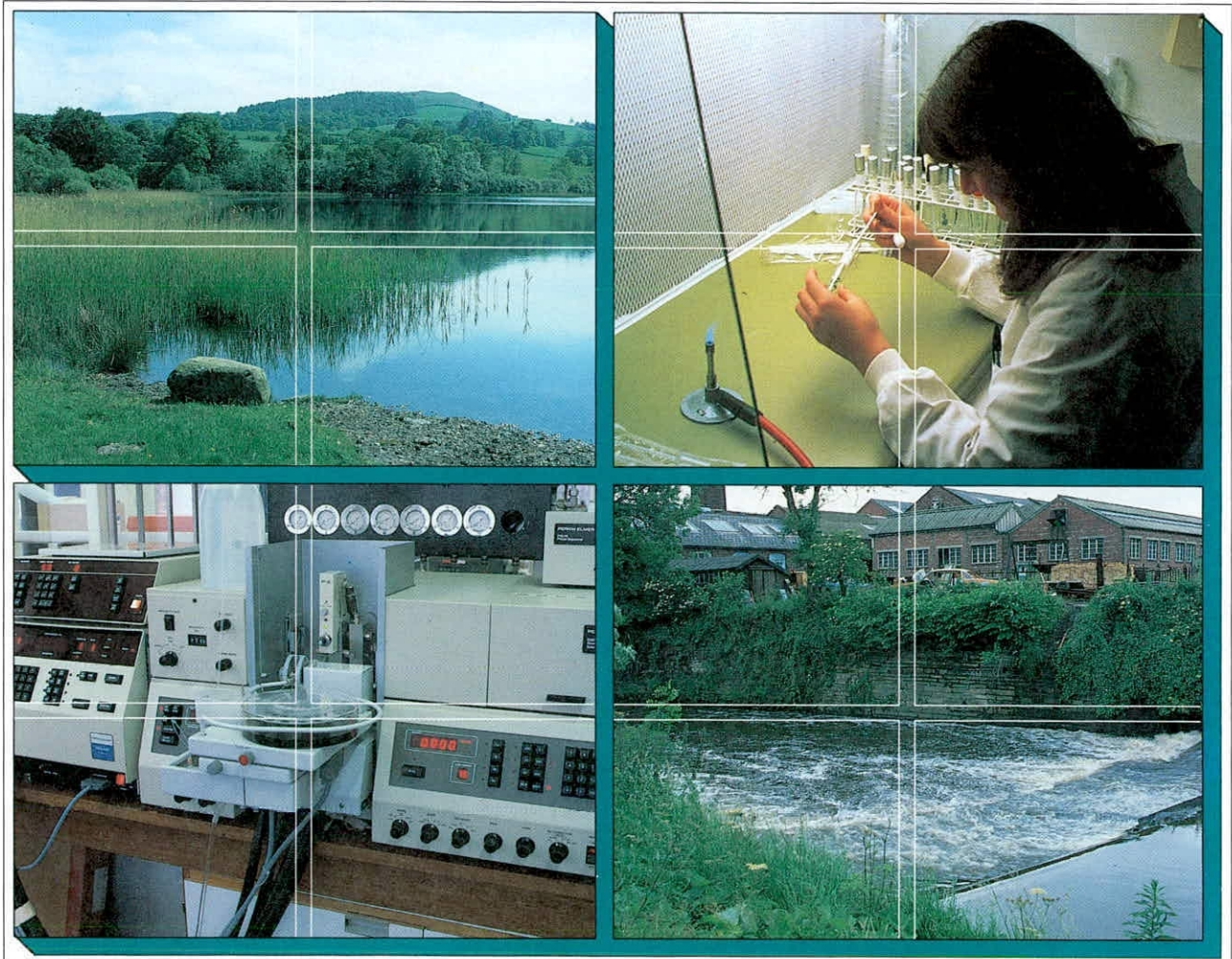


# Transportation of pesticides by colloids

W.A. House, PhD CChem FRSC  
G.P. Irons, PhD GRSC

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







**Institute of  
Freshwater  
Ecology**

**River Laboratory**  
East Stoke  
WAREHAM Dorset  
BH20 6BB

Tel: 01929 462314  
Fax: 01929 462180

# **Transportation of pesticides by colloids**

**W.A. House, PhD CChem FRSC**  
**G.P. Irons, PhD GRSC**

Project Leader:	W.A. House
Report Date:	June 1995
Report End Date:	1 December 1995
Report To:	Department of the Environment Romney House, 43 Marsham Street London SW1P 3PY
Contract No:	EPG/1/9/32
IFE Report Ref. No:	RL/T11059N2

