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Transportation of pesticides by colloids

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GLOSSARY

C_f: Concentration of pesticide in the filtrate, $\mu g\ l^{-1}$
C_s: Concentration of pesticide in the supernatant, $\mu g\ l^{-1}$
C: Concentration of colloids, $mg\ l^{-1}$
CFC: Continuous-flow-centrifugation
DCM: Dichloromethane
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 vaporiser injector (GC)
spe: Solid phase extraction
SS: Suspended sediment
UFC: Ultrafiltration cell

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 the colloids are likely to flocculate, and dispersion in near coastal waters.

2. Programme of work

The following stages were planned in the first two years:

1. Development of an automated ultrafiltration unit with low molecular weight cut-off (500-10,000) 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 ultrafiltration experiments containing the smaller colloids. Initial tests with resins will be carried out at this stage in preparation for research on the $<$ 1000 molecular weight components.

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 (7.5-8.5).

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

Items 1-3 will be completed in the first year and items 4-5 in the second.

3. Development of an automated ultrafiltration unit.

No apparatus is commercially available to enable measurement of the distribution of microorganic compounds in true solution and in naturally occurring colloids. Previous research has shown that the dialysis method of measuring the distribution of pesticides between solution and colloids is limited because of the large volume of solution/colloid needed for the analysis at the low concentrations of the pesticide found in natural waters. One method to solve this problem is to use a large diameter ultrafiltration membranes (76 mm) installed in a 500 ml

stirred cell and perform the separation of the dissolved and colloidal material by the application of high pressure (ca 50 psi) above the colloid and collecting the filtrate. An analysis of the supernatant and filtrate for pesticides content then enables the concentration of the pesticides associated with the colloids to be calculated. If the concentration of colloids in known or can be measured, the appropriate distribution coefficient may be calculated.

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

The following points were considered in the design of the ultrafiltration unit:

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

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

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

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

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

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

Previous studies in this laboratory have used an automated adsorption cell incorporating membrane filters such as GF/F glass microfibre or cellulose nitrate 0.45 to 0.01 μm pore size, and a syringe pump to remove filtrate for chemical analysis. This system is connected to a gas line (CO_2/N_2) and autoburette for the addition of the adsorbate with a suspension maintained by a stainless steel paddle stirrer mounted about 2 mm above the membrane. This system works very well and as been used extensively in studies of the interaction various microorganic compounds with minerals and natural river sediments, e.g. House and Farr, 1989; Marchesi et al, 1991. However, it is not suitable for experiments with high concentrations of colloids, e.g. clays such as illite and montmorillonite or natural organic matter (NOM) of colloid size. With these materials, the membrane filter either blocks or the flow rate decreases to an extent

that the collection of sufficient volumes of filtrate is impracticable. The maximum differential pressure across the membrane is about 15 psi by suction. Even with the smallest size membrane filter (0.01 μm), , judged by the sample colour and turbidity, the filtrates contain appreciable amounts of colloid material.

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

3.1 Tests of performance of the ultrafiltration unit with PM series membranes of 10,000 Dalton size (PM10)

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

3.1.1 Preconditioning the ultrafilter membranes

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

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

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

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

Initial test were done using aqueous solutions of 2 mM $CaCl_2$ containing a mixture of pesticides: simazine, atrazine, propazine, desmetryn, prometryn, terbutryn and parathion. The

stock multi-pesticide solution was made by the addition of 2 ml of 0.5 $\mu g\ ml^{-1}$ in ethyl acetate (EtAc) to a 500 ml volumetric and evaporation of the solvent before the addition of the $CaCl_2$ solution. This was mixed for 3 h prior to use to produce a nominal concentration of 2 $\mu g\ l^{-1}$ of each compound in the $CaCl_2$ solution.

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

The pesticides were extracted using IFE, River Laboratory SOP: 9/13.08.92. This is available to DoE on request. In brief the extraction is with 500 mg C18 (silica bonded phase), with pre-conditioning with methanol and elution with EtAc with the C18 column placed above a drying column of Na_2SO_4. The 2 ml EtAc eluate was collected using a vacuum manifold and injected directly into a capillary GC with a PTV injector and detection with NPD ceramic bead. The chromatograms were processed using a Perkin Elmer 1020 integrator and quantified for simazine, atrazine, propazine and parathion. Typical analyte recoveries by this method are $> 95\%$ with standard deviations $< 8\ \%$. The results of the GC analysis are shown in Table 1. They indicate that pesticide concentrations in the $CaCl_2$ solution are $< 2\ \mu g\ l^{-1}$ and therefore more time is needed during the dissolution stage to ensure the compounds are dissolved. In addition there is a difference between the pesticide concentrations in the filtrate and supernatant. The most likely reason for this is sorption of the compounds on the PM10 membrane.

