5.
Movement Beyond the Root Zone

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MAPPING THE VULNERABILITY OF AQUIFERS AND SURFACE WATERS TO PESTICIDE CONTAMINATION AT THE NATIONAL/REGIONAL SCALE

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ABSTRACT

Aquifer and surface water vulnerability assessments are built up by integrating a soil vulnerability classification, based on soil hydrology and organic matter content, with a physico-chemical classification of pesticide active ingredients. For each combination of soil vulnerability and pesticide classes individual assessments are made using simple mathematical models incorporating soil and substrate, pesticide and climatic properties, to predict the likelihood of pesticides reaching ground or surface waters in concentrations greater than 0.1 µg per litre. The spatial distribution of these assessments is shown by using a relational database system to overlay the distribution of soil vulnerability classes, derived from soil maps, on important climatic variables. As a final stage, land use factors are introduced to exclude areas where target crops are not grown or are inextensive.

INTRODUCTION

The recently imposed EC limit of 0.1 µg per litre for the concentration of individual pesticide compounds or their metabolites in drinking waters has focussed attention on the possibility of pesticide movement beyond the root zone. Although detailed mathematical models such as RUSTIC, GLEAMS and LEACHP exist for predicting the environmental fate and behaviour of pesticides in individual situations, their extensive data requirements often preclude spatial extrapolation to broad regional or national scales. There is thus the need for a more general comparative assessment of the relative vulnerability of water sources to pesticides so as to identify those areas most at risk.

A METHODOLOGY FOR ASSESSING THE RELATIVE VULNERABILITY OF WATER SOURCES

Vulnerability assessments are built up by integrating a soil and substrate hydrological classification - HOST (Boorman and Hollis 1990) with a broad classification of topsoil organic matter content, to produce soil vulnerability classes. Because the mechanisms and rates of water movement to aquifers are different from those to surface waters, separate classes are necessary for each type of water source. The soil vulnerability classes are in turn integrated with a classification of pesticide compounds based on their relative mobility and persistence. For each combination of soil vulnerability and pesticide classes, individual vulnerability assessments are made using simple mathematical models to predict the likelihood of pesticide compounds reaching ground or surface waters in concentrations greater than 0.1 µg per litre.

Soil vulnerability classes

Hydrological factors included in the soil vulnerability classes for aquifers are, depth to the aquifer or seasonally saturated layer, presence or absence of 'by-pass flow' to a permeable substrate, and the predominant type of unsaturated flow (simple intergranular flow as in loose unconsolidated sands, loamy sands or sandy loams, or more complex flow as in structured loams and clays). For surface water vulnerability classes, soil hydrological groupings are based on the predicted standard percentage run-off (SPR) and Base Flow Index (BFI) for each HOST class. Standard percentage run-off and Base Flow Index are stream flow characteristics which indicate the proportion of rainfall that reaches streams within a few hours or a few days. They are strongly correlated with soil HOST classes (Boorman and Hollis 1990).

The broad classification of topsoil organic matter content is based upon a preliminary analysis of arable topsoils within the National Soil Inventory dataset, which comprises analytical data from about 6,500 samples taken at 5 km grid intersects throughout England and Wales. Topsoils are classed as having either low organic matter with an average organic carbon content of 1.1%, moderate organic matter with an average organic carbon content of 2.5%, or high organic matter with a minimum organic carbon content of between 4.5 and 7% depending on clay content. Topsoils with high organic matter are not placed in the usual soil vulnerability classes for aquifers or surface waters because of their very large capacity to adsorb and effectively immobilise most pesticide products (MAFF, 1984). The properties used to define each soil vulnerability class are set out below.

p Soils with high organic matter

Soil vulnerability classes for Aquifers

a1 Soils with by-pass flow and a seasonally saturated layer within 40 cm depth.

a2 Soils with by-pass flow and a seasonally saturated layer between 40 and 100 cm depth.

a3 Soils with low organic matter, simple unsaturated flow and a seasonally saturated layer between 40 and 100 cm depth.

