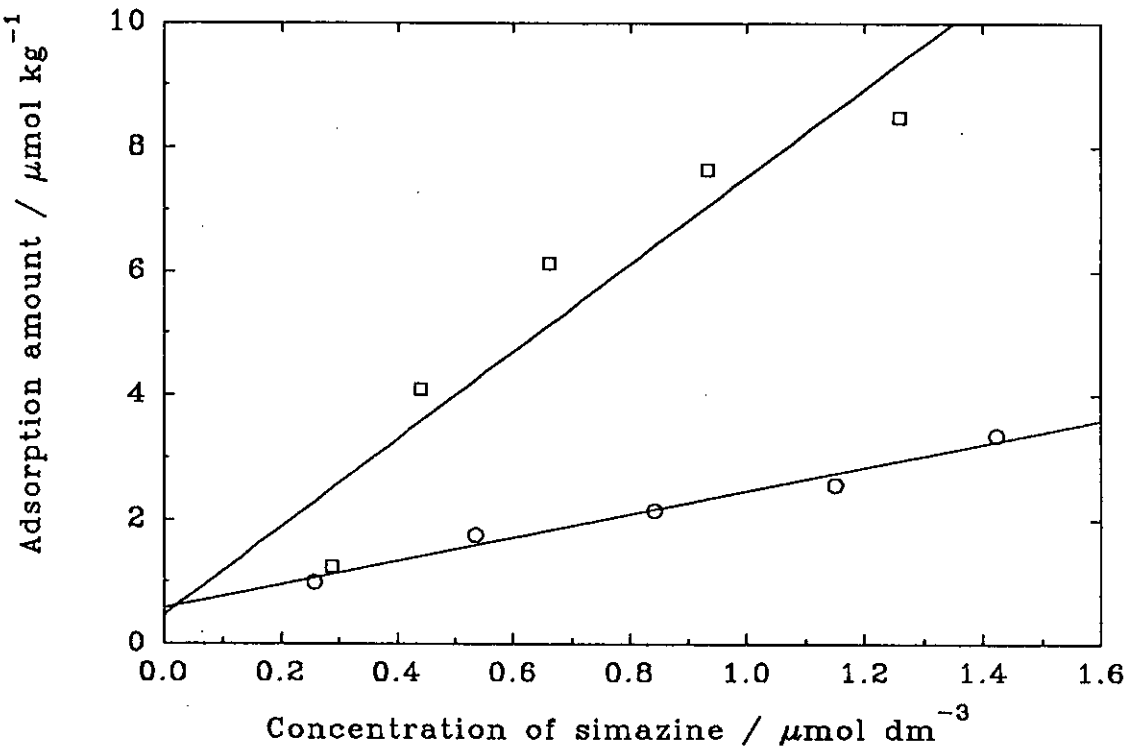


Figure 7.7 **Adsorption isotherms for simazine on sediment B measured using the adsorption cell at 5°C, ○ , and 25°C, □ .**

The results at 5°C were also recalculated in terms of a distribution coefficient based on the organic matter content of the sediment, K_{om}, ie

$$K_{om} = 100\ K_d\ /OM \qquad (7.2)$$

where OM is the percentage organic matter. This transformation leads to values of log K_{om} in better agreement (table 7.3) but much lower than the values for the pyrethroids and organochlorine pesticides eg for permethrin values of log K_{om} vary between 3.3 and 3.8.

In adsorption studies, it is usual to express the amount of adsorption in units of mass per unit area. If K_d is transformed:

$$K_A\ (m) = K_d\ (dm^3\ kg^{-1}) \times 10^{-6} / \Sigma\ (m^2\ g^{-1}) \qquad (7.3)$$

then the values of K_A shown in table 7.3 are obtained. Again, the difference in the adsorption becomes less marked.

Table 7.3 **Comparison of adsorption results for sediments A and B at 5°C by normalisation of K_d with respect to organic matter, K_{om}, and specific surface area, K_A**

sediment code	specific surface area /m^2 g^{-1}	K_d /dm^3 kg^{-1}	K_{om} /dm^3 kg^{-1}	log K_{om}	K_A /10^{-6} m
A	5.34	4.84	59.0	1.8	0.91
B	8.24	9.56	43.1	1.6	1.2

7.7 Discussion of results

The field distribution coefficient for site G was estimated in §4 as 147 ± 50 dm^3 kg^{-1}. This value is much higher than expected from the laboratory experiments and the other data in the literature on adsorption of simazine on soils. The last application of simazine in the area was in February 1989 ie approximately 17 months prior to the field sampling. Possible reasons for the difference are:

1. The sediment has been exposed to high concentrations of simazine during storm events ie >70 µg dm^{-3}. The fast adsorption kinetics indicated that in these conditions the sediment and suspended solids would adsorb simazine to an amount exceeding 280 µg kg^{-1} (assuming a K_d of 4 as determined for sediment A, See table 7.2). It is therefore possible that the simazine is only slowly released from the sediment.

2. It is expected that the stream sediment was derived mainly from suspended solids from field-runoff. These solids may have a high loading of simazine because of the direct application of the herbicide to the soil. Again, the large difference between the aqueous concentration of simazine and sediment concentration at site G may be caused by the slow kinetics of release and partially irreversible nature of the interaction.

3. Some components of the sediment have a specific chemical interaction with the simazine effectively binding it and preventing subsequent release. This interaction may take the form of intercalation with a clay or uptake by organisms and incorporation in lipophilic tissue. The latter explanation appears unlikely because similar behaviour is not observed for the more lipophilic pesticides found at this site, §4.

Recent results obtained for atrazine sorption to soils (Pignatello & Huang, 1991) also indicate that contaminated samples collected from the field can contain a large fraction of atrazine in a slowly reversible sorbed state and that this more recalcitrant fraction increases with the time of exposure of the soil to the herbicide. They found that the apparent sorption constant, K_{app}, calculated after equilibration of the contaminated soils for 24 hour, ranged between 2.3 and 42 times greater than the distribution coefficients measured after 24 hour using herbicide supplements.

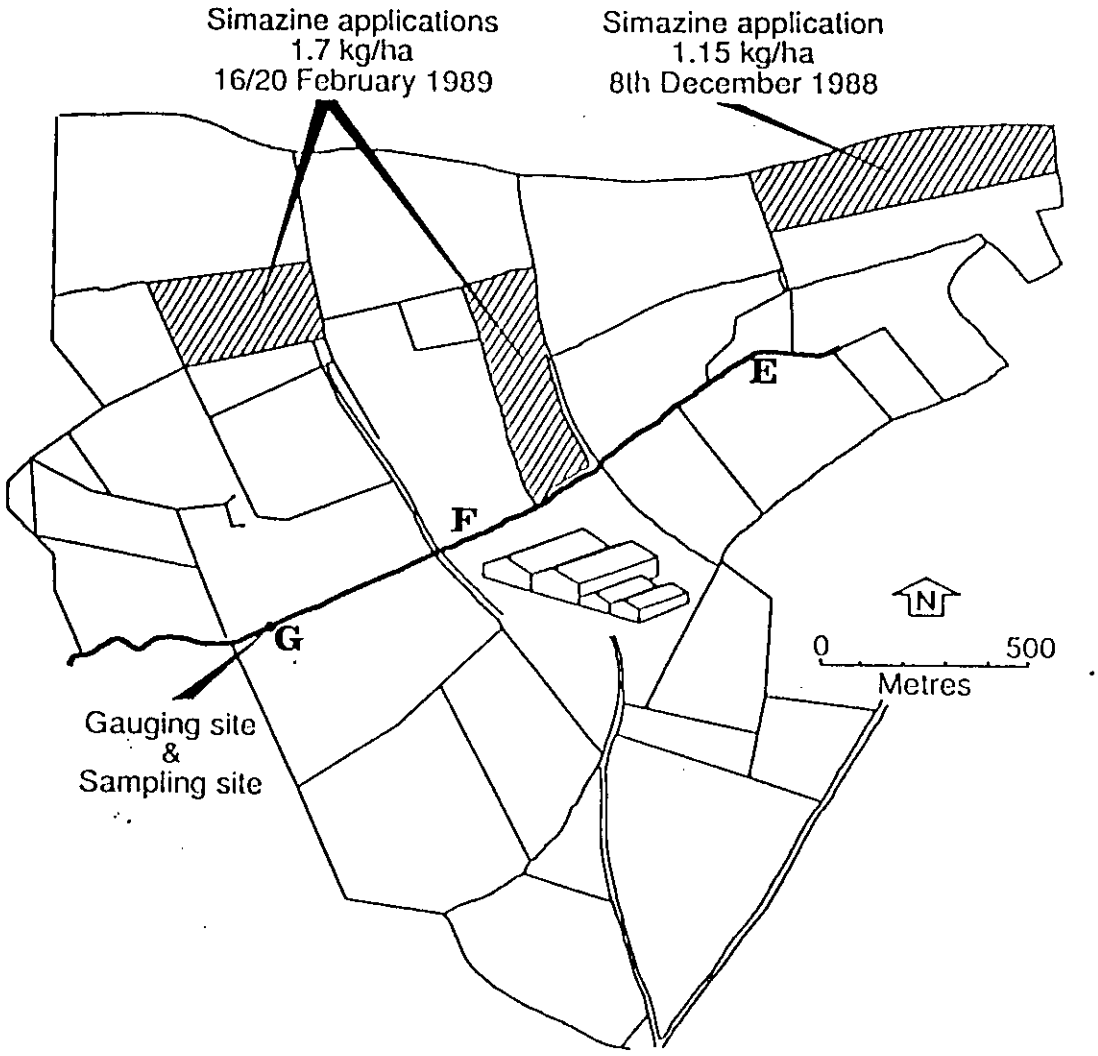
Table 7.4 Comparison of the distribution coefficients for soils with those obtained in this work for river sediments

No. of soils	Temp.	% OM[a] or % OC[b]	K_d	CV,%	$K_{om/oc}$	CV,%	Reference
25	RT	0.6-4.9[a]	3.7	54	160	33	Talbert & Fletchall 1965
21	25	1.0-10.9[b]	2.0	97	58	31	Williams 1968
5	25	0.8-4.3[a]	3.3	63	161	51	Basile *et al.* 1990
1	RT	-	7.0	-	215	-	Brown & Flagg 1981
†1	25	8.2[a]	3.8	-	46	-	this work
†1	25	22.2[a]	1.9	-	8.5	-	this work

Note: RT - room temperature
OM - organic matter, % mass
OC - organic carbon, % mass
† - river sediments

The adsorption data of Talbert & Fletchall (1965) may be used to calculate the adsorption energy for simazine and atrazine interaction with a silty clay soil between *ca* 5 and 50°C. The calculation produces values of 13.9 and 8.9 kJ mol^{-1} for simazine and atrazine respectively. The results of Albanis *et al.* (1989) produce values of 13.3 and 13.7 kJ mol^{-1} for atrazine adsorption. Although the available information on the temperature dependence of the adsorption is limited, the results obtained here for sediments indicate a high variability with the possibility of a specific interaction of simazine with some component of the sediment (see table 7.2).

APPENDIX 7.1 Location of sites E, F and G on the stream sampled in the field survey (NGR SO 555478).



8. RELEASE OF LINDANE, SIMAZINE, DIELDRIN, DDE, TDE, DELTAMETHRIN AND PERMETHRIN FROM NATURAL SEDIMENTS

The partition and concentration of pesticides on river sediments after exposure to polluted waters may subsequently lead to their release from the sediment when the concentration of the pesticides in the associated water diminishes. The reversibility of the adsorption interaction with sediments has not been previously studied in detail and to a large extent, sediments have been considered as "sinks" for pesticides. However, it is expected that many pesticides will be released into the interstitial water and through diffusion or convective transport, enter the main flow of the river. In this situation, the release rate of the pesticide from the sediment will control the speed of recovery of the system.

It was decided to examine river sediments which had been contaminated in the field through either agricultural or industrial usage of the pesticides rather than sediments spiked with pesticides in the laboratory. This choice does lead to a number of disadvantages eg the history of the sediment is unknown and the composition is largely dictated by the occurrence of the pesticide in the river. However, this is preferable to using an uncontaminated sediment and spiking with a mixture of pesticides and then examining the release into water. The interaction and specific mode of binding of pesticides to sediments is not well understood and so it is important at this stage to use sediments contaminated in 'natural' conditions.

The choice of sediments used in the studies was determined by the previous survey research on the analysis of the field samples, §4. Two sediments were chosen for detailed study:

(i) Rosemaund Farm, sediment G in table 4.1. This was used to examine the release and degradation of lindane, simazine, dieldrin, DDE, TDE and deltamethrin.

(ii) R. Stour (Worcestershire), sediment I in table 4.1. This was used to examine the release and degradation of permethrin.

8.1 Experimental procedure for measuring the release of pesticides from river sediments

The experiments were designed to investigate the distribution and degradation of the selected pesticides after incubation at 25°C in the dark for periods of 2 days and 14 days. Duplicate recovery experiments were done with incubation in the dark for 2 days. At the end of each incubation period, the sediments and waters were separated and analysed for the pesticides. The results in §6, on the methodology of separation of solids from water, indicated possible problems caused by the adsorption of pesticides to the glass containers and filtration membranes used for the separation. Hence special procedures were adopted to enable the construction of a mass-balance of each pesticide including residuals on the glass filter holder, filter and glass container.

8.1.1 Procedure for the recovery evaluation

A summary of the method is given in figure 8.1. 2 ml of a 0.05 mg dm^{-3} multistandard pesticide containing simazine, dieldrin, DDE, TDE, lindane, deltamethrin and permethrin in 5% acetone/hexane solvent was added to two 100 ml capacity glass bottles with PTFE lined screw caps. The solvent was evaporated using a gentle stream of dried nitrogen gas and 100 ml of 10 mmol dm^{-3} $KHCO_3$ was then added. These were incubated in the dark at 25°C for 2 days (Gallenkamp, orbital incubator operated at 150 rpm) and then extracted using DCM (dichloromethane), following the IFE River Laboratory operating procedure (SOP: 1/17.10.91) which is similar to the method described in §3.2.1. The extract was concentrated using a micro-Kuderna-Danish concentrator (40 ml) and solvent exchanged to 1.0 ml of 5% acetone in hexane using dry nitrogen gas over the solvent surface.