---

## **INTELLECTUAL PROPERTY RIGHTS**

### **CONFIDENTIALITY STATEMENT**

*'In accordance with our normal practice, this report is for the use only of the party to whom it is addressed, and no responsibility is accepted to any third party for the whole or any part of its contents. Neither the whole nor any part of this report or any reference thereto may be included in any published document, circular or statement, nor published or referred to in any way without our written approval of the form and context in which it may appear.'*

---

## CONTENTS

### Summary

1.	Introduction	2
2.	Programme of work	2
3.	Progress to date	3
4.	Application of spe techniques to the isolation of pesticides in organic colloids	3
5.	Tests of the performance of the UFC with 1000 Dalton membrane	5
6.	Ultrafiltration experiments with Humber river waters	5
7.	Other work in progress	7
8.	Progress on the LOIS programme	7
9.	Future work	8
Table 1.	Performance of C18 spe columns in the presence of organic colloids	4
Table 2.	Comparisons of the colloid distribution coefficients for the river Swale and Ouse	6
Table 3.	Comparison of the colloid distribution coefficients for the R. Aire	7
Figure 1.	Comparison of the DOC and absorbance values for Humber river waters analysed to date	9
Figure 2.	Examples of the concentration of simazine in the rivers Trent and Aire for the period March 1994-March 1995. The river discharge data are also shown.	10

## GLOSSARY

$C_f$ :	Concentration of pesticide in the filtrate
$C_s$ :	Concentration of pesticide in the supernatant
$C$ :	Concentration of colloids, $\text{mg l}^{-1}$
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)
spe:	Solid-phase extraction
SS:	Suspended sediment
UFC:	Ultrafiltration cell

## SUMMARY

Progress of the project between June and December 1995 is reported. Tests of the performance of the ultrafiltration cell have been continued using different waters including the rivers Ouse, Swale, Calder and Aire in Yorkshire. In addition, tests have been started to examine the use of solid-phase extraction columns to isolate pesticides from solutions containing high concentrations of humic substances. The results so far indicate the C18 (EC) columns give the best performance at concentrations of humic acid up to 200 mg/l and pesticide concentrations in the range of 0.2 to 7 µg/l.

Results are presented for the measurement of the distribution coefficients,  $K_{dc}$ , (distribution coefficient normalised with respect to the dissolved organic carbon). A comparison of the values derived from a bulk sample of the R. Ouse using a 1000 Dalton membrane are much higher than the corresponding values from a 10,000 Dalton membrane for simazine, atrazine, propazine, desmetryn and parathion. Other results for the rivers Swale, Aire and Calder lead to a range of distribution coefficients of 5 to 75 l g<sup>-1</sup>.

Other work in progress is briefly summarised including the characterisation of the suspended sediments from the rivers Ouse and Swale, the measurement of the absorbance characteristics of the dissolved organic carbon and the progress of the LOIS (Land Ocean Interaction Study) on pesticides in the Humber rivers.

### 1. 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 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. 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 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. Progress to date**

The development of the automated ultrafiltration cell was described in the last 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 application of solid-phase-extraction columns for the isolation of pesticides associated with organic colloids. This work has centred on humic/fulvic acids with bound pesticides with the purpose of developing procedures for the extraction of pesticides in waters containing high dissolved organic carbon.
- (b) 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.
- (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. Application of solid-phase-extraction (spe) techniques to the isolation of pesticides in organic colloids**

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

Previous work on this project used C18 (end-capped, EC) solid-phase-extraction (spe) columns to isolate the pesticides from solution. Although humic substances were clearly sorbed to the C18 matrix, some fractions eventually broke through the column and reached the effluent at the bottom of the column. If pesticides are bound to the humic substances, they may not interact effectively with the C18 bonded phase. One method to avoid breakthrough is to mount an anion exchanger on top of the C18 column. However, preliminary experiments

indicated this to be ineffective at high humic concentrations (300 mg/l). Thus, although the anion exchanger retained more of the humic fraction than the C18 column, a more retentive matrix is needed for waters containing high organic carbon. The graphitised carbon column also permitted the penetration of the humic substances leading to breakthrough of the colloids in the effluent. The recoveries of the pesticides were also very variable; for this reason no further work was attempted with either the anion exchanger or graphitised carbon columns.