a4 Soils with moderate organic matter and a seasonally saturated layer within 40 cm depth, OR soils with low organic matter, simple unsaturated flow and an aquifer at between 2 and 10 m depth.

a5 Soils with moderate organic matter, complex unsaturated flow and a seasonally saturated layer at between 40 and 100 cm depth, OR soils with low organic matter, simple unsaturated flow and an aquifer below 10 m depth.

a6 Soils with by-pass flow and an aquifer below 2 m depth.

a7 Soils with moderate organic matter, complex unsaturated flow and an aquifer between 2 and 10 m depth.

a8 Soils with moderate organic matter, complex unsaturated flow and an aquifer below 10 m depth.

a9 Soils with no by-pass flow, over a concealed aquifer.

Soil vulnerability classes for surface waters

s1 Soils with by-pass flow, OR soils with a SPR of >50% and a BFI <0.36

s2 Soils with a SPR of >50% and a BFI ≥0.36, OR with a BFI between 0.25 and 0.36

s3 Soils with a SPR of 30-50%

s4 Soils with a SPR of 10-30%

s5 Soils with a SPR of <10%

Pesticide mobility and persistence classification.

Two commonly determined physico-chemical properties of pesticide compounds, the soil/water partition constant based on organic carbon content (Koc) and the half life in soil (Ts1/2), have been used to define five classes of mobility and four classes of persistence. Both Koc and soil half life are commonly determined from laboratory and field studies. Although they have a natural variability within any particular soil type, when determined under standard conditions, they provide acceptable parameters for comparing the relative mobility and persistence of pesticide compounds (Gustafson, 1988).

Initially a range of mobility and persistence classes were developed from a number of sources. These include Helling (1971), who used Rf values (Helling and Turner 1968) determined from soil thin layer chromatography in a standard soil to define five classes of mobility, Hamaker (1978), who used chromatographic theory to correlate Koc with these Rf values, Gustafson (1988), who used the relationship between Koc and half life to develop a reliable leaching index for a series of compounds used in California, and the latest guidelines for the testing of agrochemicals in the Federal Republic of Germany, relating to the use of lysimeter tests (BBA, 1990).

In order to test the validity of these mobility and persistence classes the relationship between Koc, half life and the presence (at concentrations of at least 0.1 microgrammes/l) or absence in water sources of a range of pesticide compounds was examined. To eliminate bias, the compounds studied were selected from those identified by MAFF scientists as being commonly used on cropped land in an area around Claverley in eastern Shropshire and western Staffordshire. The results of this study, shown graphically in Figs. 1 and 2, suggest that the following classes of pesticide mobility and persistence may be relevant to vulnerability assessments in the UK:

Mobility class	Koc cc/g	Persistence class	Ts1/2 days
Non-mobile	>4,000	Impersistent	<5
Slightly mobile	4,000-500	Slightly persistent	5-21
Moderately mobile	499-75	Moderately persistent	22-60
Mobile	74-15	Very persistent	>60
Very mobile	<15		