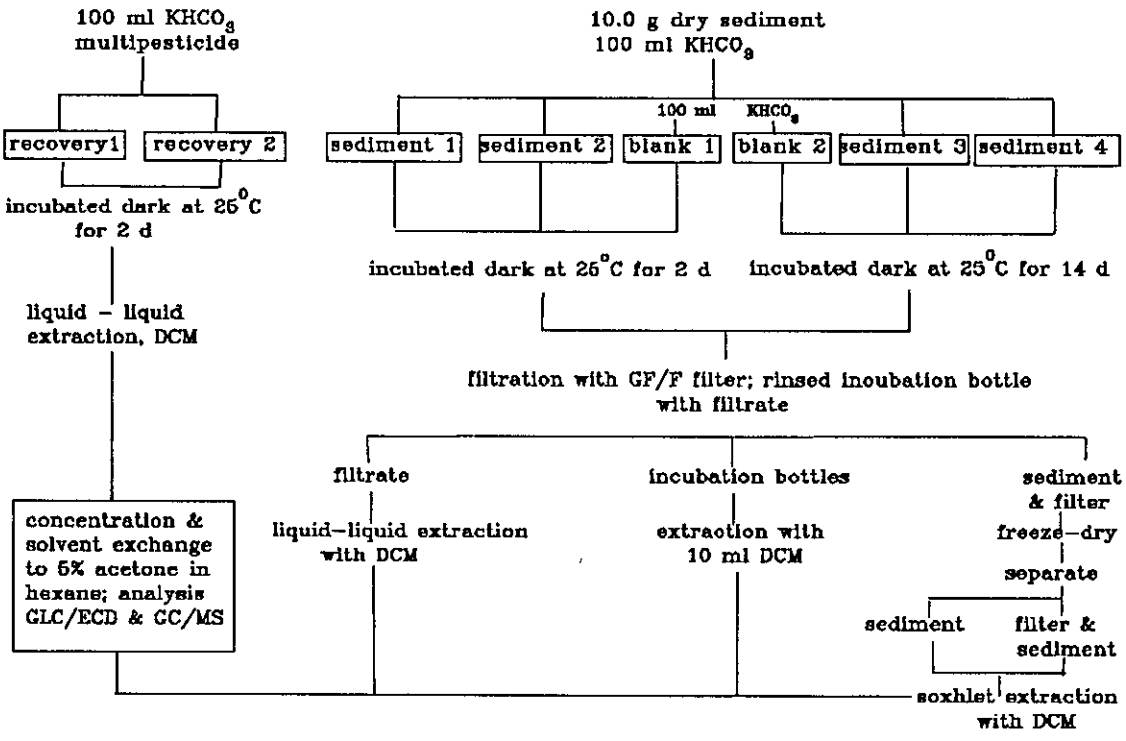


Figure 8.1 **Flow chart to demonstrate the procedure used for the separation, extraction and analysis of the water-sediment systems in the pesticide release experiments**

8.1.2 Procedure for the sediment incubation experiments

Experiments were performed in duplicate with a blank control sample for each incubation period. A summary of the procedure is shown in figure 8.1.

10 g of homogenized freeze-dried sediment was added to each 100 ml incubation bottle (wide-necked with PTFE screw cap). The blank control samples did not contain sediment. 100 ml of 10 mmol dm^{-3} $KHCO_3$ solution was added to each bottle and the suspensions incubated at 25°C in the dark for 2 days. After the requisite incubation period, the suspensions were filtered immediately using a GF/F filter (pretreated by heating at 550°C overnight and stored in a desiccator prior to use) in a glass filter holder. The exposure of the suspensions to the glass filter holder was kept as low as possible to avoid unnecessary losses. The incubation bottles were rinsed with three aliquots of 10 ml of the filtrate. The filters were partially dried for 2 minutes prior to freeze-drying.

The incubation bottles were extracted overnight with 10 ml of DCM. The extracts were then evaporated and solvent exchanged to 5% acetone in hexane prior to GLC analysis. The upper glass surface of the filter holders were also extracted with DCM and kept for separate analysis.

The filtrates were extracted by liquid-liquid extraction as described in §8.1.1. Each aliquot of DCM used to extract the filtrate was also used to rinse the collecting conical flask and filter support glassware. The extracts were concentrated and solvent exchanged to 5% acetone in hexane as described previously.

The sediments were transferred to a soxhlet extraction thimble (pretreated to remove any pesticide residues) and freeze-dried overnight. The sediments and filters were separated and extracted for 5 h with 60 ml DCM using a soxhlet apparatus (operated at 1 cycle every 25 minutes). The extracts were then concentrated and solvent exchanged to 5% acetone in hexane. All necessary weights were recorded to enable the determination of the sediment residues on the filter, the amount of sediments extracted and the volumes of water extracted. The pH and total ion concentrations in the final filtrates were also measured.

The GLC analysis was by the methods described in §3.6 for the organochlorine and pyrethroid insecticides and using the GLC with NPD with a 25 m DB5 (5% phenyl-methyl silicone stationary phase) capillary column for the determination of simazine. Linear calibration was performed with standards of 0.05, 0.1 and 0.5 mg dm^{-3} of simazine with prometryn as the internal standard (0.4 mg dm^{-3}).

Separate experiments were performed over the first 2 d of incubation to measure the changes in the solution following the addition of the sediment to the potassium hydrogen carbonate solution. This included the measurement of pH, conductivity and oxygen saturation at intervals over the first incubation period.

8.2 Results obtained from sediment G

8.2.1 Results of the recovery trials for the 2 day incubation

The duplicated recovery experiments performed in parallel with the pesticide release experiments, produced the results shown in table 8.1. All of the recoveries are lower than expected, with the highest of ~ 60% obtained for dieldrin; the standard deviations, <15%, are acceptable.

Table 8.1 **Results of the recovery trials with a nominal concentration of 1 µg dm^{-3} in each pesticide dissolved in 10 mmol dm^{-3} $KHCO_3$**

pesticide	% recovery	standard deviation %
lindane	34.6	9
DDE	39.7	10.6
dieldrin	60.4	12.5
TDE	58.6	11.9
deltamethrin	28.0	4.5
simazine	53.4	8.0
permethrin	47.1	8.8

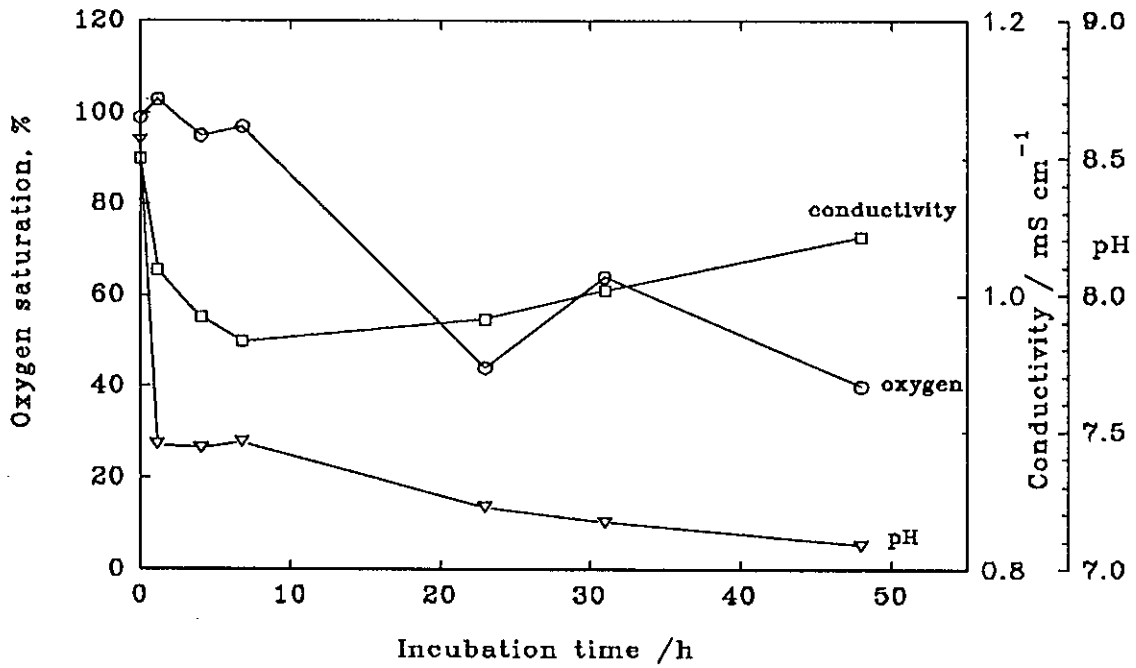


Figure 8.2 **Illustration of the pH, oxygen saturation and conductivity in the suspension during the first 2 days of incubation.**

8.2.2 Results of the measurement of the solution composition

The change in the pH, conductivity and oxygen saturation during the first 2 days of incubation is shown in figure 8.2 and the major-ion composition of the filtrate at the end of the 2 days is shown in table 8.2.

Table 8.2 Results of the analysis of the filtrate from the pesticide release experiments obtained after incubation for 2 days at 25°C.

Ion	Ca	Mg	Na	K	HCO_3	NO_3	PO_4	Cond.
	mmol dm^{-3}						µmol dm^{-3}	/µS cm^{-1}
	2.26	0.27	1.98	2.94	10.02	0.05	24.0	1001

The results indicate a rapid change in conductivity and pH in the first hour of the incubation with the pH falling from 8.6 to 7.5. The oxygen saturation (at 1 atmosphere pressure) is close to saturation with respect to the atmosphere during the first 7 hours but falls overnight to about 40% saturation thus indicating the onset of aerobic activity of bacteria in the suspension. After the initial fall in conductivity and pH, there is a trend of increasing conductivity and decreasing pH over the remaining incubation with the oxygen saturation fluctuating between 40 and 64%. It is evident (table 8.2) that the most significant changes in the solution composition are the release of Ca, Mg and Na and decrease of K with both nutrients, NO_3 and PO_4 present in solution. The hydrogencarbonate concentration is virtually unchanged which could mean that the dissolved Ca is from ion-exchange reactions of the suspended matter rather than the dissolution of calcite. The pH and conductivity of the filtrates, given in table 8.3, do not apply to the suspension at the end of the incubation because of the subsequent loss of CO_2 during filtration causes a rise in pH and decrease in conductivity.

8.2.3 Results from the pesticide release experiments

The analysis at the end of the two incubation periods resulted in 4 extracts for each suspension:

(a) the extract from the sediment
(b) the extract from the filter
(c) the extract from the filtrate
(d) the extract from the glass filter holder.

Table 8.3 Information from the pesticide release experiment with sediments 1 to 4 (see figure 8.1)

Sediment No.	incubation period /d	mass of sediment in soxhlet extraction /g	volume of filtrate /ml	pH filtrate	contact area of filter holder /cm^2
1	2	9.5725	76.80	8.86	135
2	2	9.5201	83.88	8.83	50
3	14	9.5614	53.95	8.66	33
4	14	9.5463	88.06	9.06	33

The sediment codes and incubation periods are shown in figure 8.1 and table 8.3. In all instances over 95% of the added sediment was recovered from the suspension and filter. The recovery of the filtrate was lower (54-88%) because of evaporation losses during filtration and subsequent processing. The whole filters used for the separation of sediments 3 and 4 were isolated intact together with *ca* 90%, 50% of filters used for sediments 1 and 2 respectively. It was also found possible to remove the majority of the sediment from the freeze-dried filters with < 10 mg of sediment remaining on the filters prior to soxhlet extraction.

The analysis of the control blanks (see figure 8.1) at the end of each incubation period gave concentrations of the pesticides of ≤ 0.0007 μg ml^{-1} in the extract (equivalent to 7 ng dm^{-3} in the filtrate and 0.07 μg kg^{-1} in the sediment) with simazine and deltamethrin not detected. The 'carry-over' following the analysis of the multistandard pesticide solution was determined to be ≤ 0.0007 μg ml^{-1} and similar in magnitude to the results from the analysis of the blank samples. Hence the results obtained for the sample analysis were corrected by subtraction of the 'carry-over' or blank signal depending which was the greater.

No pesticides were detected in the filter extracts; this corroborates the use of the filter matrix (§6) and procedure for separating the sediment. No pesticides were detected on the glass filter holder for sediments 1 and 2. Traces of dieldrin and deltamethrin (1% and 2% of the total respectively) were found in the analysis of sediment 3 holder and DDE and deltamethrin (0.23%, and 0.36% of the total respectively) on sediment 4 holder. Only a trace (<0.3%) of simazine was detected on the glass bottle used for sediment 2 with no pesticides detected on the other bottles.

Apart from lindane and simazine, all the pesticides recovered after incubation were found to be in the sediment. No DDE, dieldrin, TDE or deltamethrin was detected in the filtrate indicating concentrations ≤ 7 ng dm^{-3}. The recoveries of the pesticides from the sediments, expressed as a percentage of the initial concentrations, are shown in figure 8.3. The concentrations in the sediments, expressed as μg kg^{-1} (dry weight), are collated in tables 8.4 and 8.5.

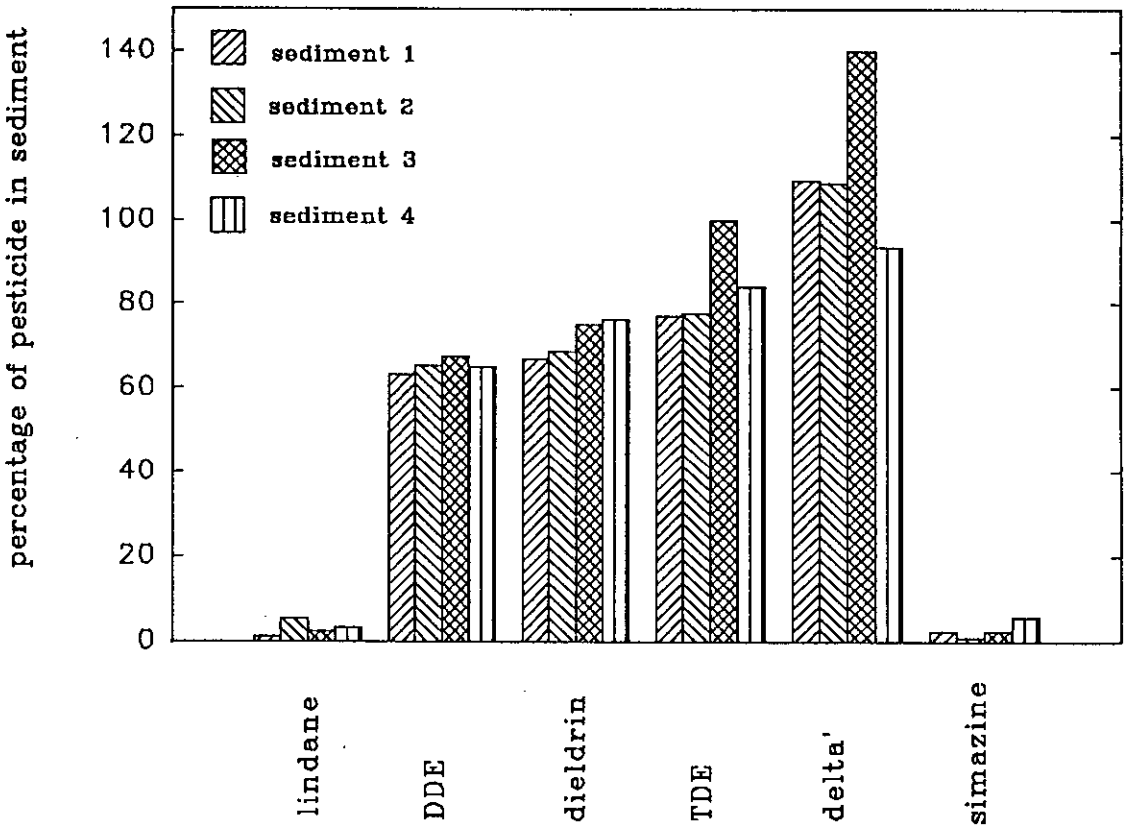


Figure 8.3 **Recovery of the pesticides from the sediments used in the incubation experiments expressed as a percentage of the initial concentration.**

The sediment codes 1 and 2 refer to 2 days incubation and codes 3 and 4 to 14 days incubation both at 25°C in the dark.