The results from the extraction of a spiked solution of pesticides in distilled water and 300 mg/l humic acid (Aldrich) are shown in Table 1. The humic acid solution was prepared by adding 0.3 g humic acid to 1 l of 2 mM CaCl<sub>2</sub> and dissolving over 48 h, followed by filtration through a 0.7 µm GF/F glass fibre pad. A multipesticide mixture was prepared by adding 1 ml of 10 mg/l EtAc solution of simazine, atrazine, propazine, desmetryn, prometryn, terbutryn, fenitrothion, malathion, cyanazine and parathion (multipesticide mixture) to a 1 litre volumetric flask, evaporating the EtAc with nitrogen, and dissolving overnight in 2 mM CaCl<sub>2</sub> solution. The multipesticide solution was then filtered through a GF/F glass fibre pad prior to use. The compounds were then extracted using the protocol, SOP: 9/13.08.92, and final elution with 2 ml of EtAc through the C18 (EC) column in-line with a sodium sulphate drying column. The results show that at this concentration of pesticide, there is no significant difference (t-test, 95 %) between the two sets of results. This indicates either that the majority of the pesticides are not associated with the humic material or that the interaction of the pesticides with the C18 matrix is greater than with the humic molecules. Further work is needed to examine the performance of the spe technique at lower concentrations of the pesticides.

**TABLE 1. Results of the comparison of the performance of the C18 (EC) spe columns for extracting pesticides from solutions with and without humic acid. The concentration of humic acid was 300 mg/l. The figures are the pesticide concentrations in µg/l.**

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



## 5. Tests of the performance of the UFC with 1000 Dalton membrane (code YM1)

Initial tests were done with the multistandard pesticide solution in 2 mM CaCl<sub>2</sub> filtered through a GF/F glass microfilter. 300 ml was added to the UFC and left stirring for two hours. After discarding the first 50 ml of filtrate, a further 100 ml was collected for analysis together with 100 ml of the supernatant. The results indicated a substantial difference (mean difference of 25 % for the triazines: simazine, atrazine, propazine and desmetryn and a mean difference of approximately 38 % including all the compounds) between the concentration of the pesticides in the supernatant and filtrate. This is in agreement with the results given in the previous report for the 10,000 Dalton membrane. Following this, it was decided to recirculate the filtrate to enable the pesticides to reach an equilibrium adsorption to the membrane and UFC components. Recirculation of a single-cell volume reduced the difference to 7.5 % for the triazines (14.7 % overall) which for the triazines is close to the analytical uncertainty of the method. Repeating the experiment but with a two-volume recirculation produced similar results to the single-volume recirculation. It was concluded that a single-volume recirculation is necessary for this group of compounds.

## 6. Ultrafiltration experiments with Humber river waters

Further experiments were performed with: (a) R. Ouse water after continuous-flow-centrifugation (CFC) (sample as in the previous report, RL/T11059n1), (b) concentrated R. Swale water, (c) R. Calder water and (d) R. Aire water.

(a) The colloids in the R. Ouse water from the CFC (for details of the preparation see report RL/T11059n1) were concentrated 10 fold using a 1000 Dalton membrane. A multipesticide mixture was added to the cell and the contents recirculated to obtain a two-volume change. Samples of the filtrate and supernatant were retained for spectrometric and DOC analysis. The distribution for the colloid material (here normalised with respect the DOC) was then calculated from the equation:

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

where C is the concentration of the DOC and C<sub>s</sub> and C<sub>f</sub> are the concentrations of the pesticide in the supernatant and filtrate respectively. The distribution coefficient is in units of ml g<sup>-1</sup> or dm<sup>3</sup> kg<sup>-1</sup>. The results of the calculation of the distribution coefficient, normalised with respect to DOC, are shown in Table 2 and compared with the previous results for the R. Ouse (report RL/T11059n1) obtained using a 10,000 Dalton membrane. A comparison of the results using the different size membranes suggests that the colloidal material between 1000 and 10,000 Dalton in size is an important fraction influencing pesticide interactions in this sample.