Figure 1

Pesticide characteristics and presence in Groundwater sources

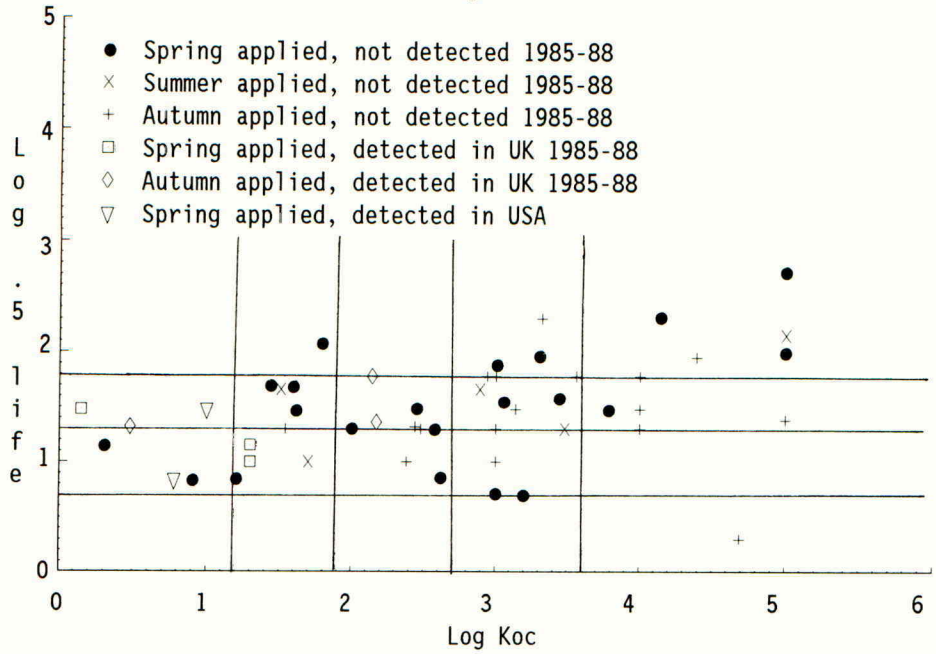
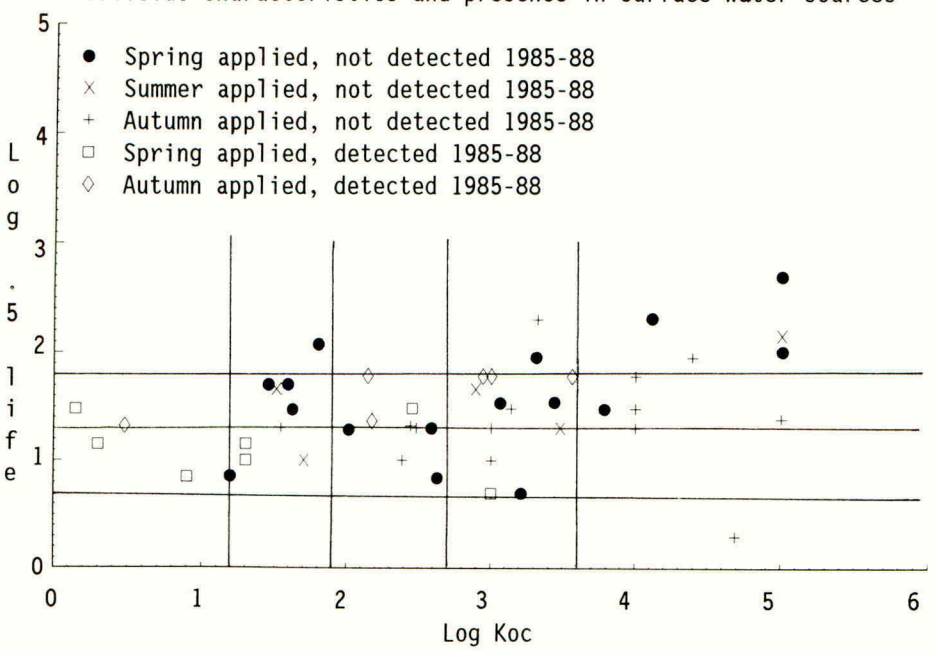


Figure 2

Pesticide characteristics and presence in Surface water sources



Integration of climatic variables.

Apart from temperature, which has a significant effect on soil microbial activity and hence the half life of pesticide compounds, the most important climatic properties relating to pesticide leaching are the duration of the field capacity period and the amount of excess winter rain during this period. Average annual values for the duration of field capacity and the amount of excess winter rain have been calculated at 5km grid intersects within England and Wales (Jones and Thomasson 1985). They can be used to calculate average daily soil water fluxes either during the field capacity period or, if travel times to water sources are longer than the field capacity period, during the year.

Climatic variations across the country have been incorporated into aquifer vulnerability assessments by examining the effect of different soil water fluxes on travel times of pesticide compounds with specified mobility and persistence characteristics within each of the soil vulnerability classes defined for aquifers.