The results for deltamethrin indicate no difference in concentration over the 12 days incubation with good agreement with the initial concentration measured prior to incubation. In spite of the high sediment concentration, no release of deltamethrin into the water could be detected.

Table 8.4 **Concentrations of pesticides in sediments detected after 2 d incubation. SD = standard deviation.**

pesticide	initial concentration /µg kg^{-1} (dry wt)	sediment 1	sediment 2	mean ± SD
		µg kg^{-1}		
lindane	4.8	0.05	0.24	0.15 (0.13)
DDE	26.4	15.9	16.4	16.2 (0.4)
dieldrin	6.0	3.8	3.9	3.9 (0.1)
TDE	16.4	12.8	12.1	12.5 (0.5)
deltamethrin	8.4	8.8	8.7	8.8 (0.1)
simazine	44.0	0.9	0.4	0.7 (0.4)

Table 8.5 **Concentrations of pesticides detected after 14 d incubation together with the results of the t-test (5%). SD = standard deviation.**

pesticide	sediment 3	sediment 4	mean ± SD	t-test	P
	/µg kg^{-1} (dry wt)				
lindane	0.11	0.14	0.13 (0.02)	NS	0.85
DDE	17.0	16.4	16.7 (0.4)	NS	0.32
dieldrin	4.3	4.4	4.4 (0.1)	S	0.02
TDE	15.7	13.1	14.4 (1.8)	NS	0.28
deltamethrin	11.3	7.5	9.4 (2.7)	NS	0.77
simazine	0.9	2.4	1.7 (1.1)	NS	0.33

Note t-test: NS, no significant difference between the concentration of pesticide in the sediment after 2 d and 14 d incubation; S: significant difference was determined; P is the probability that the assertion is incorrect.

The results for DDE, dieldrin and TDE are similar. With the exception of the result for TDE after 14 d incubation, all the coefficients of variation for the duplicates are less than 4%. Again, no release of the pesticides into the solution was detected. The lower concentrations in the sediments 1 to 4, compared with the analysis prior to incubation, does raise some questions concerning the mass balance. The missing fraction cannot be accounted by losses through adsorption to the filter or glassware and therefore it may be possible that the pesticides are more strongly bound or incorporated into organic matter (biotic or otherwise) during the incubation, thus affecting the extraction efficiency. The results indicate this is a rapid process taking < 2 d and that the longer-term incubation in the conditions employed here, do not affect the binding and therefore extraction efficiency.

Table 8.6 Concentrations of lindane and simazine measured in the filtrates from sediments 1 and 2 (2 d incubation) and sediments 3 and 4 (14 d incubation)

pesticide	sediment 1	sediment 2	mean ± SD	sediment 3	sediment 4	mean ± SD
	ng dm^{-3}					
lindane	83.3	83.5	83.4 (0.1)	61.2	27.3	44.3 (24.0)
simazine	20.8	11.9	16.4 (6.3)	150.1	ND	-

A comparison of the results obtained after 2 d and 14 d incubation (figure 8.3 and tables 8.4 and 8.5) confirms that no significant release of pesticide or degradation of the sediment bound fraction occurs. The distribution coefficients for dieldrin, DDE, TDE and deltamethrin may be estimated for the sediment using the Collander relationship (equation 4.2) to predict K_{om}'s and an organic matter content of 9.2% (table 4.1) for the sediment. These may then be compared with the maximum K_d's that can be evaluated from these experiments using the concentrations in solution corresponding to the limits of determination of each pesticide and the mean concentration of each pesticide in the sediment for the duplicate experiments after 2 and 14 days incubation. The maximum K_d's are 280, 2800, 13,500 and 9100 $dm^3\ kg^{-1}$ for dieldrin, DDE, TDE and deltamethrin respectively. Apart from dieldrin, the predicted K_d's are all much lower eg 350, 164 and 194 $dm^3\ kg^{-1}$ for DDE, TDE and deltamethrin, indicating that some release of the pesticides into solution is expected eg for DDE, dieldrin, TDE and deltamethrin equilibrium concentrations in solution of 47, 6.5, 82, 46 ng dm^{-3} respectively are expected. Only the prediction for dieldrin is below the limit of determination for this experimental configuration.

Table 8.7 Total amounts of lindane and simazine recovered after 2 and 14 d incubation

	2 d incubation / ng			14 d incubation / ng		
	sediment 1	sediment 2	mean	sediment 3	sediment 4	mean
lindane	6.90	9.40	8.15	4.40	3.80	4.10
simazine	11.0	5.8	8.40	16.2	24.0	20.1

The results for simazine and lindane are more difficult to interpret because of the biodegradation of the compounds during the incubation period. Less than 21% of the original lindane was recovered after 2 days incubation. A significant difference (t-test, 5%) was found between the total amounts recovered after 2 and 14 d incubation (see table 8.7) with a majority of the lindane occurring in aqueous phase (table 8.6 and figure 8.4). In contrast, the recovery of simazine was lower *ca* < 6% but with a significant (t-test, 5%) increase in the total recovery after 14 d incubation (see table 8.7). As shown in figure 8.4, the majority of the simazine was found in the sediment.

The distribution coefficients for lindane and simazine may be calculated from the data obtained after 2 and 14 d incubation. The mean value for lindane for the four samples is 3.34 ± 2.06 $dm^3\ kg^{-1}$ with no significant change between the 2 and 14 d incubation results. The distribution coefficient, K_d, for simazine is 48.1 ± 11.5 $dm^3\ kg^{-1}$ after 2 d incubation and 6.2 $dm^3\ kg^{-1}$ after 14 d. The result obtained after 14 d incubation is in better agreement with adsorption results in §7.6, table 7.2. The change in K_d with the incubation time may reflect the slow release of the more recalcitrant fraction of the bound simazine.

The loss of lindane observed in these experiments is in accord with other results reported for lindane biodegradation. The review by Smith *et al.* (1978) noted that lindane in a thick anaerobic sludge was more than 95% degraded after several days and that the transformation was more effective in anaerobic than aerobic conditions. Similarly it was reported that lindane incubated for 3 weeks in samples of river water and sediments was 80% degraded compared with more than 95% recovery after 12 weeks in sterilised conditions. The hydrolysis reaction will contribute a significant amount to the degradation at alkaline pH (Saleh *et al.* 1982).

There is less information concerning simazine degradation, although it is likely that abiotic hydrolysis is an important process in the conditions employed here. A wide range of bacteria is able to biodegrade simazine but this is expected to be slow and the effects of aeration on the degradation rate are uncertain (Goswami & Green 1971; Jessee *et al.* 1983). For soils in aerobic conditions, the degradation depends on the soil moisture and temperature (Walker 1976) with half-lives ranging from 36 d to 234 d. In anaerobic conditions, the half-lives varied between 8-12 weeks. Similar measurement for aquatic sediments do not appear to be available.

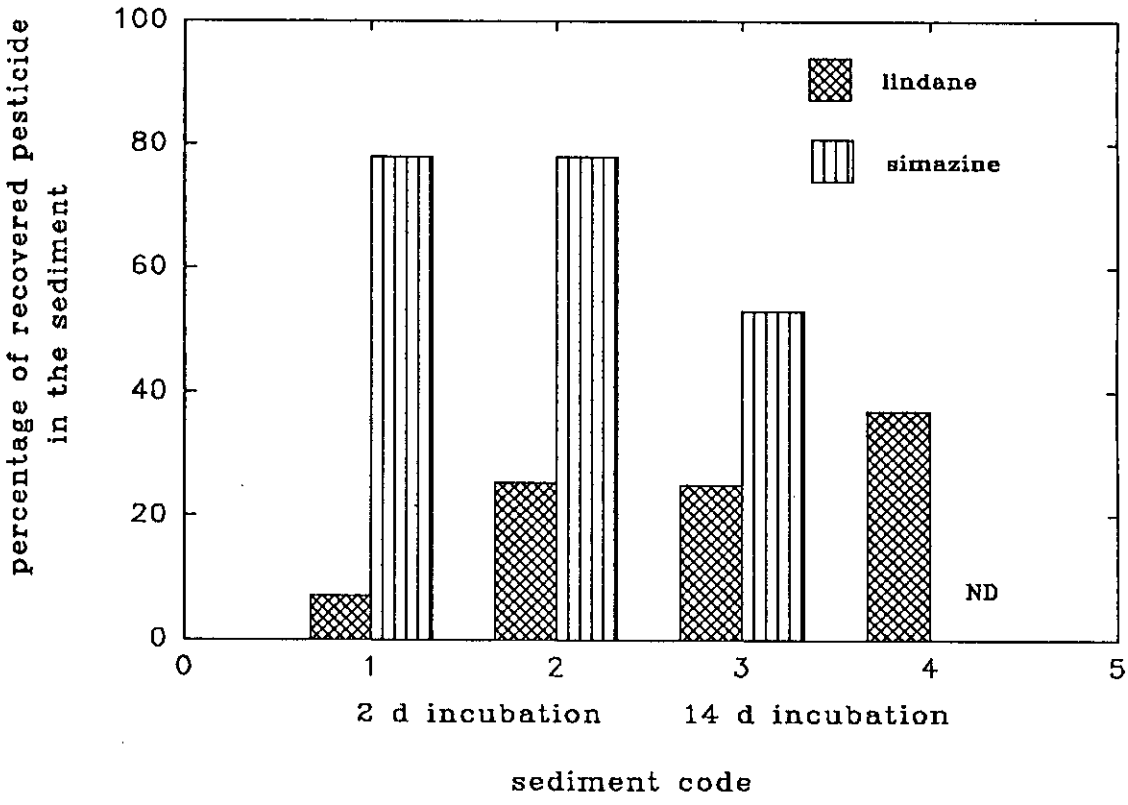


Figure 8.4 Distribution of lindane and simazine between the sediment and solution at the end of the 2 and 14 days incubation

The results obtained in this work, although tentative, indicate a rapid initial loss of simazine during the first 2 d of incubation. This loss does not appear to be consistent with the biodegradation or hydrolysis rates reported for soils. No significant change in the sediment concentration occurred during the 12 d of further incubation.

8.3 Results obtained from sediment I

The release of *cis*-permethrin from sediment I was studied using the procedure described above. The initial analysis of the sediment by soxhlet extraction with DCM without further clean-up gave a concentration of *cis*-permethrin in the sediment of 10.3 μg kg^{-1} (dry weight). The concentration of permethrin in this freeze-dried sediment stored at room temperature had previously been found to be stable over a period of 1 year.

Unfortunately, problems were encountered during the analysis of the samples extracted after 2 days of incubation which resulted in the loss of the water and sediment extracts. The experiments were continued for 14 days of incubation and the extracts from the filtration, bottle, filter and filter holder were analysed as described in §8.1. No permethrin was found in the filtrate with only trace quantities in the bottle, filter and filter holder extracts in similar amounts determined in the corresponding control blank samples. The concentration of *cis*-permethrin in the duplicate sediment samples was 1.6 ± 0.2 μg kg^{-1} corresponding to approximately 15% of the original concentration.

Hill (1989) has reviewed the degradation of permethrin in soil and natural waters including studies on a wide variety of soil types. In all soils, under aerobic conditions, degradation is fairly rapid (half-life of 5-55 d) with conversion to carbon dioxide as the ultimate product. The hydrolysis of permethrin in water is likely to contribute to the degradation (half-life reported as ~ 64 d for *cis*-permethrin at pH = 7, NRCC 1986). However, microbial degradation is the most important pathway although the identification of the species that degrade pyrethroids and the rates of degradation are largely unknown (NRCC 1986). Previous studies (for review see Hill (1989) and NRCC (1986)) have indicated that *cis*-permethrin is more persistent than the *trans*-isomer and that permethrin is more persistent in reducing conditions than oxic eg Gambrell *el at.* (1981) found less than 3% recovery of permethrin after 3 weeks incubation in well-oxidized suspensions compared with 33% to ~ 100% recovery in strongly reducing conditions. The degradation was also found to be pH dependent.

The low concentration of permethrin in sediment I after incubation is expected to produce low concentrations in the associated water. The elution of peaks close to *cis*-permethrin in the ECD chromatograms, limited the detection to ~ 0.005 mg dm^{-3} in the extract which corresponds to 0.05 μg dm^{-3} in the filtrate. In these conditions it is not possible to determine K_d's > 30 dm^3 kg^{-1} (Log $K_{OM} \leq 3.5$). The field distribution coefficients (table 4.7), log K_{omf}, were 3.5 and 4.1 indicating that the equilibrium solution concentration of permethrin in the release experiments is likely to be below the limits of detection in the present configuration.

Parallel incubation experiments in the dark at 25°C over 14 days were also performed using sediment I fortified with permethrin at 100 μg kg^{-1} (dry weight). In two of the bottles, the pesticide was added in water prior to freeze-drying and in a further two bottles, permethrin was added to the freeze-dried sediment in a solvent followed by rotary evaporation at 40°C. The total recovery of *cis*-permethrin was 89-96% with fractions in the water, sediment, filter, filter holder and glass bottle. Similar results were obtained for all four samples with between 83 and 89% of the total permethrin recovered found to be in the sediment. The calculated K_d's varied between the samples with a mean of 343 dm^3 kg^{-1} (SD = 262 dm^3 kg^{-1}) ie log K_d = 2.54. The calculated log K_{OM} values fall within the range of 4.00 to 4.83 which is slightly higher than the field values (log K_{omf}) reported in §4. The K_d's are at least a factor of 100 lower than the distribution coefficient determined for the interaction of permethrin with the sediment colloids ie log K_{dc} = 4.48, in §5.4. However, because the distribution coefficient for the colloid fraction was normalised with respect to the humic acid content, it is more realistic to compare K_{om} and K_{dc}. In this case the value for the colloids of log K_{dc} = 4.48 is within the range of log K_{om} for the sediment I ie 4-4.83.

