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TRANSPORTATION OF PESTICIDES BY COLLOIDS

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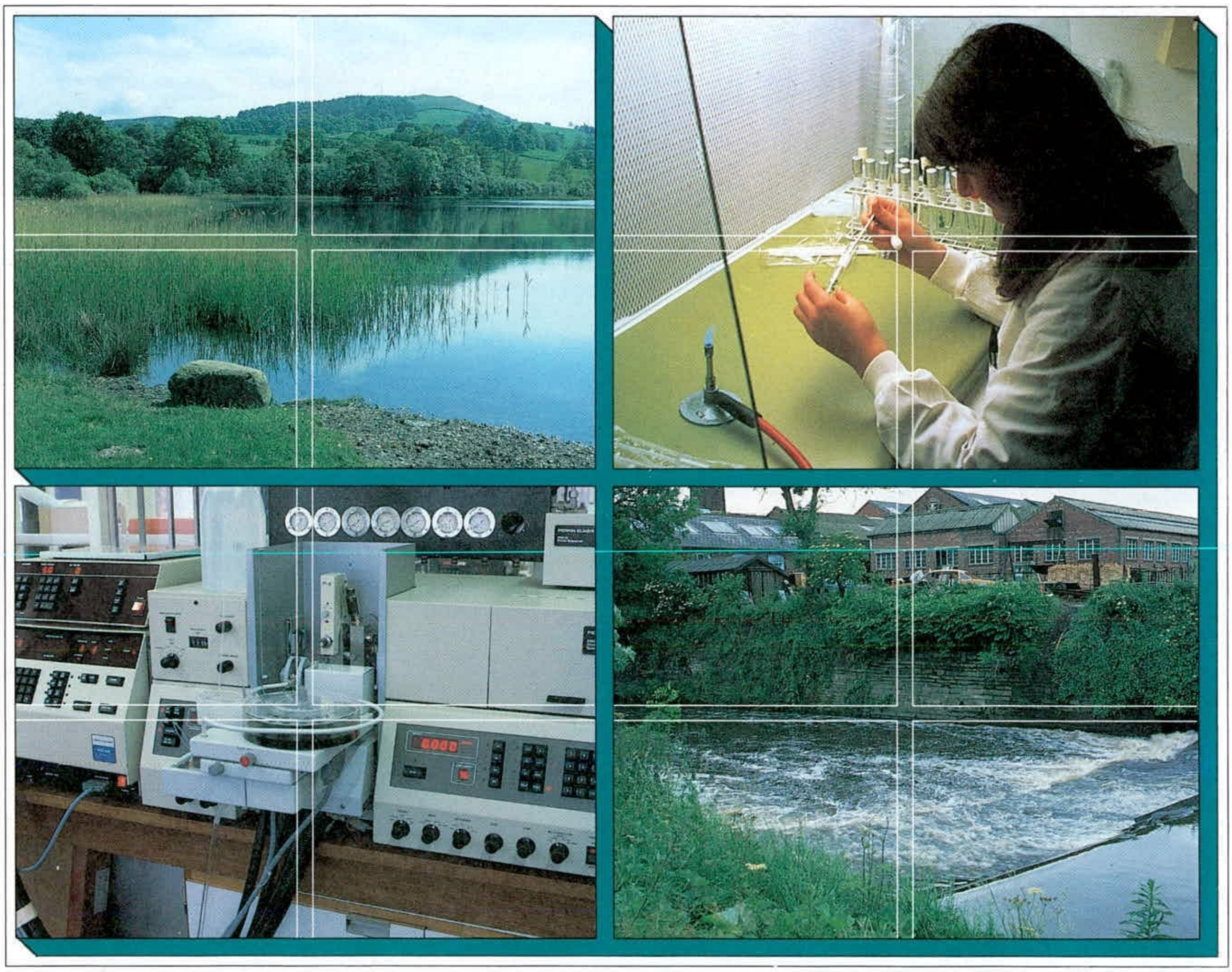
Report To: Department of the Environment
CEH Project No: T11059N2
IFE Report Ref.No: RL/T11059N2/3