(b) A sample of R. Swale water (sampled on 21.9.94) was concentrated 6.3 fold using a 1000 Dalton filter. The concentrate was stored at 6 °C in the dark prior to the experiments. The UFC experiment was conducted using a similar procedure as described in (a) above with a two-volume change. The results of the calculation of the distribution coefficient are shown in Table 2. In this instance, the k<sub>dc</sub>'s are lower than those calculated for the R. Ouse sample with the same size of membrane in the UFC.

(c) The R. Calder water was collected on 3/7/95 from Methley bridge (SE409258) in a 10 l container. This was transported to the River Laboratory and stored at 5 °C in the dark prior to use. One litre of this water was filtered through a 0.45 µm membrane filter before adding the UFC. The UFC was used to determine the  $K_{dc}$  values for the multipesticide mixture. The distribution coefficients are higher than those obtained for the R. Ouse sample with the 10,000 Dalton membrane but smaller than the results from the 1000 Dalton membrane, e.g. for simazine and atrazine the  $K_{dc}$ 's for the R. Calder water were 19.3 and 23.8 l g<sup>-1</sup> respectively compared with 1.1 and 3.0 l g<sup>-1</sup> respectively for the R. Ouse with the same porosity membrane. The results for the R. Calder sample are tentative as the DOC from the spectrometer scan at 340 nm was used to estimate the DOC; the calculations will be corrected when DOC measurements are available.

(d) Further research has been done on a sample of R. Aire water collected on 24.8.95 from Beale (SE534255) near the NRA gauging station at the tidal limit of the river. The initial experiments consisted of filtering the river water through GF/F glass membrane pad and concentrating two-fold with a 1000 Dalton membrane in the UFC and then adjusting the volume with a multipesticide mixture. This was then recirculated to produce a 1.4 volume change before the filtrate and supernatant were separated for pesticides analysis. The preliminary results are shown in Table 3. A similar experiment was performed with the unfiltered R. Aire water and the results are shown in Table 3. The suspended solids content of the water was measured using the protocol (SOP: ) as 13.5 mg l<sup>-1</sup>. The results will

TABLE 2. Comparison of the distribution coefficient,  $k_{dc}$  in units of l g<sup>-1</sup>, obtained from the UFC experiments.

compound	DOC = 4.86 mg l <sup>-1</sup>		
	R. Ouse (expt. 10) 1000 Dalton	R. Ouse (expt.6C) 10000 Dalton	R. Swale (expt.11C) 1000 Dalton
simazine	19	1.1	5.3
atrazine	122.1	3.0	6.2
propazine	159.5	5.2	9.9
desmetryn	104.9	5.0	10.5
prometryn	150.0	-	32.9
terbutryn	-	33.3	8.5
fenitrothion	160.4	-	35.1
malathion	-	-	36.0
cyanazine	153.0	-	25.5
parathion	50.8	20.6	7.7

recalculated when the DOC data are available. The distribution coefficients are similar to those calculated for the R. Calder water discussed above but generally much lower than the values shown in Table 2 for the R. Ouse (expt. 10). The distribution coefficients for the

unfiltered water are higher than the filtered because of the presence of larger particulate matter (>0.45 µm) in the sample. Hence the DOC is an underestimate of the colloid and particulate concentrations. These samples are currently being analysed for DOC and TOC (total organic carbon) to enable better estimates of the normalised distribution coefficients.

TABLE 3. Comparison of the results using the R. Aire water collected on 24.8.95 obtained using the UFC with 1000 Dalton membrane.

DOC = 21.9      20/11/96  
DOC = 15.8      p39 lab book  
exp 16      DOC =

compound	$K_d$ for pre-filtered water <del>1.5</del> <del>1.5</del> <del>1.5</del> $l\ g^{-1}$	$K_d$ for unfiltered water <del>1.5</del> <del>1.5</del> <del>1.5</del> $l\ g^{-1}$
simazine	9.5	12.4
atrazine	11.8	17.3
propazine	11.4	20.7
desmetryn	8.2	11.0
prometryn	6.4	5.4
terbutryn	6.1	-
fenitrothion	7.1	25.6
malathion	-	74.9
cyanazine	24.5	32.6
parathion	3.6	10.6

## 7. Other work in progress

Samples of suspended sediment/colloids from the R. Ouse are being analysed for mineralogy and particle size distribution. This information will be used to assess the importance of the <0.45 µm fraction to the total mineral and organic matter content of the sediment. In addition, the visible absorbance of all river waters, filtrates and supernatants from the UFC are being measured at 460, 440, 400, and 340 nm and compared with independent DOC measurements (see Fig. 1).