In the case of surface water vulnerability assessments, average daily soil water fluxes are less important than individual rainfall events because soil vulnerability classes are based on parameters that predict the proportion of rain from an average event that reaches a water course relatively rapidly. The critical factors for surface water vulnerability assessments are thus the length of time between application of a pesticide and a significant rainfall event and the amount of rain in that event. For any location, the amount of rain in an individual event is extremely variable, but the range of that variation does not differ significantly accross the country. Instead, the main climatic variation is in the frequency of rainfall events. For surface water vulnerability assessments therefore, the effect of climatic variation within England and Wales was examined by using differences in the duration of field capacity to assess differences in the average time period between pesticide application and a significant rainfall event.

Simple model for aquifer vulnerability assessment

The equations used to model aquifer vulnerability are based on the work of Rao et al (1985) and Leonard and Knisel (1988). They calculate the Pesticide Attenuation Factor (AF), defined as the proportion of the pesticide applied at the surface that reaches ground water. Attenuation factors for individual pesticides are calculated from the travel time to ground water (Tr), based on the depth to ground water, the soil water content, the net recharge rate (i.e. the average soil water flux) and a retardation factor for pesticide flow, and the first order rate constant for pesticide degradation expressed as 0.693/half life in soil (T1/2)

$$\text{Thus: } AF = \text{Exp.}\left[-Tr * \frac{0.693}{T1/2} \right]$$

Full details of the equations and their calculation are given by Hollis (1990).

Attenuation factors are calculated for each combination of soil vulnerability and pesticide classes using a climatically representative range of soil water fluxes and average values for each of the required soil properties, calculated from the SSLRC soil physical property database. The

likelihood of a pesticide reaching ground water in concentrations greater than 0.1 micrograms per litre of soil water is then assessed by comparing the calculated attenuation factors with 'critical' attenuation factors for pesticides applied at a low and a high rate. These critical factors are based on the ratios required to achieve a pesticide concentration of 0.1 micrograms per litre in soil water reaching a ground water table. Where the attenuation factor calculated by the model is greater than the critical attenuation factor for low pesticide application rates, there is a high risk of pesticide reaching ground water at concentrations greater than 0.1 micrograms per litre. Conversely, where the calculated attenuation factor is smaller than the critical attenuation factor for high application rates, the risk is low. Where the calculated attenuation factor is between the critical factor for low and for high application rates, the risk is moderate. Using this system, vulnerability assessments for groups of pesticides with specific characteristics can be made for each soil vulnerability class under a range of different climatic regimes. By combining such matrices, overall vulnerability assessments can be built up for groups of pesticides with specified ranges of mobility and persistence. An example of the overall assessment matrix for very mobile, slightly persistent pesticides is shown in Table 1.

Table 1. Overall aquifer vulnerability assessments for very mobile, slightly persistent pesticides

Soil vulner. class	Excess Winter Rain (mm)					
	<175	175-200	200-300	300-400	400-750	>750
a1	High/Mod	High/Mod	High/Mod	High/Mod	High	High
a2	High/Mod	High/Mod	High/Mod	High/Mod	High	High
a3	Mod/Low	Mod	Mod	Mod	High/Mod	High/Mod
a4	Mod/Low	Mod	Mod	Mod	High/Mod	High/Mod
a5	Mod/Low	Mod/Low	Mod	Mod	High/Mod	High/Mod
a6	Mod/Low	Mod/Low	Mod	High/Mod	High/Mod	High/Mod
a7	Mod/Low	Mod/Low	Mod/Low	Mod	High/Mod	High/Mod
a8	Mod/Low	Mod/Low	Mod/Low	Mod	High/Mod	High/Mod
a9	Low	Low	Low	Low	Low	Low

Simple model for surface water vulnerability assessment.

The equations used to model surface water vulnerability, predict pesticide concentrations in soil water entering streams, either through field drains or natural fissure/macropore systems. This situation is likely to occur only in soil vulnerability classes s1 to s4 and consequently, surface water vulnerability assessments for s5 soils are always low irrespective of climate, pesticide characteristics or application rates.