8.4 Conclusion

The results illustrate the need to examine the release of pesticides from sediments already contaminated rather than laboratory "spiked" sediments eg using radiolabelled compounds in short-term experiments. For those compounds studied here which are degradable during the release experiments eg simazine and lindane, it is not as yet possible to predict their fate in sediments, even in controlled laboratory conditions. However, certain conclusions may be drawn:

(i) The organochlorine compounds studied, DDE, TDE, dieldrin and also the synthetic pyrethroid, deltamethrin, remain bound to the sediment. The expected release of DDE, TDE and deltamethrin as predicted from equilibrium adsorption/desorption calculations, was not evident.

(ii) The synthetic pyrethroid, deltamethrin, was not degraded or released from the sediment in the conditions studied.

(iii) Lindane was degraded to an extent in general agreement with information from the soil literature.

(iv) Simazine demonstrated some anomalies which warrant further study. In particular the fast degradation during the initial incubation and the change in the distribution of simazine between the sediment and the solution during the incubation period.

9. IMPLICATIONS OF THE OCCURRENCE OF PESTICIDES IN SEDIMENTS, SUSPENDED SOLIDS AND WATER TO THEIR TOXICITY TO AQUATIC INVERTEBRATES

Information on the toxicity of simazine, permethrin and lindane is reviewed to enable an assessment of their effect on invertebrates at concentration levels found in the field survey (§4). Particular attention is given to any information available on the toxicity effects of the pesticides when they are associated with suspended solids or sediments. The implications regarding the occurrence of the pesticides is summarized and the limitations of the available toxicology information is identified.

9.1 Toxicity of simazine to aquatic invertebrates

Toxicity of simazine to invertebrates in the literature uses several criteria eg EC_{50}, TL_{50}, LC_{50} (table 9.1). These terms are generally synonymous in this context in that the effect measured for EC_{50} was mortality and the tolerance limit for TL_{50} was also death as is usual for LC_{50} values. Simazine toxicity to zooplankton is in the range 1-4 mg dm^{-3} for experiments of 48 and 96 h. Values for *Gammarus fasciatus* are very variable with 48 h LC_{50} values ranging from 21 to >100 mg dm^{-3}. All other crustacea tested, *Asellus*, *Palaemonetes* and *Orconectes* had TL_{50} values greater than 100 mg dm^{-3}, the maximum concentration used in the experiments. There are only two laboratory produced toxic values for insects, one for the stonefly *Pteronarcys* (96 h LC_{50} 1.9 mg dm^{-3}) and one for the chironomid family Tendipedidae which has a LD_{50} of 28 mg dm^{-3}. Field experiments using 0.5-2 mg dm^{-3} did not affect this family, nor did it affect phantom midges (*Chaoborus*) and dragonflies and there was only marginal reduction in numbers of Trichoptera. Mosquitos and biting midges were badly affected, the former being eliminated from the ponds for 14 months and the latter for 8 weeks. Ephemeroptera and Coleoptera showed *c.* 90% reduction in numbers in the first week and depressed numbers for 11-14 months (Walker 1964). Work on the ephemeropteran *Hexagenia* showed no effect to concentrations of 3 mg dm^{-3} (Mauck *et al.* 1976a).

Molluscs were badly affected (100% mortality for 8 weeks) but leeches were unaffected. Oligochaeta had a LD_{50} of *c.* 28 mg dm^{-3} in the laboratory and a 50% mortality in the field experiments at 0.5-2 mg dm^{-3}.

Sanders (1970) noted the behaviour of some aquatic invertebrates to simazine. His first criterion was "irritability or excitability" and in the extreme case the glass shrimp *Palaemonetes kadiakensis* jumped out of the water. This phase was followed by loss of equilibrium and lack of coordination or immobilization. Death followed this phase.

9.1.1 Effect of sediment on simazine toxicity

The concentration of simazine in the sediment is directly proportional to the application rate (Mauck *et al.* 1976a). Although residues decline, it is persistent in the sediment being found 456 days after application. Bioacccumulation was evident in invertebrates for the first 86 days and simazine was found in invertebrates after a year (Mauck *et al.* 1976a).

There is little evidence of simazine bound in the sediment affecting free swimming invertebrates. This herbicide, applied as a preflooding treatment to bass rearing ponds, did not affect the zooplankton populations which are very sensitive to simazine (Snow 1964).

As previously stated, many of the invertebrates affected are associated with the sediment. Walker (1964) concluded that there was a localization of the herbicide at the sediment water interface caused by the accumulation of simazine onto the sediment surface. This formed a concentrated chemical barrier to emergence of chironomids and subjected sediment associated invertebrates with concentrations many times higher than the application rates.

9.1.2 Summary

There appear to be three concentrations of simazine that affect aquatic invertebrates in laboratory experiments. Values of a few mg dm^{-3} will affect zooplankton and some insects such as stoneflies. Concentrations of 10-30 mg dm^{-3} affect many benthic invertebrates, particularly those associated with sediment, eg Oligochaeta, *Gammarus*, mosquitos and chironomids. Other groups are unaffected by concentrations of 100 mg dm^{-3}. These include *Asellus*, crayfish and glass shrimps even though they may be associated with sediment as well.

There is no information about the direct effects of simazine adsorbed to sediment on benthic animals associated with sediment. It is therefore impossible at the moment to assess how concentrations as high as 200 µg kg^{-1} found in this study at sites F and G affect such animals (table 4.6). The literature does indicate that many invertebrates affected are living in the sediment environment, although it is not clear whether simazine associated with the interstitial water or sediment bound material is causing the toxicity.

In the aqueous phase, the literature shows that toxic effects on animals are only observed for simazine concentration >500 µg dm^{-3}. Concentrations as high as this have not been observed in this study. It is possible that streams directly draining treated land may reach this high level during storm events. The indications from laboratory toxicity studies are that concentrations as low as 1-2 µg dm^{-3} will have no adverse effects on many invertebrates, at least over a 96 h period.

9.2 Toxicity of permethrin to aquatic invertebrates

In section 4, concentrations of *cis*- and *trans*-permethrin were presented for aqueous and sediment materials. *Cis*-permethrin was found in river waters from several sites at concentrations between 17 and 468 ng dm^{-3}. *Trans*-permethrin was also found at some sites but at a lower concentration *viz* 39-82 ng dm^{-3}. The compounds were also detected in some of the sediments with the *cis*-isomer at a slightly higher concentration, 9-11 µg kg^{-1}, compared with the *trans*-isomer, 4-7 µg kg^{-1}. The values of the field partition coefficient, log K_{om}, were determined as 3.4 and 4.1 which compare with predicted values of 3.3-3.8.

In view of the analytical data obtained at the river sites it was necessary to make some evaluation of the likely toxic effects to invertebrates, particularly those normally associated with sediments.

Data for individual species taken from the literature are given in table 9.2. The toxicity test or concentration of permethrin used in each case is given along with the reference. Results have been collated into invertebrate groups and the range of concentrations affecting each group are given in table 9.3.

Table 9.4 gives the minimum effect concentration reported in the literature for each invertebrate species or group.

Crustaceans are the most sensitive group of animals to permethrin with reported LC_{50} values starting at ≤0.3 µg dm^{-3} for *Daphnia, Gammarus* and crayfish species.. Reported concentrations for *Gammarus* were all ≤1 µg dm^{-3} even for LC_{96} values. Crayfish values ranged from 0.3 to 3 µg dm^{-3} *Daphnia* had a slightly narrower range with highest LC_{50} reported being 2.5 µg dm^{-3} The cladoceran *Scapholeberis* does not fit with the generally sensitive crustaceans having a LC_{50} of 13 µg dm^{-3}.

Many insects are also very sensitive to permethrin. Mayflies and mosquito LC_{50} values start below 10 µg dm^{-3} and caddisflies, chironomids and stonefly LC_{50} values are reported ≤2 µg dm^{-3}. *Simulium* species are more resistant with $LC_{50\text{-}95}$ values between 3.8 and 5 µg dm^{-3}. The only reported LC_{50} value for dragonflies was 7 µg dm^{-3} although many studies report effects on dragonfly mortality in experimental ponds or natural situations at concentrations very much lower than this value, the lowest reported effect concentration being 2.6 µg dm^{-3}. Although no LC_{50} values are given for beetles, a concentration of 2.3 µg dm^{-3} in a natural watercourse caused mortality of Dytiscidae, Staphilinidae and Gyrinidae and the hemipterans Gerridae and Notonectidae.

The most resistant animals include the caseless caddis *Hydropsyche* which has a $LC_{90\text{-}95}$ value of 100 µg dm^{-3}, and the microcrustaceans *Cyclops* and *Podura aquatica* which showed only partial mortality of a population at the same concentration in outdoor ponds. However no effect was found at this high concentration on a range of aquatic organisms including *Rhynchelmis*, Turbellaria, Hirudinea, Mollusca and Ostracoda in the same study.

9.2.1 Effect of sediment on permethrin toxicity

Generally the effect of sediment on a range of pesticides has been shown to depend on the organic nature and particle size of the sediment. Pesticides become bound on organic sediment and small particle sizes which give high surface areas. Decreasing organic fraction and increasing particle size made pesticides more available to animals and uptake by aquatic invertebrates increased.

Relatively few studies are available on the effects of sediment on permethrin toxicity. Early work concentrated on quantifying the persistence of the chemical in aquatic habitats but no effects on animals were considered. Rawn *et al.* (1980) gave a concentration of permethrin in sediment of 4.9 µg kg^{-1} (dry wt) 232 days after treatment of artificial pools with 28 g dm^{-3}.

Kingsbury & Kreutzweiser (1979) found a concentration of 40 µg kg^{-1} in the sediment after an application of 17.5 g ha^{-1}. This had reduced to 10 µg kg^{-1} after 28 days. The maximum concentration found in the water was only 2.66 µg dm^{-3} and this reduced very quickly so that permethrin was undetected in the water after only 48 h.

One of the first studies involving aquatic invertebrates used a simulated application of 7.3 g ha^{-1} of permethrin to water and river sediment. The initial concentration in water was 7.63 µg dm^{-3} and the maximum mean concentration in the sediment after 1 and 7 days was 30 and 50 µg kg^{-1} (dry wt) respectively. Nymphs of *Hexagenia rigida* were exposed to contaminated river sediment and eight days after application there was 100% mortality.

The experiments of Muir *et al.* (1983) were more involved and were designed to show the toxic effects of contaminated sediment at different organic contents and particle sizes. For *Chironomus tentans* larvae held in water above spiked sediment, uptake of permethrin by the larvae was greatest above sand. At a concentration of 50 µg kg^{-1} in sand uptake was significantly greater than that above pond (75% clay) or river (silt/clay mixture) sediment spiked at 500 µg kg^{-1}. Uptake by larvae above pond sediment was consistently slightly higher than for animals above river sediment. Larvae were also allowed to burrow in the sediment. Uptake by animals in sand was again significantly greater than in river or pond sediment and at the higher concentration (500 µg kg^{-1}) uptake was greater in river sediment than in pond sediment.

In all cases the bioconcentration factor was greater for animals kept in sediment than for animals kept above the sediment although this was only significantly different in sand at both concentrations and for pond sediment at the lower concentration.

9.2.2 Summary

Permethrin is extremely toxic to many groups of aquatic invertebrates and very low concentrations can have significant effects on populations. Studies in the literature on the effect of permethrin are difficult to compare because they have used a wide range of physical and chemical variables in their experimental design and conducted their experiments and observations over a wide time scale. Table 9.4 shows the lowest concentration of permethrin recorded in the literature for each animal mentioned. Values quoted are for laboratory and field experiments, LC_{50} and LC_{90} values or EC concentrations ie for some specified behavioural change. The table shows that concentrations of ≤2 µg dm^{-3} affect a very wide range of aquatic invertebrates and show also that behavioural changes can have larger effects on population densities than mortality. This is shown by massive drift changes eg 20,000 times higher than normal for Leuctridae. Drift is a common reaction to sublethal concentrations of permethrin affecting Ephemeroptera, Trichoptera, Plecoptera, Diptera and Amphipoda.

The time element of observations is very important. This is shown in the case of *Brachycentrus* where the $LC_{90\text{-}95}$ value is 1.0 µg dm^{-3} but a concentration of 0.02 µg dm^{-3} although showing no immediate mortalities, resulted in 55% deaths after 28 days.

It is evident that some overlap occurs between the observed concentrations in water ie 0.02 ~ 0.5 μg dm^{-3}, §4, and observed lethal and acute toxic effects to certain organisms (see tables 9.3 and 9.4) particularly with the prolonged exposure expected at sites downstream of sewage works discharging permethrin.

It is more difficult to evaluate the effects of permethrin in the sediment because of the dynamic exchange of permethrin in solution with sediment bound material. There is no information available about the reversibility of this process. Another uncertainty is the effects of naturally occurring polyacids eg humic and fulvic acids, or the transport of permethrin from the particulate surfaces to the solution. This type of interaction, which has been reported for organochlorine pesticides, may lead to enhanced concentrations in interstitial water. However, in the absence of such enhancement, it is possible to estimate interstitial water concentrations from the field K_d (§4 and taking the average value of 1.8 dm^3 kg^{-1}) and surficial sediment concentration, ie ≈ 10 μg kg^{-1}, as 0.16 μg dm^{-3} at the River Stour site (samples H and I). Again, some groups of organisms such as crustaceans will be affected in these conditions eg *Daphnia magna* LC_{50} ≈ 0.2 μg dm^{-3}, with many other animals being affected over longer periods of exposure.

9.3 Toxicity of lindane to aquatic invertebrates

Results of the effect of Lindane on aquatic invertebrates are difficult to compare owing to the differing experimental procedures and variations in temperature and water chemistry (tables 9.5 and 9.6). LC_{50} values have been determined for a wide period of time. Canton *et al.* (1975) give values for *Daphnia magna* for 11 time periods from a value of >2000 μg dm^{-3} for 5 day LC_{50} to only 200 μg dm^{-3} for 25 day LC_{50}, a reduction of one order of magnitude in concentration over a 20 day period. Increasing the exposure time decreases the LC_{50} value. This can also be seen when determining TL_m values. The concentration reduced from 860 μg dm^{-3} to 640 μg dm^{-3} by increasing the exposure time of *Lymnaea luteola* to lindane from 12 h to 96 h (Agrawal 1984).

LC_{50} values have little meaning when determining the upper limit concentration to be allowed in freshwater. More useful are effect concentrations determined in laboratory experiments as EC_{50} values although field experimentation or observations on pollution of natural waters can point to significant effects on invertebrates at much lower levels than even EC_{50} values. The 48 h EC_{50} for *Daphnia magna* is 460 μg dm^{-3} (Sanders & Cope 1966). The effect is immobilization which does not necessarily lead to death. This concentration is considerably less than the corresponding LC_{50} value but is likely to have a similar devastating effect on a natural population. The LC_{50} exposure time for this concentration is 19 days.