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CONTENTS

GLOSSARY

C_f:	Concentration of pesticide in the filtrate
C_s:	Concentration of pesticide in the supernatant
C:	Concentration of colloids, mg l^{-1}
CFC:	Continuous-flow-centrifuge
DOC:	Dissolved organic carbon
EtAc:	Ethyl acetate
k_d:	Distribution coefficient
k_{oc}:	Distribution coefficient normalised with respect to organic carbon
k_{dc}:	Distribution coefficient for colloids
NOM	Natural organic matter
NPD:	Nitrogen phosphorus detector (GC)
PTV:	Programmable temperature vapouriser injector (GC)
SFE:	Supercritical fluid extraction
spe:	Solid-phase extraction
SS:	Suspended sediment
UFC:	Ultrafiltration cell

SUMMARY

Progress of the project between December 1995 and June 1996 is reported. The work covers further experiments with the ultrafiltration cell, initial trials to investigate the performance of XAD resins and characterisation of sediments isolated by continuos-flow centrifugation from the Humber rivers.

Previous work with the ultrafiltration cell employed either 1000 or 10,000 Dalton membranes. The application has now been successfully extended to the use of 500 Dalton membranes to permit investigations of the interaction of pesticides with a wider range of colloids and DOC.

Initial comparisons of the performance of XAD resins for measurements of pesticide-colloid interactions by competitive adsorption have proved encouraging. The tests so far indicate that of the four resins tested, the DAX-8 resin is the most convenient to use and produces high K_d's with rapid equilibium in solution. A good correspondence has been obtained between the amount of pesticide removed from solution and that recovered by extraction of the DAX-8 using ethyl acetate. Further work is necessary before the method can be compared with the results from the UFC or applied to river waters.

The progress of the LOIS CORE programme and special topic project on particle-pesticide interactions in the Humber rivers is also summarised. The first years pesticide monitoring data have been examined in some detail and the results accepted for publication; the abstract of the paper is attached.

1.0 Introduction

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

The project seeks to improve the understanding of the role of colloids in the long-range transportation of contaminants, and in particular of pesticides, both in riverine movement to estuaries, where colloids are likely to flocculate, and dispersion in near coastal waters.

2.0 Programme of work

The first two years are planned as follows:

1. Development of an automated ultrafiltration unit with low molecular weight cut-off (500-10000 Daltons) for sorption measurements.

2. Measurement of the sorption affinity of pesticides using the adsorption cell with 0.01 μm membrane filter, to enable some comparisons with the ultrafiltration experiments containing the smaller colloids. Initial tests with XAD resins will also be carried out at this stage.

3. Test the performance of the ultrafiltration unit in experiments without a membrane and also in experiments with a membrane but without colloids present.

4. Measure sorption isotherms in freshwater conditions and over a range of pH.

5. Measure isotherms to determine the affinity of the pesticides to the colloids in solutions of different salinity.

Items 1-3 are expected to be completed in the first year and 4-5 in the second year.

3.0 Progress to date

The development of the automated ultrafiltration cell was described in the report (RL/T11059n1, December to June 1995). This included the construction of parts of the system, interfacing the valves and ancillary equipment to a computer and testing the performance. The development of the control software was also outlined in the last report. This development work has continued with further tests of the performance summarised here.

Research has also continued in the following areas:

(a) The analysis of natural waters from the Humber rivers to ascertain the importance of colloids in the transportation of selected pesticides. The research has used the ultrafiltration cell (UFC) developed in the project.
(b) Development of a competitive adsorption method using XAD resins
(c) Research is in progress to characterise natural suspended sediments and colloid fractions in the rivers Ouse, Aire, Calder and Swale in Yorkshire.

This report covers the items (a) to (c) above and further development in the LOIS (Land Ocean Interaction Studies) concerning the distribution of pesticides in the Humber rivers.