## 8. Progress on the LOIS programme

Weekly measurements of a range of compounds in the Humber rivers have continued over the last year. The compounds studied include those in the multipesticide mixture used in this project. Generally, the southern rivers are the most contaminated; this includes the rivers Trent, Don, Aire and Calder. The LOIS CORE programme is also measuring the DOC, suspended solids, UV/visible absorbance, TOC and particulate organic matter on a weekly basis. This information will be invaluable to the current project in determining the controls of pesticide movement to the inter-tidal zones of the rivers and to the estuary. Examples of the concentration of pesticides in the rivers Aire (at Beale, the tidal limit) and Trent (at Cromwell Lock, the tidal limit) are shown in Figs 2 (a) and (b) together with the river

discharge data. Similar results are obtained for atrazine and isoproturon. Peaks in concentration appear in the spring for both rivers which are not related to increases in discharge. Both rivers however show peaks in herbicide concentrations during the first major autumn storms and some indications that the compounds are also flushed from land during later winter storms. Research is now in progress on a special topic project as part of LOIS to investigate the partition of a range of compounds between river waters, suspended solids and bed-sediments in the rivers Trent, Don, Swale, Aire and Calder (the main inputs into the Humber estuary). All the sites are coincident with the LOIS core monitoring sites at the tidal limits of the rivers and close to NRA gauging stations.

## 9. Future work

The research is behind the original schedule and a request to reschedule the finances has been made to DoE. This situation has arisen because the detailed and more expensive tests with the UFC have been delayed. It is now intended to place more effort on this aspect of the work during the remaining of this financial year (95/96). This will involve the following work:

1. Characterisation of the sediments previously collected from the R. Ouse and Swale by XRD and particle size analysis to assess the fraction of colloidal clay minerals as aggregates and primary particles.
2. Re-examine the interaction of the multipesticide mixture with both aldrich humic and natural humics from the Humber rivers including the extension of the use of the UFC to 500 Dalton membranes.
3. Continue the research with the UFC using different river waters to measure the distribution coefficient,  $K_{dc}$ . This will also include experiments to pre-concentrate the colloid components.
4. Examine the performance of the UFC with different groups of pesticides to include a pyrethroid, carbamate and organochlorine pesticide found in the Humber rivers.

Fig 1. Comparison of DOC and Absorbance (340 nm and 4 cm path length)