The LC_{50} value for *Lymnaea* was calculated as >300 μg dm^{-3} by Bluzat & Seuge (1979). They found by decreasing the concentration that no effect on mortality occurred at 100 μg dm^{-3}. However there was an effect on fecundity with a decrease of 36% at this concentration and also an effect on embryogenesis with double and multiple embryos in 11.6% of the population. A concentration of 2000 μg dm^{-3} decreased fecundity by 66%.

Temperature also had an effect on toxicity. There is a negative correlation with temperature as toxicity increases with decreasing temperature. This is shown by Almar *et al.* (1988) when toxicity to the snail *Melanopsis* increased from 22.85 mg dm^{-3} to 19.8 mg dm^{-3} as the temperature decreased from 29°C to 15°C. It has also been shown in the cladoceran *Simocephalus* where the 24 h EC_{50} (immobilization) value increased from 520 µg dm^{-3} to 880 µg dm^{-3} (ie decreasing toxicity) for a temperature rise of 10°F (Canton *et al.* 1975). The opposite effect however was documented as early as 1950 by Guthrie who wrote that lindane was more toxic at higher temperatures. This was also found by Agrawal (1984). He quotes values of 860 µg dm^{-3} and 590 µg dm^{-3} for 12 h TL_m values for *Lymnaea luteola* for temperatures of 18-21°C and 31-34°C respectively. Also Fisher & Wardleigh (1985) found that there was a positive temperature correlation with LC_{50} values of 13.43 µg dm^{-3} at 15°C and 6.63 µg dm^{-3} at 25°C for *Chironomus riparius*. A further 10°C increase did not affect the toxicity.

Both effects are seen by the toxicity of lindane to the tubificid *Branchiura sowerbyi* where 100% mortality is recorded at 4.4°C and 32.2°C but zero mortality occurred at 21°C (Naqvi 1973). Thus it seems likely that toxicity may increase with decreasing temperature and increasing temperature from some middle range temperature, the value of which depends on the invertebrate species being considered.

Toxicity also changes with life stage or size of the invertebrate. First year class *Pteronarcys california* (stonefly) were 4.5 times more susceptible to lindane than 2nd year class animals (Sanders & Cope 1968).

9.3.1 Effect of sediment on lindane toxicity

There are very few studies concerning the effect of sediment on lindane toxicity. In a terrestrial situation lindane was sprayed onto 'peat soil' and the activity of the insecticide was measured by toxicological studies using *Asellus aquaticus*. Uptake by the peat was low and this contaminated sediment did not affect the test animals (Kaminski *et al.* 1969).

In experiments with the tubificid *Branchiura sowerbyi* Naqvi (1973) found that the addition of 'mud' reduced the effect of a known concentration of lindane in water from 100% to zero mortality.

9.3.2 Summary

The highest concentration of lindane determined in river water in this work is 0.04 µg dm^{-3} at the R. Stour site (H, §4). Although lindane was the most commonly occurring pesticide found in the water samples, the concentrations were always low *viz* <0.02 µg dm^{-3}. This is in agreement with other survey work that we carried out during 1989-90 in the Great Ouse catchment in East Anglia where concentrations between 0.016-0.019 µg dm^{-3} were determined at sites in the main river, side channels and a marina. At all locations the corresponding concentration of lindane in the river sediments was ≤1.2 µg kg^{-1} (see §4).

Lindane is toxic to a wide range of aquatic invertebrates and a concentration of ≤10 μg dm^{-3} causes mortality to some microcrustacea, and insect groups (table 9.5). Molluscs and Oligochaeta are in general very tolerant to lindane with effect concentrations usually above 1000 μg dm^{-3} and often considerably higher (*Lymnaea* LC_{50} 7300 μg dm^{-3} and *Melanopsis* LC_{50} *c.* 20,000 mg dm^{-3}). Sediment appears to have a detoxifying effect, removing lindane from solution where it becomes unavailable or reduced in effect as a toxin.

9.4 Conclusion

It is difficult to evaluate the toxic effects of the pesticides when they are associated with suspended solids or river/lake sediments. This is because of the limited amount of published information relating to particulate bound material; in cases where sediments have been incorporated in a toxicology test, the observed effects are likely to be a result of the sorption of the pesticide onto the solids and concomitant reduction in the concentration in the aqueous phase. One approach is to estimate the concentration of pesticide in interstitial water and relate this to the aqueous toxicity. The concentration in the interstitial water may be measured directly by specialized procedures for abstraction and measurement or calculated from the distribution coefficient of the pesticide with the sediment. Neither approach takes account of the speciation of the pesticide in the interstitial water, *viz* soluble, colloid and suspended solids, but does provide a first approximation not applied at the moment.

Table 9.1 Results of simazine toxicity tests and experiments from the literature on invertebrates

	Conc. of simazine mg dm^{-3}	Toxicity	Reference
Crustacea			
Zooplankton	1-1.5	No effect	Snow 1964
"	2	96 h mortality slight	Snow 1963
"	4	96 h mortality 10%	"
Daphnia magna			
(immature)	1.1	96 h EC_{50}	Johnson & Finley 1980
Daphnia magna	1.0	48 h TL_{50}	Sanders 1970
Cypridopsis vidua	3.2	48 h TL_{50}	"
" " (mature)	3.7	48 h EC_{50}	Johnson & Finley 1980
Asellus brevicaudus	>100	48 h TL_{50}	Sanders 1970
Gammarus fasciatus	40	24 h LC_{50}	Sanders 1969
" "	21	48 h LC_{50}	"
" "	13	96 h LC_{50}	"
" "	>100	96 h LC_{50}	Johnson & Finley 1980
" "	>100	48 h TL_{50}	Sanders 1970
Palaemonetes kadiakensis			
(glass shrimp)	>100	48 h TL_{50}	"
Orconectes nais (crayfish)	?100	48 h TL_{50}	"
Diptera			
Tendipedidae	28	LD_{50}	Walker 1964
"	0.5-2	not affected	"
biting midges	0.5-2	100% mortal. for 8 weeks	"
phantom midges	0.5-2	unaffected	"
mosquitos	0.5-2	100% mortal. for 14 mths	"
Ephemeroptera	0.5-2	88% mortal. after 1 week depressed for 14 months	Walker 1964
Hexagenia	1-3	unaffected	Mauck *et al.* 1976a
Trichoptera	0.50-2	marginal reduction	"
Odonata	0.5-2	unaffected	Walker 1964
"	0.1-0.3	"	Mauck *et al.* 1976a
Pteronarcys			
(2nd year class)	1.9	96 h LC_{50}	"
Coleoptera	0.5-2	90% reduction in 1 week depressed for 11 months	"
Mollusca	0.5-2	100% mortality for 8 wks recovered in 4-6 months	"
Leeches	0.5-2	unaffected	"
Oligochaeta	0.5-2	50% mortality in 1 week recovered in 4-6 months	"

Table 9.2 Results of permethrin toxicity tests and experiments from the literature on invertebrates

	Conc. of permethrin µg dm^{-3}	Toxicity	Reference
Crustacea			
Daphnia magna	0.2-0.6	48 h LC_{50}	Stratton & Corke 1981
" "	1.0	100% mortality	" " "
" "	1.4-2.5	48 h LC_{50}	Thurston *et al.* 1985
Daphnia	2.0	100% mortality	Rettich 1980b
Daphnia rosea	0.75-1.5	100% mortality	Yasuno *et al.* 1988
Scapholeberis kingi	13	3 h LC_{50}	Sun 1987
Tropocyclops pracinus	10	mortality	Yasuno *et al.* 1988
Cyclops	100	"	Rettich 1980b
Podura aquatica	100	"	" "
Asellus aquaticus	5.0	mortality	Rettich 1980b
" "	10.0	100% mortality	" "
Gammarus pseudolimnaeus	0.25-0.37	LC_{50}	Helson *et al.* 1986
Gammarus	1.0	24 h LC_{90-95}	Muirhead-Thompson
"	0.5	Drift	1978
Gammarus pseudolimnaeus	17.5 g ha^{-1}	mortality	" "
			Helson *et al.* 1986
Orconectes	3.0	48 h LC_{50}	
Procambarus clarkii			Poirier *et al.* 1988
8-12 mm	0.39	96 h LC_{50}	
20-30 mm	0.62	96 h LC_{50}	Jolly *et al.* 1978
		0.1 ppb for 10 wks	" " "
		No effect on growth	
8-12 mm		1 ppb left for 24 d	" " "
		No mortal. after 96 h	
20-30 mm		1 ppb left for 16 d	" " "
		No mortal. after 96 h	
			" " "
Diptera			
Tanytarsus	2.5	48 h LC_{50}	Thurston *et al.* 1985
Glyptotendipes paripes	2.4	24 h LC_{50}	Ali 1981
" "	5.3	24 h LC_{90}	" "
Chironomus decorus	4.5	24 h LC_{50}	" "
" "	11.0	24 h LC_{90}	" "
Goeldichironomus holoprasinus	2.4	24 h LC_{50}	" "
" "	3.1	24 h LC_{90}	" "

	Conc. of permethrin µg dm^{-3}	Toxicity	Reference
Chironomids 17.5 g ha^{-1}	(2.66)	40-90% mortality	Kingsbury & Kreutzweiser 1979
"	5	No effect	Rettich 1980b
"	10	100% mortality	" "
Chaoborus flavicans	0.75.1.5	100% mortality	Yasuno *et al.* 1988
Aedes aegypti	0.69-1.85	LC_{50}	
" " 28 g ha^{-1}	(15)	after 0-12 h 100% m.	Helson *et al.* 1986
		after 24 h 24% mort.	Rawn *et al.* 1980
		after 72 h 0% mort.	" " "
			" " "
Aedes albopictus	2.5 (trans)	LC_{50}	
" "	2.2 (cis)	LC_{50}	Gill 1977
" "	4.5 (trans)	LC_{90}	" "
" "	3.8 (cis)	LC_{90}	" "
			" "
Aedes nigromaculis	11-28 g ha^{-1}	high mortality	Mulla *et al.* 1975
" " (larvae)	0.5	LC_{50}	Mulla *et al.* 1980
" " "	0.8	LC_{90}	" " "
" " (pupae)	2	LC_{50}	" " "
" " "	4	LC_{50}	" " "
Aedes taeniorhynchus			
" " (larvae)	0.5	LC_{50}	Mulla *et al.* 1980
" " "	1.3	LC_{90}	" " "
" " (pupae)	2	LC_{50}	" " "
" " "	4	LC_{90}	" " "
Aedes cantans (larvae)	4.7	LC_{50}	Rettich 1979
" " "	15.4	LC_{90}	" "
" " (pupae)	1	LC_{50}	" "
" " "	6	LC_{90}	" "
" " (larvae)	5	LD_{100}	Rettich 1980b
" " (pupae)	10	LD_{100}	" "
" "	0.02-0.75 g m^{-2}	Substantial reduction in numbers	Rettich 1980a
Aedes sticticus (larvae)	2.7	LC_{50}	Rettich 1979
" " "	6.8	LC_{90}	" "
" " (pupae)	1	LC_{50}	" "
" " "	2.5	LC_{90}	" "

		Conc. of permethrin µg dm^{-3}	Toxicity	Reference
Aedes vexans	(larvae)	2.1	LC_{50}	Rettich 1979
" "	"	6.3	LC_{90}	" "
" "	(pupae)	0.8	LC_{50}	" "
" "	"	2.5	LC_{90}	" "
" "	(larvae)	100	LD_{100}	Rettich 1980b
Culex quinquefasciatus				
" "	(larvae)	1.4	LC_{50}	Mulla *et al.* 1980
" "	"	2.5	LC_{90}	" " "
" "	(pupae)	1	LC_{50}	" " "
" "	"	5	LC_{90}	" " "
Culex tarsalis	(larvae)	2	LC_{50}	Mulla *et al.* 1980
" "	"	4	LC_{90}	" " "
" "	(pupae)	6	LC_{50}	" " "
" "	"	16	LC_{90}	" " "
" "		28-56 g ha^{-1}	excellent control	Mulla *et al.* 1975
Culex pipiens	(larvae)	2.1	LC_{50}	Rettich 1979
" "	"	4.1	LC_{90}	" "
" "	(pupae)	2.4	LC_{50}	" "
" "	"	4.9	LC_{90}	" "
Culex p. molestus	(larvae)	1.4	LC_{50}	Rettich 1979
" " "	"	2.8	LC_{90}	" "
" " "	(pupae)	11.2	LC_{50}	" "
" " "	"	16.9	LC_{90}	" "
Culex peus		28-56 g ha^{-1}	excellent control	Mulla *et al.* 1975
Culiseta annulata	(larvae)	5.9	LC_{50}	Rettich 1979
" "	"	10.7	LC_{90}	" "
" "	(pupae)	13.1	LC_{50}	" "
" "	"	29.8	LC_{90}	" "
Culiseta incidens	(larvae)	3.0	LC_{50}	Mulla *et al.* 1980
" "	"	5.0	LC_{90}	" " "
" "	(pupae)	0.7	LC_{50}	" " "
" "	"	1.4	LC_{90}	" " "
Culiseta inornata		28 g ha^{-1}	100% mortality	Mulla & Darwazeh 1976
" "		5.6-11.2	some mortality	" " "

	Conc. of permethrin µg dm^{-3}	Toxicity	Reference
Pscorphora columbiae			
" " (larvae)	3.0	LC_{90}	Mulla *et al.* 1980
" " "	3.0	LC_{90}	" " "
" " (pupae)	2	LC_{50}	" " "
" " "	4	LC_{90}	" " "
" "	28 g h^{-1}	100% mortality	Mulla & Darwazeh 1976
" "	5.6-11.2	some mortality	" " "
Culicidae	17.5 g ha^{-1}	95% mortality	Kingsbury & Kreutzweiser 1979
Simulium	5.0	24 h LC_{90-95}	Muirhead-Thomson 1978
"	10 ppb for 15-16 min	86% mortality	" " "
"	3.8	48 h LC_{50}	Poirier *et al.* 1988
"	1.8	Short term effect	Kingsbury & Kreutzweiser 1979
Ephemeroptera			
Baetis	1.0	24 h LC_{90-95}	Muirhead-Thomson 1978
Baetidae	1.8	40-90% reduction in benthos. Increase in drift	Kingsbury & Kreutzweiser 1979
Hexagenia rigida	0.58-2.06	6 hr LC_{50}	Friesen *et al.* 1983
" "	7.63	100% mort. after 7 d	" " "
Heptageniidae	1.8	Immediate drift. *c.* 100% mortality	Kingsbury & Kreutzweiser 1979
Isonychia	4.4	48 h LC_{50}	Poirier *et al.* 1988
mayflies	1.1 g ha^{-1}	toxic in short term	Mulla *et al.* 1978
	5.6 g ha^{-1}	toxic	Mulla & Darwazeh 1976
Plecoptera			
Leuctridae	1-16	Drift increased by x20,000	Kingsbury & Kreutzweisr 1979
Pteronarcys dorsata	0.21	90% immobility in 5 h	Anderson 1982
	0.064	100% " in 48 h	" "
	0.042	100% " in 21 d	" "