TABLE 1. Results of trial experiment in the absence of colloids and no recirculation. UFC: ultrafiltration cell

compound	pesticide concentration in solution / $\mu g\ l^{-1}$		
	not exposed to UFC	filtrate	supernatant
simazine	1.44	0.49	0.75
atrazine	1.45	0.34	0.68
propazine	1.60	0.34	0.81
parathion	0.80	0.025	0.073

3.1.3 Test of performance of ultrafiltration cell in the absence of colloid but with recirculation.

The procedure above (2.1.2) was repeated with the PM10 membrane but with the following modifications:

(a) The $CaCl_2$ solution was mixed with the pesticide residues overnight and then filtered through a 0.45 μm membrane filter before use in the ultrafiltration cell.
(b) The concentration of compounds in the solution was increased to approximately 10 $\mu g\ l^{-1}$.
(c) The solution in the ultrafiltration cell was recirculated using the "AUTOUFC" (Appendix 1) program by connecting the autoburette to the filtrate collection vessel. The volume of the cell was replaced 2.5 times during the recirculation over a period of 3 h. The results of the GC analysis of the stock solution, filtrate and supernatant are shown in Table 2.

TABLE 2. Results of trial experiment in the absence of colloids and with recirculation. UFC: ultrafiltration cell

compound	pesticide concentration in solution / $\mu g\ l^{-1}$		
	not exposed to UFC	filtrate	supernatant
simazine	10.51	4.29	3.80
atrazine	9.58	4.24	4.20
propazine	9.68	4.41	4.70
desmetryn	8.13	3.86	3.58
prometryn	8.19	2.40	2.30
terbutryn	7.96	1.22	1.35
parathion	10.06	9.18	10.65

The results show better agreement of the measured concentrations with the nominal value (10 $\mu g\ l^{-1}$) and general agreement between the filtrate and supernatant concentrations of all the pesticides. Hence although there is a loss of pesticides to the cell components, the recirculation procedure is sufficient to allow an equilibrium to be established. During these experiments the ultrafiltration cell was found to operate satisfactory and able to perform the main functions for which it was designed. The gas purging system has not been fully tested yet during a sorption isotherm measurement.

3.1.4 Test of the performance of the ultrafiltration cell in the presence of colloids and with recirculation.

A preliminary test of the performance of the apparatus was completed using the sample of natural water from the river Ouse (Naburn Lock, York). A 50 l quantity of this water was continuous-flow-centrifuged (CFC); see section 4 for details. One litre of the CFC water was placed through the ultrafiltration unit and the supernatant reduced to ca 100 ml using the

autoburette to deliver the CFC water to the cell. The filtrate was collected for UV absorbance measurements. 100 ml of the stock $CaCl_2$ solution from the experiment in 2.1.3 was then added to the cell and mixed. This was then circulated, (16x25 ml to give 2 volume replacements), through the cell using the autoburette to deliver the filtrate to the ultrafiltration cell. Samples of the filtrate and supernatant were taken as described above, extracted and analysed by GC. The results in Table 3 show that in samples of this type, further concentration of the colloid component, separated with the 10,000 PM10 ultrafilter, is need to measure K_{oc}'s (see Appendix 2 for more details) as low as 1000.

TABLE 3. Results of the trial experiment with R. Ouse water (code: ??) after continuous-flow- centrifugation. The distribution coefficients are normalised with respect to organic carbon (DOC=7.9 mg l^{-1}); see equation (5) in appendix 2. UFC: ultrafiltration cell.

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

4. Field sampling and results.

Part of the project involves the collection of colloidal material and its characterisation to prepare for more intensive field work in the third year of the project. The field study site originally proposed was the Humber rivers and estuary. This is also the study area for the NERC, LOIS (Land Ocean Interaction Study) programme and it is planned to share some of the storm sampling in the third year with a project in this programme to enable more storms and samples to be analysed.