4.0 Development of a competitive adsorption method

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

4.1 Selection of resin

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

A known weight (approximately 2 g) of each wet resin was shaken overnight at 10 °C with 100 ml of nominal 15 µg l^{-1} pesticide multistandard in teflon bottles. A control bottle containing an equal volume of the multistandard was incubated at the same time. The resins were then filtered off, and the pesticides remaining in the waters extracted by solid phase extraction and analysed by GC-MS. As this stage no efficient method had been identified for extracting the pesticides from the collected resin, approximate K_d were calculated from the loss of free pesticides from solution; these are tabulated in Table 1. The K_d values obtained indicate that the 2 g of wet resin used was capable of adsorbing far more than 50 % of the pesticides from 100 ml of the 15 µg l^{-1} solution used, and that future experiments should be based around smaller quantities of resin for the same type and quantity of pesticide solution.

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

To obtain better estimates of the distribution constants (K_d) for the pesticides and some measure of the recovery that could be obtained from the resins a further screening experiment was performed. For each resin and pesticide, the mass of wet resin required to remove half of the pesticide from 100 ml of volume of 15 µg l^{-1} pesticide solution was calculated. These were averaged to obtain M, the average mass of resin required to remove half of the pesticides from the solution. Four bottles were used for each resin containing 0 , 0.5 M, 1.5 M and 2 M of resin and a 100 ml of the pesticide solution. These were incubated for 48 hours before being filtered, the aqueous phases extracted and analysis performed by GC-NPD. Again K_d values were calculated based on the loss of free pesticide from solution and these are also shown in Table 1 below.

Two experimental extractions were performed on collected resins, this involved passing four 0.5 ml aliquots of ethyl acetate through the column of collected resin. The eluate from each set of resin was dried, and analysed by GC-NPD. The data from these extracts was used to calculate the recoveries shown in Table 2. The recoveries from the resin DAX-8 are in general far better than the recoveries from XAD-2. The result for dimethoate were unreliable because of the comparatively large uncertainties in the measurement of this particular pesticide at low levels.

The resin DAX-8 was selected for further study as it gave reasonable recoveries from a simple extraction procedure which could be easily performed with only small modifications to the procedures.

Table 1 Initial and second estimates of K_d ($dm^3\ kg^{-1}$)values

	Initial values				Second estimates	
	XAD-2	XAD-4	XAD-7	DAX-8	XAD-2	DAX-8
Trifluralin	966	899	215	1039	2453	2571
Dimethoate	nd	nd	nd	nd	370	495
Simazine	995	957	714	1343	3167	1506
Atrazine	nd	nd	nd	nd	3244	1845
Propazine	956	857	1437	1250	3265	2217
Desmetryn	1086	1294	1323	1311	2250	1268
Prometryn	1022	1092	1806	1473	2269	1762
Terbutryn	1345	1436	2204	1811	3174	3092
Fenitrothion	nd	nd	nd	nd	4303	4127
Malathion	nd	nd	nd	nd	2479	3399
Cyanazin	nd	nd	nd	nd	2453	1780
Parathion	2052	2200	1399	1498	4832	4401

Table 2. Pesticides recovered from resin as percentage of pesticide lost from solution

	XAD 2	DAX 8
Trifluralin	50	114
Dimethoate	137	-
Simazine	19	72
Atrazine	21	73
Propazine	21	133
Desmetryn	28	99
Prometryn	27	93
Terbutryn	47	113
Fenitrothion	40	99
Malathion	35	96
Cyanazin	23	95
Parathion	30	93

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

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

The adsorption kinetics of the pesticides were studied first as they must be known before accurate experiments to measure the adsorption isotherm can be designed. Five pairs of bottles were prepared, each pair consisting of a control containing no resin and an second bottle containing a known mass of resin (approximately 0.25 g wet resin per bottle). An aliquot of pesticide solution (50 ml nominally 15 $\mu g\ l^{-1}$) was added to each bottle, and the pairs shaken at 10 °C for various lengths of time. The distribution coefficients were calculated for each pair, using the loss of pesticide from solution in each pair to estimate the uptake of pesticide onto the resins. This data was used to calculate the half-life of the uptake process. Typical half-life values are tabulated below with predicted percent deviation from equilibrium at 24 hours.

In most cases the distributions of the compounds are within 1 % of their equilibrium values within twenty four hours, of the resin being mixed with the liquid. Therefore the kinetics for the adsorption of the pesticide into the resin will not introduce significant errors into the method if the samples are incubated for 24 hours or more. This type of check will have to be repeated to ensure that in the final method, the distribution of pesticide between the solution and the colloids in real samples is also given sufficient time to reach a good approximation of its equilibrium values.