	Conc. of permethrin µg dm^{-3}	Toxicity	Reference
Trichoptera			
Brachycentrus	1.0	24 h LC_{90-95}	Muirhead-Thomson 1978
"	5 ppb for 30 min	No effect	" "
"	0.52	behavioural change in 6 h	Anderson 1982
"	0.064	All affected after 24 h	" "
"	0.03	No effect after 2 days	" "
"	0.03	55% mort. after 28 d	" "
Brachycentrus americanus	0.17	21 day LC_{50}	
Hydropsyche	100	24 h LC_{90-95}	Muirhead-Thomson 1978
"	0.5 ppb for 30 min	50% drift after 2-4 h	" "
"	5 ppb for up to 1 h	high survival	Muirhead-Thomson 1979
Rhyacophila	10 ppb for 15 min	100% mortality after 24 h	Muirhead-Thomson 1979
Pycnopsyche	7.0	48 h LC_{50}	Poirier *et al.* 1988
Trichoptera	2.0	100% mortality	Rettich 1980b
	1-16	Drift increase, benthos reduction	Kingsbury & Kreutzweiser 1979
Odonata	5.6 g ha^{-1}	toxic	Mulla & Darwazeh 1976
	1.1 g ha^{-1}	no effect	Mulla *et al.* 1978
	17.5 g ha^{-1} (2.66)	mortality within 24 h	Kingsbury & Kreutzweiser 1979
Ophiogomphus	7.1	48 h LC_{50}	Poirier *et al.* 1988
Coleoptera	17.5 g ha^{-1} (2.66)	Surface beetles affected	Kingsbury & Kreutzweiser 1979
Dytiscidae	2.0	100% mortality	Rettich 1980b
Helodidae	5.0	some mortality	" "
"	10.0	100% mortality	" "
Hemiptera			
Gerris lacustris	2.0	100% mortality	" "

	Conc. of permethrin µg dm^{-3}	Toxicity	Reference
Molluscs *Helisoma trivolvis*	0.33 100	Behavioural change for 7 days only No effect	Spehar *et al.* 1982 Rettich 1980b

Table 9.3 Toxicity of invertebrate groups to permethrin

affected

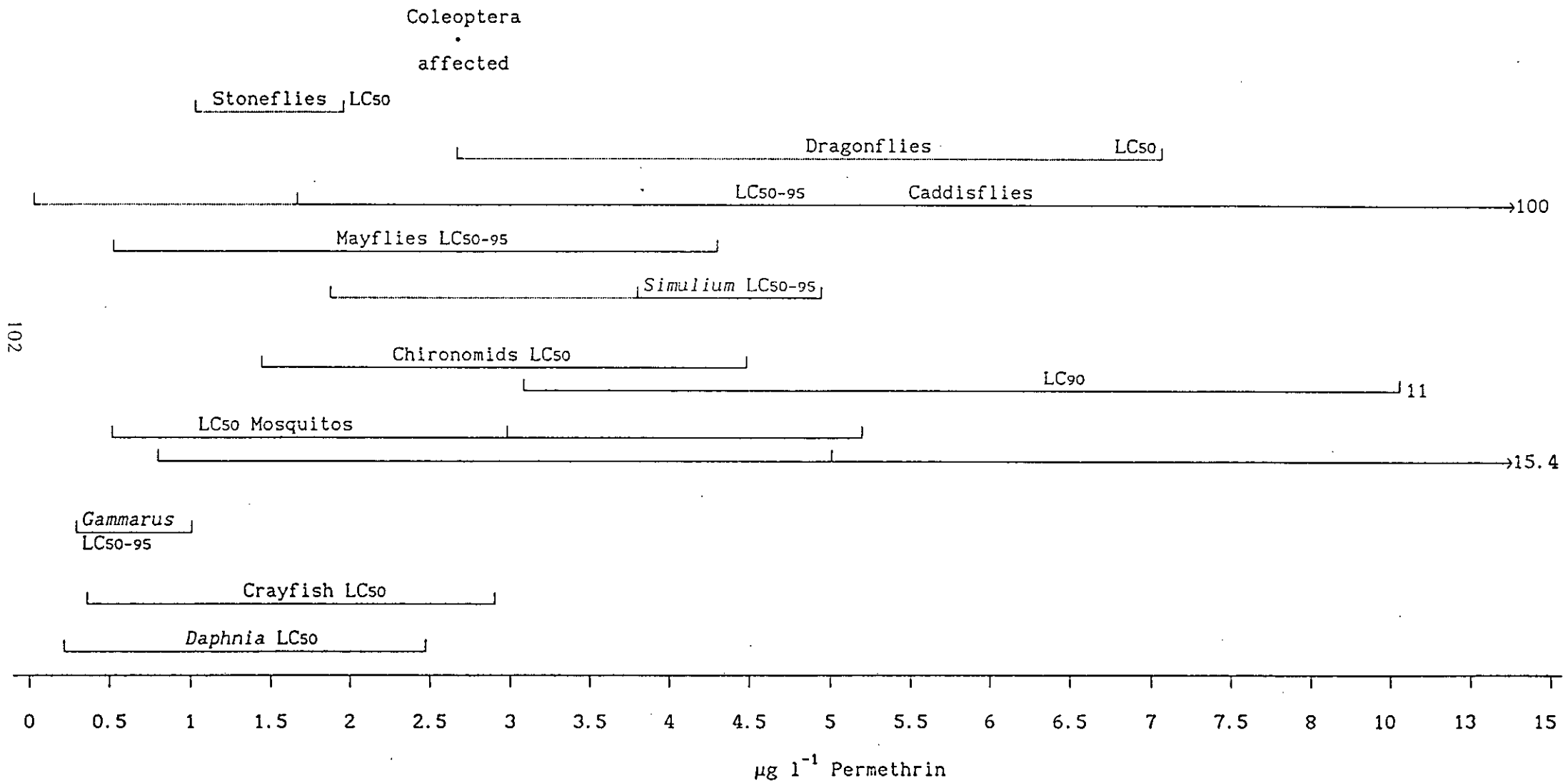


Table 9.4 Minimum effect concentrations of permethrin reported in the literature for invertebrates

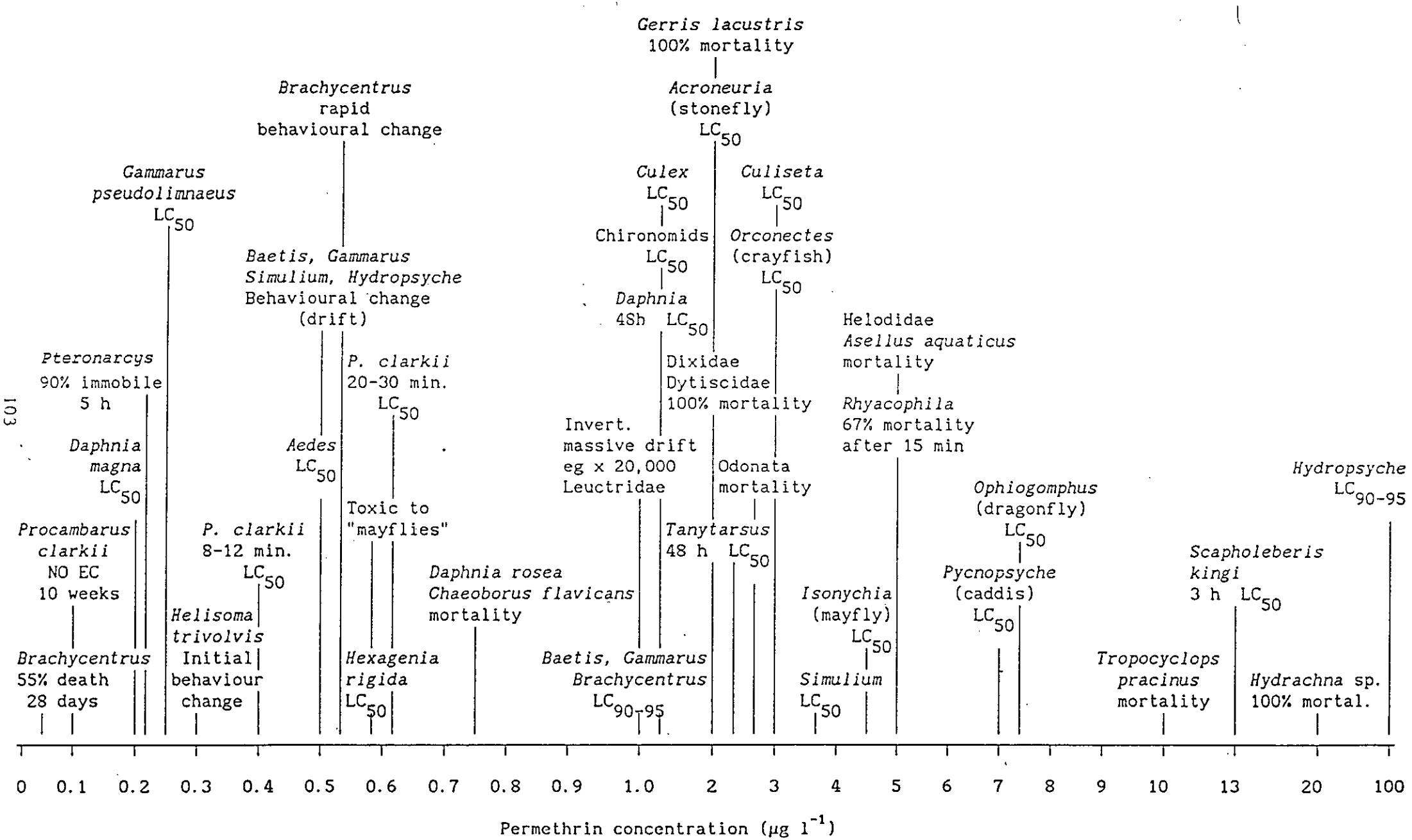
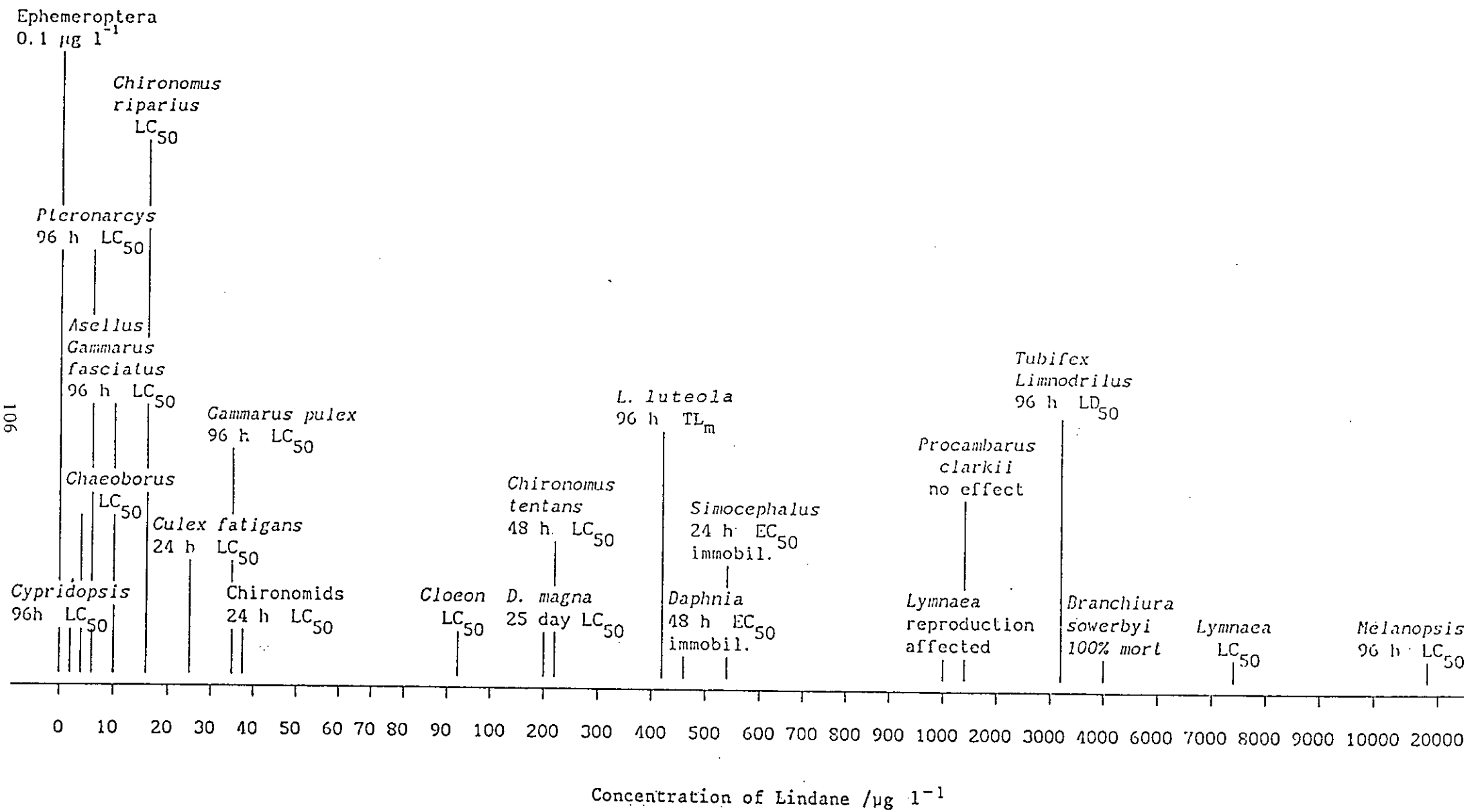


Table 9.5 Results of lindane toxicity tests and experiments in the literature on invertebrates