The water samples taken from the Ouse, Swale and Aire rivers are listed in Table 4, together with the parameters that have been measured and a note of the measurements planned in future work. The main focus of this research will be on the R. Ouse at the tidal limit (Naburn Lock) and down stream to Goole in the upper estuary. Weekly samples from the Humber rivers, analysed over the last year, indicate that the major contributors to the pesticide load to the Humber are the rivers Ouse, Aire, Don and Trent. The rivers from the upland catchments, such as the Swale, Ure and Wharfe are much less important, although they do have the highest concentrations of DOC. The DOC concentrations in the river Ouse at York

vary between 3 and 10 mg l^{-1} with the highest values during storms. The samples listed in Table 4 are briefly described below:

(i) Sample C1 from the river Swale was taken during the first major storm in the autumn of last year. Two extracts have been taken from this sample, both using the ultrafiltration cell with a YM1, 1000 Dalton hydrophillic membrane; these were prepared before the unit was automated. The first extract was 1070 ml reduced to 170 ml (concentration factor of 6.3) and the second was 1400 ml reduced to 40 ml (concentration factor of 35 fold). These samples will be used to evaluate the sorption of pesticides with the automated unit.

(ii) Two litres were taken according to the protocol (SOP:7/09.01.92). Dichloromethane was added on site, and the samples extracted on return to the River Laboratory. The extracts have been dried and reduced in volume ready for analysis by GC/MS in full scan to identify compounds which may be present but are not being analysed in the routine weekly work.

TABLE 4. Field samples from the Humber rivers. SS: suspended solids measured by filtration through a GF/F glass microfibre filter; DOC: dissolved organic carbon; A: absorbance of filtered sample at 340 nm using 4 cm cell; UFC: ultrafiltration cell; CFC: continuous-flow-centrifugation.

site	NGR	date of collection	purpose	SS /mg l^{-1}	DOC /mg l^{-1}	$A^{(340\ nm)}$ @ 4cm	sample
R. Swale		21.9.94	concentration of colloids; UFC expts.				10 l unfiltered water
R. Ouse		2.3.95	analysis of pesticides by solvent extraction				unfiltered water
R. Ouse		10.4.95	CFC; UFC expts. and suspended sediment analysis for pesticides and mineralogy	10.3	3.03	0.107	50 l unfiltered water
R. Aire Beale		10.4.95	DOC; suspended solids	6.5	7.43	0.442	unfiltered water
R. Aire Airmyn		10.4.95	DOC; suspended solids	8.5	5.77	0.281	unfiltered water
R. Ouse Boothferry		10.4.95	DOC; suspended solids	7.0	4.94	0.180	unfiltered water
R. Ouse Drax		10.4.95	DOC; suspended solids	6.0	5.25	0.139	unfiltered water

(iii) 50 l of water were sampled from Naburn Lock on the river Ouse at the tidal limit. This was transported to the River Laboratory and subject to continuous-flow-centrifugation (CFC) at 10 ^{0}C over a period of ca 9 h. The centrifuge was operated at 12,000 rpm with a flow rate of 100 ml min^{-1} through the centrifuge cell. The supernatant contained no suspended material when analysed for suspended solids by the normal laboratory procedure (SOP: 36/6/5/95). The solid material was then isolated from the centrifuge cell and concentrated by successive centrifugation so that the final volume was less than 5 ml. This solid isolate will be use for pesticide analysis and mineralogy studies. The supernatant is being used to test the automated ultrafiltration unit (see section 2.1.4). The results of the DOC and absorbance

studies are given in Table 5.

(iv) Samples C4-C7 were taken from the rivers Aire and Ouse. Sample C4 was from the NRA harmonised monitoring site near Beale, C5 from the river Aire near its confluence with the river Ouse, C6 from Boothferry in the Humber and C7 from a site upstream of the river Aire confluence and near the Drax power station. This part of the field work enabled other down stream sites to be visited and assessed for future use in the sampling programme. The samples were used for DOC, suspended solids and absorbance measurements; the results are given in Tables 4 and 5.