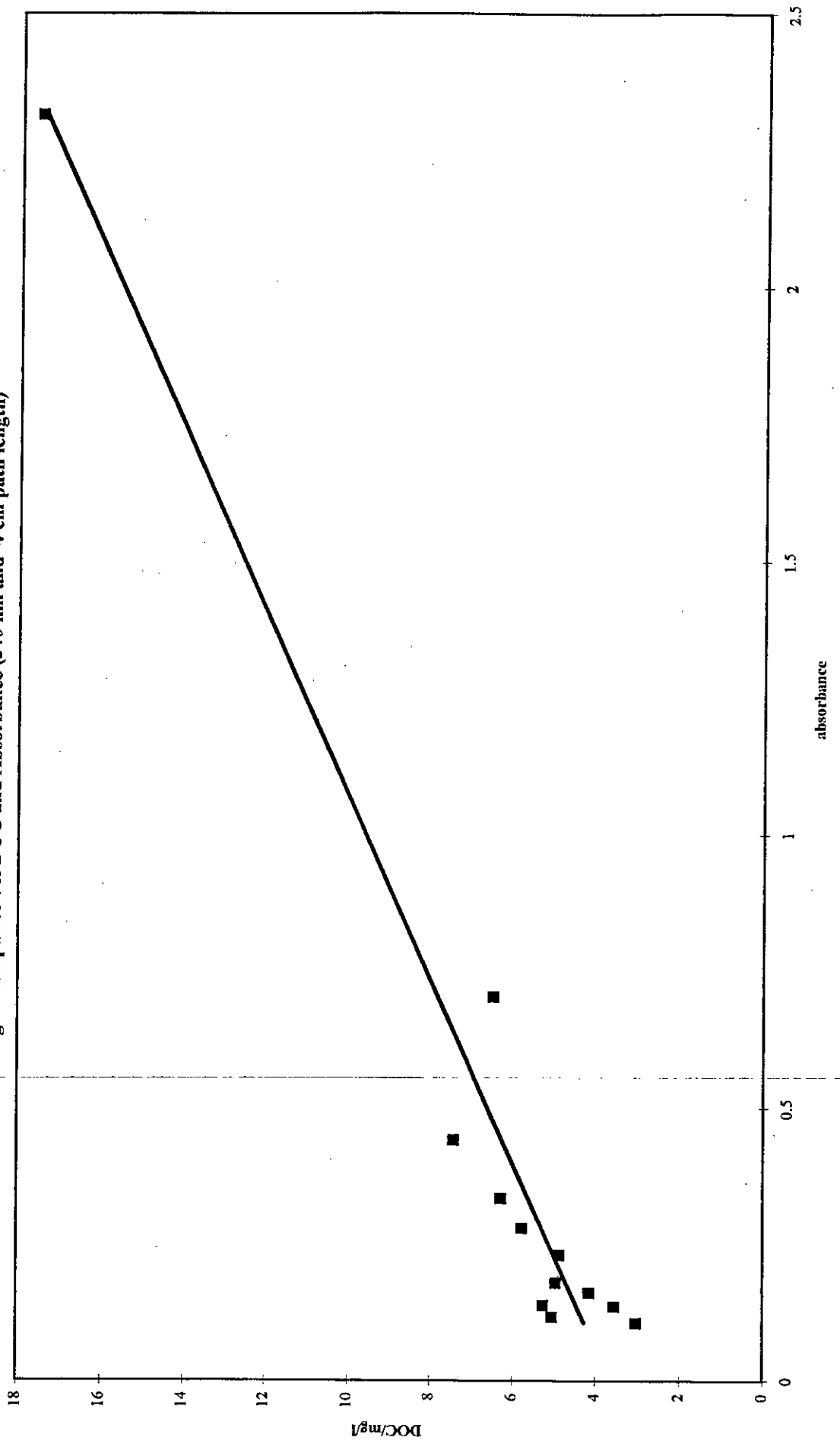
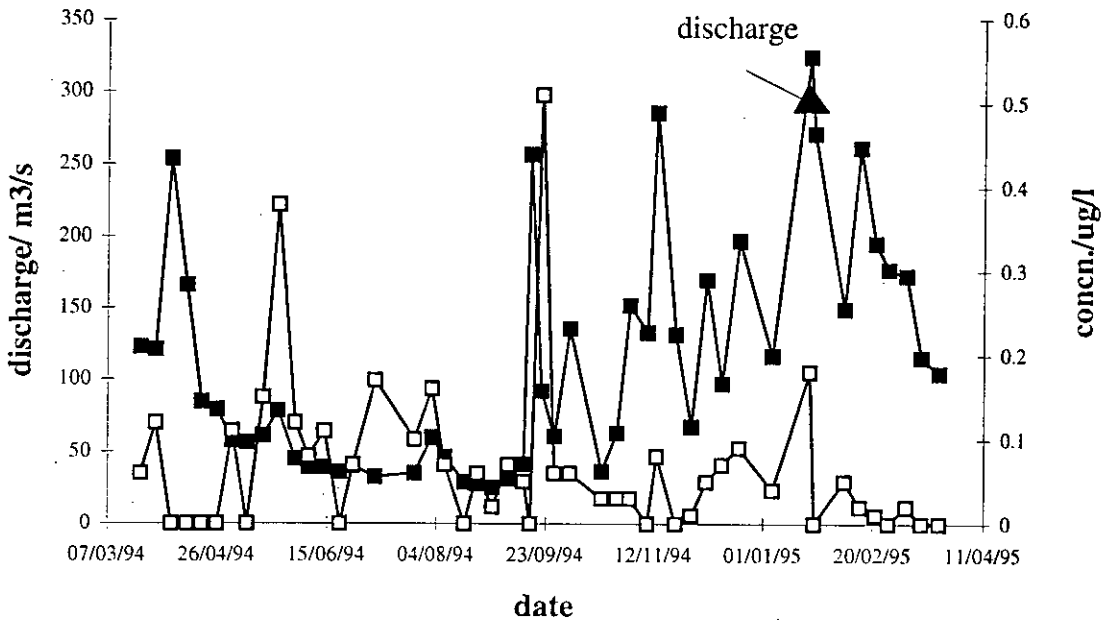


Figure 2.

(a) Comparison discharge & simazine concentration for the R. Trent (94-95)



(b) Comparison of discharge and simazine concentration for the R. Aire