	Isomer	Conc. of lindane µg l^{-1}	Temper-ature	Toxicity	Reference
Crustacea					
Daphnia	γ	460	15.6°C	48 h EC_{50}	Sanders & Cope 1966
Daphnia magna (immature)	γ	460	15°C	48 h EC_{50}	Johnson & Finley 1980
Daphnia magna	γ	2000		5 day LC_{50}	Canton *et al.* 1975
" "	γ	800		15 day LC_{50}	" " "
" "	γ	200		25 day LC_{50}	" " "
" "	γ	207		48 h LC_{50}	Macek et al. 1976
Simocephalus (immature)	γ	520	60°F	24 h EC_{50}	Sanders & Cope 1966
"	γ	880	70°F	24 h EC_{50}	" " "
"	γ	520		48 h EC_{50}	Johnson & Finley 1980
Cypridopsis (mature)	γ	3.2	21°C	96 h LC_{50}	" " "
Asellus (mature)	γ	10	15°C	96 h LC_{50}	" " "
Asellus aquaticus		21		LC_{50}	Tscheu-Schlueter & Skibba 1986
Gammarus fasciatus (mature)	γ	10	15°C	96 h LC_{50}	Johnson & Finley 1980
Gammarus lacustris	γ	120	21.1°C	24 h LC_{50}	Sanders 1969
" "	γ	88		48 h LC_{50}	" "
" "	γ	48		96 h LC_{50}	" "
" "	γ	88	21°C	96 h LC_{50}	Johnson & Finley 1980
" "		30		48 h LC_{50}	Bluzat & Seuge 1979
Gammarus pulex	γ	34		96 h LC_{50}	Abel 1980
" "		10		116h LT_{50}	" "
" "		20		102 h	" "
" "		50		27 h	" "
" "		100		20 h 20 h	" "
" "		200		9.4 h 9.4 h	" "
" "		500		5.4 h 5.4 h	" "
" "		1000		2.4 h 2.4 h	" "
" "		2000		0.57 h	" "
" "		4000		0.70 h	" "
Gammarus fasciatus	γ	39		48 h LC_{50}	Macek *et al.* 1976
Procambarus clarkii	γ	1120		No effect	Andreu-Moliner *et al.* 1986

	Isomer	Conc. of lindane µg l^{-1}	Temper-ature	Toxicity	Reference
Diptera					
Chironomus tentans	γ	207		48 h LC_{50}	Macek *et al.* 1976
Chironomus riparius	γ	13.43	15°C	LC_{50}	Fisher & Wardleigh 1985
" "		6.63	25°C	LC_{50} "	" "
" "		6.77	35°C	LC_{50} "	" "
chironomids		38.81	28°C	24 hr LC_{50}	Joshi *et al.* 1975
Tendipes crassicaudatus	γ	20		89-99% mortality	Patterson 1964
Glyptotendipes paripes	γ	20		79-93% mortality	" "
Chaoborus		8		48 h LC_{50}	Bluzat & Seuge 1979
Culex fatigans	γ	27		24 h LC_{50}	
Baetis rhodani & *Caenis moesta*		0.1		reduction in survival	Harper *et al.* 1977
Cloeon		92		LC_{50}	Bluzat & Seuge 1979
Pteronarcys californica (2nd year class)	γ	4.5	15.5°C	96 h LC_{50}	Sanders & Cope 1968
1st year class				4.5 times more susceptible	" " "
Pteronarcys californica		2		48 h EC_{50}	Cope 1965
Mollusca					
Melanopsis dufouri		19800	15°C	96 h LC_{50}	Almar *et al.* 1988
		21030	22°C		" " "
		22850	29°C		" " "
Lymnaea		7200		48 h LC_{50}	Bluzat & Seuge 1979
"		1000		36% decrease in fecundity	" " "
"		2000		66% " " "	" " "
Lymnaea luteola		860	18-21°C	12 h TL_m	Agrawal 1984
" "		640	"	96 h TL_m	" "
" "		590	31-34°C	12 h TL_m	" "
" "		420	"	96 h TL_m	" "
Oligochaeta					
Branchiura sowerbyi	γ	4000	4.4°C	100% mortality after 72 h	Naqvi 1973
" "	γ	4000	32.2°C	" " " " "	" "
Tubifex tubifex	γ	4000		No effect after 72 h	Naqvi & Ferguson 1968
Tubifex & *Limnodrilus* 45%	γ	8080	20°C	24 hr LD_{50}	Whitten & Goodnight 1966
		5660	"	48 hr LD_{50}	" " "
		3150	"	96 hr LD_{50}	" " "

Table 9.6 Minimum effect concentrations of lindane reported in the literature for invertebrates



10. CONCLUSIONS

The movement and partition of toxic organic compounds in rivers and lakes is of vital importance to our understanding of their impact on aquatic life and general quality of freshwater ecosystems. This project has examined particular aspects of the distribution of three groups of pesticides: the older organochlorine insecticides, the newer synthetic pyrethroids and the triazine herbicides with attention to an important member of each group viz: lindane, permethrin and simazine. Although considerable information is available from laboratory studies about the toxicity, adsorption, biodegradation, chemical reactions and fate of the individual compounds, it is not yet possible to assess their fate in complex natural systems of varying physical, chemical and biological diversity. For this reason alone it is necessary to survey river sites which are subject to pesticide exposure and determine the instantaneous distribution between the dissolved, bed and suspended sediment, colloids and biota. The information is also valuable for validation of models developed to predict the fate of the pesticides, for risk assessment related to the exposure of the chemical associated with different matrices and for the estimation of the amount of pesticides transported downstream with suspended matter in a river.

The general conclusions drawn from the survey work are that a range of the older organochlorine insecticides are still found in river sediments at concentrations much higher than in the associated water. At sites subject to exposure to pyrethroids eg permethrin and deltamethrin, the same relative concentration in the sediment compartment is observed. The triazines, simazine and atrazine, have a much lower affinity to the bed sediment and suspended matter but do exhibit anomalous adsorption behaviour, with higher loads on sediments and suspended solids found in field samples than is expected from the partitioning behaviour observed in the laboratory.

The partitioning of permethrin, DDE, lindane and dieldrin between water and surficial sediment at sites where the pesticide concentrations are not expected to fluctuate rapidly, are found to be consistent with the behaviour estimated on the basis of their distribution between the water and the organic matter content of the sediment. This has proven a useful criterion to identify anomalous distribution behaviour in complex sediments. It also provides a useful first-approximation to the evaluation of the interstitial concentrations of pesticides to which benthic feeding organisms are exposed. The summary of the invertebrate toxicology data supports the conclusion that at the moment the best estimate of the toxicity of particle-bound pesticides is from the interstitial concentrations which are expected to be higher than the corresponding bulk-water concentrations for most pesticides including the triazines.

The partition of pesticides on to suspended solids presents particular problems in the handling and separation procedures used prior to chemical analysis. Specialised methods have been developed to enable the concentration of pesticides to be measured with samples of 1 to 50 litres. In general, the concentration of lipophilic pesticides is expected to be higher on suspended sediments because of their greater organic matter content. The concentration of pesticides on suspended solids during a storm in a stream with material mainly derived from sub-surface and surface run-off, has been measured and found to be similar to the bed-sediment. The results show a substantial contribution of suspended solids to the overall pesticide transport, particularly for the synthetic pyrethroids, DDT and metabolites and dieldrin but relatively minor (<10% of the total load) for lindane and the triazines. It is

possible to estimate the contribution of suspended solids to the mass transport for neutral pesticides from information on the distribution characteristics of the pesticides and the concentration of suspended solids in the water.

Studies of the release of native (or in-situ) pesticides from bed-sediments are also necessary for the assessment of their fate and availability. It is also important to distinguish between artificially 'spiked' sediments and material containing pesticides after exposure in field conditions, ie containing native pesticide. The history of the sediment is likely to play a part in determining the release mechanism and also the kinetics of the release process. Unfortunately, most of the research in this area has been done using radio-labelled pesticides rather than native compounds. The conclusions from the present study, based on release experiments from field sediments, are that after a period of 10 days in anaerobic conditions, no release of DDE, TDE, permethrin or deltamethrin could be detected. Both lindane and simazine were released into he water. The distribution coefficient for simazine decreased from a high field value to the laboratory determined value indicating the loss of the recalcitrant fraction after prolonged exposure.

Finally, preliminary experiments with the colloid sediment fraction (<0.2 μm in size) have shown that permethrin has a strong association with colloid material compared with simazine. It has not been possible to measure the distribution coefficient for simazine but the indications are that it is <2000 l/kg. This compares with a value for permethrin of 30,000 l/kg. Further research is needed to characterize the colloid component, make more precise measurements of the affinity between pesticides and colloids and to examine differences between the behaviour of colloids derived from different sources to enable the results to be applied to riverine transport of pesticides and flocculation in estuaries and coastal waters.

11. SUGGESTIONS FOR FURTHER STUDIES

The interaction between pesticides and particulate matter in rivers and lakes is a complex area of research not only because of the multitude of pesticides in current use but also the nature of the heterogeneity of suspended matter and sediment materials. It is surprising that very little published information exists on the role of particulate bound pesticides in toxicology and also in more general terms of the transport, release, degradation and persistence of sediment bound compounds. It has already been noted in §4 that we have not found any published accounts of the concentration of pesticides in river sediments in the U.K.; the publication, §11, from this work appears to be the first.

It is inevitable that a project of this scope, even with well-defined objectives, §2, raises some important questions which suggest further studies. This is particularly true of a new area such as "pesticide-particle interactions" where new techniques have been developed enabling more reliable studies of environmental samples. Specialised procedures have been developed and tested for the analysis of organic rich sediments and suspended matter (see §3 and publications in §11) for a range of pesticides. These techniques could now be applied more widely to the evaluation of the occurrence of pesticides in river/lake sediments and suspended solids.

Apart from general survey work, perhaps linked to river load estimation, land use and longer-term monitoring studies, other more process-orientated work is summarized as follows.

11.1 Transportation of pesticides by colloids

The preliminary study presented in §5 illustrates the potential importance of colloids in riverine transport of lipophilic compounds. There is scope for the development of the automated adsorption system (§7) for the study of natural colloids with the objective of evaluating the flux of colloid bound pesticides to an estuary in a selected river catchment.

11.2 Fate of synthetic pyrethroids in river sediments

The studies in §4 and §8 provide evidence of the occurrence and persistence of two synthetic pyrethroids in river sediments. In view of the increasing market share of insecticides that the pyrethroids demand, it is pertinent to examine other compounds in the group including new insecticides. The predictive equations found successful in this work for estimating the distribution of organochlorine compounds between water and sediments need validation (or re-determination) for the synthetic pyrethroids. The fate and toxicity of pyrethroids in anaerobic river/lake sediments is of particular concern.

11.3 Fate of triazine and other water soluble herbicides in river sediments

The results obtained here, which are also supported by information in the published literature, show that simazine is bound in some sediments by at least two different mechanisms; fast reversible adsorption and much slower partially reversible sorption. This has important implications for the fate of these compounds and impact on benthic animals. Research is needed to assess whether similar results are obtained for other triazines and water soluble herbicides eg phenylureas such as isoproturon.

12. PUBLICATIONS FROM THIS PROJECT

House, W.A., Farr, I.S., Orr, D.R. & Ou, Z. (1991) The occurrence of synthetic pyrethroid and selected organochlorine pesticides in river sediments. British Crop Protection Council, No. 47. *Pesticides in soils and water.* University of Warwick, 183-192.

House, W.A. & Ou, Z. (1992) in press. Determination of pesticides on suspended solids and sediments: investigation on the handling and separation. *Chemosphere*, pp 17.

House, W.A., Ou, Z., Armitage, P.D. & Farr, I.S. (1992) The partition of selected pesticides in an agricultural drainage stream. Lecture to the presented at the joint meeting of SETAC-Europe 'Ecology/Environmental fate/Toxicology/Bioremediation' in Potsdam, Germany.

13. REFERENCES

Abel, P.D. (1980) Toxicity of γ-hexachlorocyclohexane (Lindane) to *Gammarus pulex*: mortality in relation to concentration and duration of exposure. *Freshwat. Biol.*, **10**, 251-259.

Agrawal, H.P. (1984) Toxicity of Lindane to *Lymnaea luteola* Lamarck. *J. Anim. Morphol.*, **31**, 267-272.

Albanis, T.A., Pomonis, P.J. & Sdoukos, A.T. (1989) The influence of fly ash on pesticide fate in the environment. II Hydrolysis, degradation and adsorption of atrazine in aqueous mixtures of soils with fly ash. *Toxicological & Environ. Chem.*, **19**, 171-178.

Ali, A. (1981) Laboratory evaluation of organophosphate and new synthetic pyrethroid insecticides against pestiferous chironomid midges of central Florida. *Mosq. News*, **41**, 157-161.

Almar, M.M., Ferrando, M.M.D., Alarcon, V., Soler, C., & Andreu, E. (1988) Influence of temperature on several pesticides toxicity to *Melanopsis dufouri* under laboratory conditions. *J. Environ. Biol.*, **9**, 183-190.

Anderson, R.L. (1982) Toxicity of fenvalerate and permethrin to several nontarget aquatic invertebrates. *Environ. Entomol.*, **11**, 1251-1257.

Andreu-Moliner, E.S., Amlar, M.M., Legarra, I. & Nunez, A. (1986) Toxicity of some ricefield pesticides to the crayfish *P. clarkii*, under laboratory and field conditions in lake Albufera (Spain). *J. Environ. Sci. Health*, B, **21**, (6), 529-537.

Basile, G., Arienzo, M. & Celano, G. (1990) Adsorbimento di diserbanti su suoli della campania. *Agrochimica*, **34**, 181-192.

Bluzat, R. & Seuge, J. (1979) Effets de trois insecticides (Lindane, Fenthion and Carbaryl): Toxicité aigue sur quatre especes d'invertebres limniques; toxicité chronique chez le mollusque pulmone *Lymnea*. *Environmental Pollution*, **18**, 51-70.

Bowman, B.T. & Sans, W.W. (1985) Partitioning behaviour of insecticides in soil-water systems. I Adsorbent concentration effects. *J. Environmental Quality*, **14**, 265-269.

Briggs, G.G. (1981) Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *J. Agricultural Food Chemistry*, **29**, 1050-1059.

Brown, D.S. & Flagg, E.W. (1981) Empirical prediction of organic pollutant sorption in natural sediments. *J. Environ. Qual.*, **10**, 382-386.

Canton, J.H., Greve, P.A., Slooff, W. & Van Esch, G.J. (1975) Toxicity, accumulation and elimination studies of α-hexachlorocyclohexane with freshwater organisms of different trophic levels. *Water Res.*, **9**, 1163-1169.

Coats, J.R. & O'Donnell-Jeffery, N.L. (1979) Toxicity of 4 synthetic pyrethroid insecticides to rainbow trout (*Salmo gairdneri*). *Bull. Environ. Contam. Toxicol.* **23**, 250-255.

Cope, O.B. (1965) Contamination of the fresh-water ecosystem by pesticides. *J. Appl. Ecol.*, **3** (suppl.), 33-44.

Dean, W.E. Jr (1974) Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods.

Farr, I.S. & Clarke, R.T. (1984) Reliability of suspended load estimates in chalk streams. *Arch. Hydrobiol.*, **102**, 1-19.

Fisher, S. & Wardleigh, R.W. (1985) Effects of temperature on the acute toxicity and uptake of lindane by *Chironomus riparius* (Meigen) (Diptera:Chironomida). *J. Econ. Entomol.*, **78**, 1222-1236.

Friesen, M.K., Galloway, T.D. & Flannagan, J.F. (1983) Toxicity of the insecticide permethrin in water and sediment to nymphs of the burrowing mayfly *Hexagenia rigida* (Ephemeroptera:Ephemeridae). *Canadian Entomologist*, **115**, 1007-1014.