TABLE 5. Information on DOC, suspended solids and absorbance measurements on samples C3 to C7 sampled on 10.4.95.
The ratio: A^{460}/A^{660} is used as an estimate of the molecular weight fractions of humic substances in the samples.

sample	filter	filtrate absorbance ratio, A^{460}/A^{660}	DOC/mg l^{-1}
R. Ouse, Naburn C3	0.45	6.64 (unfiltered=1.77)	3.03
R. Aire, Beale C4	0.45	3.36 (unfiltered=2.12)	7.43
R. Aire, Beale C4	10,000	8.37	5.77
R. Aire, Beale C4	GF/F	5.19	6.23
R. Ouse, Boothferry, C6	GF/F	4.37	4.94
R. Ouse, Drax, C7	GF/F	4.57	5.25
R. Ouse, Naburn C3	CFC	5.59	5.04
R. Aire, Airmyn C5	GF/F	5.23	4.15

The results show a general increase in absorbance at 340 nm in a 4 cm path length cell, with DOC ($DOC(mg\ l^{-1})=12.54\ A^{340nm}+2.464$; $R=0.773$). Filtration of the river Aire water through the 10,000 Dalton membrane produced the lowest DOC results and highest absorbance ratio indicating a move to the lower molecular weight fraction in the filtrate compared with the supernatant. Further work is needed to compare the results after ultrafiltration through lower molecular weight membranes. This change is also demonstrated with the CFC water from the river Ouse (sample C3) when 1000 ml was concentrated to 100 ml using the PM10 membrane of 10,000 Dalton. The absorbance ratio changes from 5.59 for the CFC water to 1.83 in the supernatant and 10.21 in the filtrate.

5. Future plans.

It is planned to continue the development of the ultrafiltration system by testing different membranes with molecular cut-offs between 10,000 and 500 Dalton. This will include trials without colloids and also with the R. Ouse water, sample C3 after CFC. This will include measurement of the DOC associated with the filtrates and supernatant from the ultrafiltration cell and changes in the absorbance ratio. The tests will also be extended to a greater range of pesticides including those currently found in the Humber rivers.

The suspended sediment from the river Ouse (separated by CFC from sample C3) will be analysed for pesticides, distribution of particle sizes and mineralogy. The full analysis of the extract from C2 will also be completed to give more information about the occurrence of microorganics. Further samples of freshwaters from the Ouse at York will be analysed for suspended sediment and colloids. Further methods for characterisation of the sediments and colloids will be sought.

6. Progress of LOIS on pesticides

The CORE weekly monitoring programme on pesticides started on March 1994. Initially this focused on the sites at the tidal limit of the 11 major rivers flowing to the Humber; these sites coincide with the NRA harmonisation sites. The compounds cover a range of phenylureas, triazines, organochlorine, organophosphorus and pyrethriods insecticides. Recently the list has been extended to include some PCB's and chlorinated phenols. In cooperation with the NRA, further work to extend the range to selected PAH's, common fungicides and phthalates started in April this year as part of a special topic program on pesticide particle interactions.

The weekly measurements have so far detected simazine, atrazine, lindane and isoproturon in the rivers Trent, Don, Calder, Aire and Ouse on a regular basis throughout the period. Some pyrethriods have also been detected on the rivers Aire and Calder. These results are currently being compiled for publication with the purpose of estimating fluxes of the compounds to the estuary. This will be useful information for this project and guide the eventual choice of compounds for the field work.

APPENDIX 1. Design and operational software

Control software for the ultrafiltration unit.

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

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

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

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

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

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

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

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

CONST ValvePortAddr% = &H2A0 + 3

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

2. The addition of the subroutines and function described above

3. The addition of the line:

Set (Valve1%, Powered%)

at the start of the routine responsible for adding spike solution to the cell, and the line:

```
Set (Valve1%, NoPower%)
```