Table 3. Pesticides extracted from resin as percentage of pesticide lost from solution

	Half-life (h)	% deviation from equilibrium at 24 h
Trifluralin	2.1	0.04
Dimethoate	8.9	15
Simazine	2.8	0.24
Atrazine	2.7	0.20
Propazine	2.5	0.13
Desmetryn	3.0	0.39
Prometryn	4.3	1.99
Terbutryn	2.2	0.05
Fenitrothion	1.3	0.00
Malathion	2.1	0.04
Cyanazin	2.5	0.12
Parathion	2.1	0.04

5.0 Sediment characterisation

Sediments from the Humber rivers: Ouse, Aire and Swale, have been separated from 50 litre bulk water samples using continuos-flow centrifugation (11,000 rpm at 200 ml min^{-1}). These sediments have been characterised by particle-size analysis by sedimentation and the results are shown in Table 4. The sediment from the R. Swale had a higher content of the coarser-size fraction reflecting the high discharge conditions at the time of sampling. The other two samples were of similar composition with about 30-36 % by mass of particles in the clay fraction, < 2 μm. Although these samples were ultrasonicated (300 W for 10 minutes) prior to the particle-size analysis, they were left for two days before analysis to allow the particles to equilibrate in the solutions. It is planned to analyse the samples by laser-light scattering in an ultrasonicated solution containing a dispersing agent to determine the particle-size composition of the primary particles prior to aggregation. Work is now in progress to characterise the mineralogy of the material. Results from similar samples show that kaolinite, expandable clays and illite are important components of these sediments and will contribute to the colloid fraction.

Table 4. Particle size distributions of suspended river sediments obtained after separation of the suspended material from 50 litre water samples using continuos-flow centrifugation.

River	sampling date	>20 μm	5-20 μm	2-5 μm	< 2 μm
Ouse	19.4.95	9.3	42	16.7	31.3
Aire	14.12.95	10.2	30.7	23.9	35.2
Swale	23.9.94	39.6	33.7	5.8	20.9

6.0 Ultrafiltration experiments

The application of the automated UFC has been extended with deployment of a 500 Dalton membrane. The membrane was tested by circulating a solution of 2 mM $CaCl_2$ containing a multistandard pesticide mixture of simazine, atrazine, propazine, desmetryn, prometryn, fenitrothion, cyanazine and parathion.. The results shown in Table 5, indicate the satisfactory

Table 5. Comparison of the concentrations of a range of pesticides in the filtrate and supernatant of the UFC. Results are shown for duplicate determinations.

Pesticide	F, mean concentration in filtrate/ mg/l	S, mean concentration in supernatant/ mg/l	ratio of concentrations (S/F)
simazine	5.70	5.83	1.02
atrazine	5.88	6.18	1.05
popazine	6.21	6.52	1.05
desmetryn	11.79	10.62	0.90
prometryn	10.82	12.67	1.17
fenitrothion	1.51	1.36	0.90
cyanazine	3.03	3.24	1.07
parathion	0.37	0.39	1.05

performance of the membrane in the absence of colloids for most of the compounds apart from prometryn. No further progress has been made with the UFC method in the last 6 months.

7.0 Progress in LOIS

The first years data concerning micro-organic compounds in the Humber rivers have been examined and the results compiled for publication in the journal of Science and the Total Environment. This has now been accepted for publication and an abstract is attached to this report. Further information is available on request.

Progress with the LOIS special topic project has also been made with the first years quarterly sampling due for completion in July 1996. The sampling consists of bed and suspended sediments as well as whole water samples from the rivers: Aire, Calder, Trent, Don, Swale and Ouse. The sediments are extracted using supercritical fluid extraction (SFE) with 10 % methanol modified carbon dioxide. The results so far indicate high concentrations in the sediments (> 100 ug/kg (dry wt.)) for a range of compounds including permethrin, PAH's, triazines and diazinon. These results will be compiled in the late summer and the pesticide concentrations related to the sediment properties such mineralogy, particle-size and specific-surface area. The storm sampling of each of the main Humber rivers will start in the Autumn and continue throughout the winter of 1996-97. This sampling will consist of the collection of suspended solids by continuos-flow centrifugation on site as well as whole water samples using automatic samplers specifically equipped for sampling micro-organic compounds in river waters.