Gill, S.S. (1977) Larvicidal activity of synthetic pyrethroids against *Aedes albopictus* (Skuse). *S East Asian J. trop. Med. Public Hlth*, **8**, 510-514.

Goswami, K.P. & Green, R.E. (1971) Microbial degradation of the herbicide atrazine and its 2-hydroxy analog in submerged soil. *Environ. Sci. & Tech.* **5**, 426-429.

Gschwend, P.M. & Wu, Shian-chee (1985) On the constancy of sediment-water partition coefficients fo hydrophobic organic pollutants. *Environ. Sci. Tech.* **19**, 90-96.

Guthrie, F.E. (1950) Effect of temperature on toxicity of certain organic insecticides. *J. Econ. Entomol.* **43**, 559-563.

Harper, D.B., Smith, R.V. & Gotto, D.M. (1977) BHC residues of domestic orihin: a significant factor in pollution of freshwater in Northern Ireland. *Environmental Pollution*, **12**, 223-233.

Hassett, J.P. & Milicic, E. (1985) Determination of equilibrium and rate constants for binding of a polychlorinated biphenyl congener by dissolved humic substances. *Environ. Sci. Tech.* **19**, 638-643.

Hawker, D.W. & Connell, D.W. (1988) Influence of partition coefficients of lipophilic compounds on bioconcentration kinetics with fish. *Water Research*, **22**, 701-707.

Helson, B.V., Kingsbury, P.D. & De groot, P. (1986) The use of bioassays to assess aquatic arthropod mortality from permethrin drift deposits. *Aquat. Toxicol.*, **9**, 253-262.

Hill, I.R. (1989) Aquatic organisms and pyrethroids. *Pestic. Sci.*, **27**, 429-465.

House, W.A. (1983) Adsorption on heterogeneous surfaces. *Colloid Sci., Specialist Periodical Reports*, **4**, 1-58.

House, W.A., Shelley, N. & Fox, A.M. (1988) Chemical modelling applications to experimental streams. *Hydrobiologia*, **178**, 93-112.

Jessee, J.A., Benoit, R.E., Hendricks, A.C., Allen, G.C. & Neal, J.L. (1983) Anaerobic degradation of cyanuric acid, cystine and atrazine by a facultative anaerobic bacterium. *Applied & Environ. Microbiology*, **45**, 97-102

Johnson, W.W. & Finley, M.T. (1980) Handbook of acute toxicity of chemicals to fish and aquatic invertebrates. *Washington US Dept of the Interior, fish and wildlife service*, **137**, 98 pp.

Jolly, A.L. Avault, J.W., Koonce, K.L. & Graves, J.B. (1978) Acute toxicity of permethrin to several aquatic animals. *Trans. Am. Fish. Soc.*, **107**, 825-827.

Joshi, H.C., Kapoor, D., Panwar, R.S. & Gupta, R.A. (1975) Toxicity of some insecticides to chironomid larvae. *Indian J. environ. Hlth*, **17**, 238-241.

Kaminski, A., Zawalzki, B. & Szymanska, T. (1969) Teh effect of turf soil on the tixic activity of the gamma-hexachlorocyclohexane (HCH). *Rocz. Nauk. Roln. Ser. A*, **95**, 589-605.

Kile, D.E., Chiou, C.T. & Helburn, R.S. (1990) Effect of some petroleum sulphate surfactants on the apparent water solubility of organic compounds. *Environ. Sci. Tech.*, **24**, 205-208.

Kingsbury, P.D. & Kreutzweiser, D.P. (1979) Impact of double applications of permethrin on forest streams and ponds. *For. Pest Manage. Inst., Sault Ste Marie, Ontario.* Inf. Rep. FPM-X-27, 42 pp.

Lockhart, W.L., Billech, B.N., DeMarch, B.G.E. & Muir, D.C.G. (1983) Uptake and toxicity of organic compounds: studies with an aquatic macrophyte (*Lemna minor*). In: *Aquatic toxicology and hazard assessment, 6th Symposium; ASTM ST 802.* W.E. Bishop & R.D. Cardwell & B.B. Heidolph (Eds). American Society for Testing and Materials, 460-468.

Macek, K.J., Buxton, K.S., Derr, S.K., Deane, J.E. & Sauter, S. (1976) Chronic toxicity of Lindane to selected aquatic invertebrates and fish. *U.S. Environmental Protection Agency, Washington.* Report No. EPA-600/3-76-046.

Marchesi, J.R., House, W.A., White, G.F., Russell, N.J. & Farr, I.S. (1991a) A comparative study of the adsorption of linear alkylsulphates and alkylbenzene sulphonates on river sediments. *Colloids & Surfaces*, **53**, 63-78.

Marchesi, J.R., Russell, N.J., White, G.F. & House, W.A. (1991b) Effects of surfactant adsorption and biodegradability on distribution of bacteria between sediments and water in a freshwater microcosm. *Appl. Environ. Microbiol.* **89**, 2507-2513.

Matthiessen, P. (1988) Recent attempts to measure the behaviour and impact of pesticides in aquatic environments. In: *Field methods for the study of environmental effects of pesticides*, M.P. Greaves, P.W. Greig-Smith & B.D. Smith (Eds), *BCPC Monograph No. 40*, Thornton Heath: BCPC Publication.

Mauck, W.L., Mayer, F.L. Jr & Holz, D.D. (1976a) Simazine residue dynamics in small ponds, *Bull. Environm. Contam. Toxicol.*, **16**, 1-8.

Means, J.C. & Wijayaratne (1982) Role of natural colloids in the transport of hydrophobic pollutant. *Science*, **215**, 968-971.

Muir, D.C.G., Townsend, B.E. & Lockhart, W.L. (1983) Bioavailability of six organic chemicals to *Chironomus tentans* larvae in sediment and water. *Environ. Toxicol. Chem.*, **2**, 269-282.

Muir, D.C.G., Rawn, G.P., Townsend, B.E., Lockhart, W.L. & Greenhalgh, R. (1985) Bioconcentration of Cypermethrin, Deltamethrin, Fenvalerate and Permethrin by *Chironomus tentans* larvae in sediment and water. *Environmental Toxicology and Chemistry*, **4**, 51-61.

Muirhead-Thomson, R.C. (1978) Lethal and behavioural impact of permethrin (NRDC 143) on selected stream macroinvertebrates. *Mosquito News*, **38**, 185-190.

Muirhead-Thomson, R.C. (1979) Experimental studies on macroinvertebrate predator-prey impact of pesticides. The reactions of *Rhyacophila* and *Hydropsyche* (Trichoptera) larvae to *Simulium* larvicides. *Can. J. Zool.*, **57**, 2264-2270.

Mulla, M.S. & Darwazeh, H.A. (1976) Field evaluation of new mosquito larvicides and their impact on some nontarget insects. *Mosq. News*, **36**, 251-276.

Mulla, M.S., Darwazeh, H.A. & Majori, G. (1975) Field efficacy of some promising mosquito larvicides and their effects on nontarget organisms. *Mosq. News*, **35**, 179-185.

Mulla, M.S., Navvab-Gojrati, H.A. & Darwazeh, H.A. (1978) Toxicity of mosquite larvicidal pyrethroids to four species of freshwater fishes. *Environ. Entomol.*, **7**, 428-430.

Mulla, M.S., Darwazeh, H.A. & Dhillon, M.S. (1980) New pyrethroids as mosquito larvicides and their effects on non-target organisms. *Mosquito News*, **40**, 6-12.

Naqvi, S.M. (1973) Toxicity of 23 insecticides to a tubificid worm *Branchiura sowerbyi* from the Mississippi delta. *J. Econ. Entomol.*, **66**, 70-74.

Naqvi, S.M. & Ferguson, D.E. (1968) Pesticide tolerances of selected frshwater invertebrates. *J. Miss. Acad. Sci.*, **14**, 121-127.

NRCC (1986) Pyrethroids: Their effects on aquatic and terrestrial ecosystems. NRCC 24376, Ottawa, Ont. 303 pp.

Patterson, R.S. (1964) Recent investigations on the use of BHC and EPN to control chironomid midges in central Florida. *Mosq. News*, **24**, 294-299.

Pignatello, J>J> & Huang, L.Q. (1991) Sorption reversibility of atrazine and metolachlor residues in field samples. *J. Environ, Quality*, **20**, 222-228.

Pinder, L.C.V., Ladle, M., Gledhill, T., Farr, I.S., Casey, H. & Baker, J.H. (1982) Chalk river surveillance data. *A report to the department of the Environment*, Contract No. DGR 480/309.

Poirier, D.G. & Surgeoner, G.A. (1988) Evaluation of a field bioassay technique to predict the impact of aerial applications of forestry insecticides on stream invertebrates. *Can. Entomol.*, **120**, 627-637.

Rao, P.S.C. & Davidson, J.M. (1980) Estimation of pesticide retention and transformation parameters required in non-point source pollution models. In: Overcash, M.R. & Davidson, J.M. (eds), *Environmental impact of non-point source pollution*, Ann Arbor Science, Michigan, 23-67.

Rawn, G.P., Webster, G.R.B. & Muir, D.C.G. (1980) Bioactivity and degradation of Permethrin in artificial pools. *Can. Tech. Rep. Fish. Aquat. Sci.* **975**, 140-149.

Rettich, F. (1979) The toxicity of four synthetic pyrethroids to mosquito larvae and pupae (Diptera, Culicidae) in Czechoslovakia. *Acta entomologica bohemoslovaca*, **76**, 395-401.

Rettich, F. (1980a) The use of perethrin (NRDC 143) in pre-seasonal treatment of mosquito breeding sites. *Folia Parasitologica (Prague)*, **27**, 265-268.

Rettich, F. (1980b) Field evaluation of permethrin and decamethrin against mosquito larvae and pupae. *Acta entomological bohemoslovaca*, **77**, 89-96.

Saleh, F.Y., Dickson, K.L. & Rodgers Jr, J.H. (1982) Fate of lindane in the aquatic environment: rate constants of physical and chemical processes. *Environmental Toxicology and Chemistry*, **1**, 289-298.

Sanders, H.O. & Cope, O.B. (1966) Toxicities of several pesticides to two species of cladocerans. *Trans. Amer. Fish. Soc.*, **95**, 165-169.

Sanders, H.O. & Cope, O.B. (1968) The relative toxicities of several pesticides to naiads of three species of stoneflies. *Limnol. Oceanogr.*, **13**, 112-117.

Sanders, H.O. (1969) Toxicity of pesticides to the crustacean *Gammarus lacustris, U.S. Bureau of Sport, Fisheries and Wildlife.* Tech. paper No. **25**.

Sanders, H.O. (1970) Toxicities of some herbicides to six species of freshwater crustaceans. *J. Wat. Poll. Cont. Fed.*, **42**, 1544-1550.

Schimmel, S.C., Garnas, R.L., Patrick, J.M. Jr & Moore, J.C. (1983) Acute toxicity, bioconcentration and persistence of AC 222, 705, benthocarb, chlorpyrifos, fenvalerate, methylparathion and permethrin in the estuarine environment. *J. Agric. Food Chem.* **31**, 104-113.

Senesi, N. & Chen, Y. (1990) Toxic organic chemicals in porous media. Ed. B. Yaron, Ch. 3. pp 37-90.

Sharom, M.S., Miles, J.R.W., Harris, C.R. & McEwen, F.L. (1980) Behaviour of 12 insecticides in soil and aqueous suspensions of soil and sediment. *Water Research*, **14**, 1095-1100.

Sharom, M.S. & Solomon, K.R. (1981) Adsorption and desorption of permethrin and other pesticides on glass and plastic materials used in bioassay procedures. *Canadian J. Fish Aquat. Sci.*, **38**, 199-204.

Smith, J.H., Mabey, W.E., Bohonos, N., Holt, B.R., Lee, S.S., Chou, T.W., Bomberger, D.C. & Mill T. (1978) Environmental pathways of selected chemicals in freshwatr systems, Part II, Laboratory Studies. *U.S. Environmental Protection Agency,* EPA-600/7-78-074.

Snow, J.R. (1963) Simazine as an algicide for bass ponds. *Prog. Fish-Cult.*, **25**, 34-36.

Snow, J.R. (1964) Simazine as a preflooding treatment for weed control in hatchery ponds. *Proc. 18th Ann. Conf. of SE Assocn of Game and Fish Comm.*, Glearwater, Florida.

Spehar, R.L., Tanner, D.K., Nordling, B.R. (1982) Toxicity of synthetic pyrethroids, permethrin and AC 222, 705 and their accumulation in early life stages of fathead minnows and snails. *Aquat. Toxicol.*, **3**, 171-182.

Stratton, G.W., & Corke, C.T. (1981) Interaction of Permethrin with *Daphnia magna* in the presence and absence of particulate material. *Environmental Pollution ser. A)* **24**, 135-144.

Sun, F. (1987) Evaluating acute toxicity of pesticides to aquatic organisms: Carp, mosquitofish and daphnids. *Plant Prot. Bull (Taiwan)*, **29**, 385-395.

Talbert, R.T. & Fletchall, O.H. (1965) The adsorption of some s-triazines in soils. *Weeds*, **13**, 46-52.

Thurston, R.V., Gilfoil, T.A., Meyn, E.L., Zajdel, T.I. & Veith, G.D. (1985) Comparative toxicity of ten organic chemicals to ten common aquatic species. *Water Res.* **19**, 1145-1185.

Tscheu-Schlueter,M. & Skibba, W.D. (1986) Verleichende aquatoxikologische Ergebnisse mit ausgewaehlten Wasserschadstoff-gruppen und repraesentativen Wasserorganismen. (Comparative water toxicological results with selected groups of aquatic pollutants and aquatic organisms.) *Acta Hydrochim. Hydrobiol.*, **14**, 627-641.

Vollenweider, R.A. (1969) *A manual on methods for measuring primary production in aquatic environments*, Blackwell Scientific Publishers, Oxford, p28.

Walker, A. (1976) Simulation of herbicide persistence in soil. *Pestic. Sci.*, **7**, 41-49.

Walker, C.R. (1964) Simazine and other *s*-triazine compounds as aquatic herbicides in fish habitats. *Weeds*, **12**, 134-349.

Whitten, B.K. & Goodnight, C.J. (1966) Toxicity of some common insecticides to tubificids. *J. Wat. Poll. Contro. Fed.*, **38**, 227-235.

Williams, J.D.H. (1968) Adsorption and desorption of simazine by some Rothamsted soils. *Weed Res.*, **8**, 327-335.

Yasuno, M., Hanazato, T., Iwakamura, T., Takamura, K., Ueno, R. & Takamura, N. (1988) Effects of Permethrin on phytoplankton and zooplankton in an enclosure ecosystem in a pond. *Hydrobiologia*, **159**, 147-258.