at the end of this routine

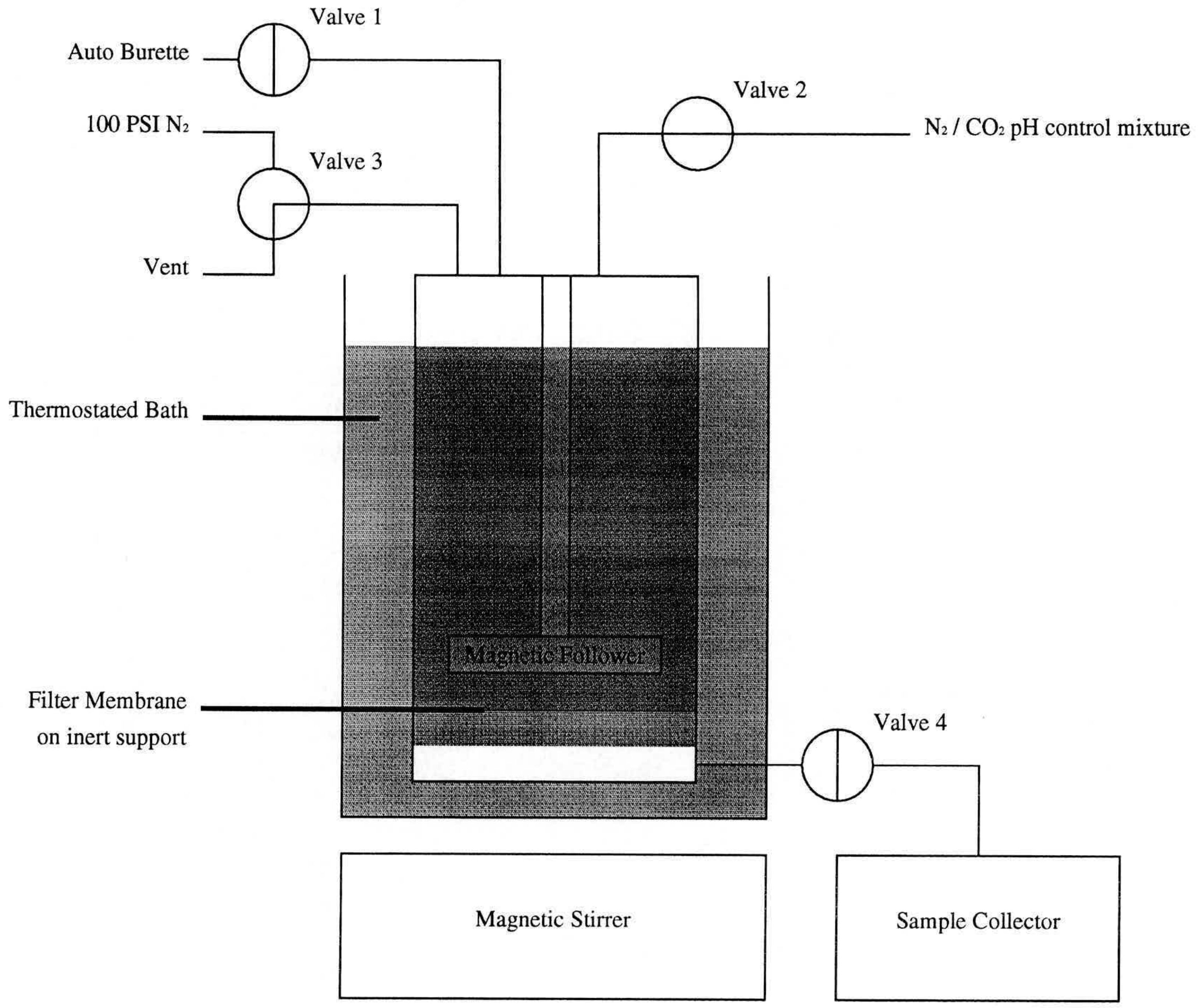
4. The sampling procedure was changed to:

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

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

PROGRAMS AVAILABLE

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


Valve 1
Auto Burette
Valve 2
100 PSI N_2
N_2 / CO_2 pH control mixture
Valve 3
Vent
Thermostated Bath
Magnetic Follower
Filter Membrane
on inert support
Valve 4
Magnetic Stirrer
Sample Collector

APPENDIX 2

Definitions of distribution coefficients

The distribution coefficient, k_d, is defined:

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

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

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

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

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

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

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

or

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

Hence if k_{dc} is constant, the ratio of the concentrations in the filtrate and supernatant of the ultrafiltration cell should be constant and independent of the pesticide concentration.

7. REFERENCES

House, W.A. and Farr, I.S. (1989) Adsorption of sulphonates from detergent mixtures on potassium kaolinite, Colloids and Surfaces, **40**, 167-180.

Marchesi, J.R., Russel, N.J., White, G.F. and House, W.A. (1991) Effects of surfactants adsorption and biodegradation on the distribution of bacteria between sediments and water in a freshwater microcosm, Appl. Microbiology, **59**, 2507-2513.