8.0. Further work

8.1 In the next 6 month period it is planned to continue research with the competitive adsorption approach using the XAD resins and in particular:

a) Obtain better final estimates of the distribution coefficients.
b) Study the kinetics of the pesticide uptake in the presence of colloids.
c) Use the data from (a) and (b) to finalise the conditions required for use in the competitive adsorption method and compare the results with those from the UFC method.

If successful the method will be applied to studying the transport of colloids in the Humber rivers in the field sampling stage of the project.

8.2 Work on the characterisation of the suspended solids from the Humber rivers will be completed with a further sample collected in June this year from the R. Aire at Beale. The solids will be separated by continuos-flow centrifugation and analysed by the methods used for the previous samples. The association of colloid-bound pesticides will be determined by the competitive adsorption and the automated UFC method (see 6.1(c)) above).

8.3 Research will be started with a more basic pesticide, flutriafol, to determine the sorption interaction with a colloidial clay (in the first instance kaolinite) before and after contact of the clay with water from the R. Aire and the Humber estuary. This will permit an estimate of the effects of adsorbed natural organic materials on pesticide interactions with colloids. The study will encompass the effects of temperature, pH and salinity on sorption behaviour.

8.4 Co-ordinate this project with the LOIS CORE programme and special topic project with the view of combining the sampling effort in the autumn and winter of this year.

9.0 Abstract of paper on LOIS CORE results:

MICRO-ORGANIC COMPOUNDS IN THE HUMBER RIVERS

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ABSTRACT

The concentrations of a range of micro-organic compounds in the Humber rivers have been measured at weekly intervals over a period of 1 year. The compounds include the triazine herbicides (simazine, atrazine, propazine, desmetryn and prometryn), selected organophosphorus insecticides (fenitrothion, malathion and parathion), phenylurea (chlorotoluron, diuron, isoproturon and linuron) and phenoxyacid herbicides (2,4-D, MCPA, MCPB and mecoprop), phenol derivatives (phenol, 2-ethylphenol, 2-chlorophenol, 4-nitrophenol, 2-methylphenol, 4-ethylphenol and 2,4-dichlorophenol), organochlorine insecticides (HEOD, DDT, TDE, DDE, HCB, a-BHC and lindane), PCB's and some synthetic pyrethroid insecticides (*cis/trans*-permethrin, fenvalerate and cypermethrin). The results indicate the high frequency of occurrence of many compounds in the southern Humber rivers Aire, Calder ,Trent and Don compared with the more occasional concentrations found in the upland rivers with catchments dominated by low intensity agriculture. The more water soluble herbicides, atrazine, simazine, isoproturon and diuron are detected frequently in the southern rivers with the highest concentrations and abundance in the rivers Aire, Calder and Trent. The most abundant phenolic compound is 2,4-dichlorophenol usually occurring at concentrations < 1ug/l. The organochlorine insecticides and PCB's are generally at concentrations < 0.01 ug/l. *cis/trans*-permethrin are the only synthetic pyrethroids detected and these are found in the rivers Aire and Calder at about equal concentrations of between 0.01 and 0.11 μg/l.

The results for the occurrence of simazine and atrazine in the rivers Trent, Don and Aire illustrate peaks in concentration near the time of applications in the spring and then later

in the year during the early autumn with the first major storm of the year after the summer. In the rivers Trent and Don, the annual exports (March 1994-95) of atrazine are lower than for simazine whereas in the R. Calder the yield of atrazine is higher than for simazine suggesting differences in use in these catchments. The maximum triazine concentration observed, i.e. 8 μg/l of atrazine in the R. Calder, could have inhibiting effects on the phytoplankton and algal growth although, because of the transient nature of the peaks, recovery is expected to be rapid. The only compounds measured at concentrations likely to produce detrimental ecotoxicological effects are *cis/trans* permethrin in the rivers Aire and Calder.