The concentration (C1) of pesticide in soil water entering streams, either through field drains or natural fissure/macropore systems is based on the concentration (C2) of pesticide in the soil water fraction at the depth (d mm) to which it has penetrated during the time (n days) between when it was applied and the first significant rainfall event, a Dilution

Factor (DF) and a Partition Factor (PFr) for rapid percolation through the topsoil and subsoil:

$$C1 = C2 * \frac{(DF)}{PFr} \quad \text{Microgrammes/litre}$$

C2 is calculated from the theoretical pesticide concentration (C3 microgrammes/litre) in the upper 1 mm of topsoil directly after application assuming rapid partitioning, the topsoil/water partition factor (PFt) and the pesticide Attenuation Factor (AF):

$$C2 = \frac{C3 * AF}{[PFt * 2 * (d-1)]} \quad \text{Microgrammes/litre}$$

Full details of the equations and their calculation are given by Hollis (1990).

As for aquifer vulnerability assessments, the SSLRC physical property database was used to calculate average values of the required soil properties for each of the soil vulnerability classes.

Using these models, assessments for classes s1 to s4 are based on the likelihood of pesticide entering streams in concentrations greater than 0.1 microgrammes per litre when it is applied at a high and a low rate. Values for high and low application rates are the same as those used for aquifer vulnerability assessments. Where predicted pesticide concentrations in drainage waters are more than 0.1 microgrammes per litre for low application rates, there is a **high** surface water vulnerability. Conversely, where predicted concentrations are less than 0.1 microgrammes per litre for high application rates, vulnerability is **low.** In between these two extremes, surface water vulnerability is assessed as **moderate.** As with aquifer vulnerability, overall assessment matrices can be built up for groups of pesticides with defined ranges of mobility and persistence. An example for very mobile, slightly persistent pesticides is shown in Table 4.

Table 2. Overall surface water vulnerability assessments for very mobile, slightly persistent pesticides

Soil vulner. class	Field Capacity Days <125	125-175	175-225	>225
s1	High	High	High	High
s2	High	High	High	High
s3	Mod	High/Mod	High/Mod	High/Mod
s4	Mod/Low	Mod/Low	Mod	Mod
s5	Low	Low	Low	Low

Definition of terms.

Vulnerability assessments made using the quantitative techniques described above can be defined more precisely than subjective ones. The

terms used to assess aquifer and surface water vulnerability for this project are defined as follows:

LOW	No pesticides in the class, except those which are misapplied, are likely to contaminate water sources.
MOD/LOW	Only the most persistent and mobile pesticides in the class, which are applied at high rates, are likely to contaminate water sources.
MODERATE	Most of the more mobile pesticides in the class and most of those with high application rates are likely to contaminate water sources.
MOD/HIGH	All except the least mobile pesticides in the class, which are applied at low rates are likely to contaminate water sources.
HIGH	All pesticides in the class are likely to contaminate water sources if applied at the recommended or higher rates.

NATIONAL/REGIONAL SCALE VULNERABILITY ASSESSMENT MAPS

By using the SSLRC Land Information System (LandIS) to overlay the spatial distribution of soil vulnerability classes on important climatic variables, 5km dot matrix sigmex maps of England and Wales showing aquifer and surface water vulnerability assessments for different pesticide classes can be produced from the vulnerability assessment matrices described above. An example for very mobile, slightly persistent compounds in aquifers is shown in Figure 3. The distribution of soil vulnerability classes is derived from digitised 1:250,000 scale soil maps of England and Wales and based on properties of the dominant soil series within 5 km blocks. The distribution of important climatic factors is derived from SSLRC agroclimatic datasets.

In order to exclude areas where aquifers or surface waters may be vulnerable to contamination by specific pesticides, but the crops to which they are applied are not grown or are inextensive, land use factors need to be taken into account. This can be done either by using regional cropping statistics to exclude regions where target crops are not grown or are uncommon, or by using crop suitability models to exclude areas of land that are unsuited or only marginally suited to target crops. Methods for assessing the suitability of different soils for individual crops are outlined in Soils and their use in South East England (Soil Survey Bulletin No. 15, Jarvis et al 1984).

Based on the crop suitability method, Figure 4 shows an example map of the vulnerability of surface waters to very mobile, slightly persistent pesticides applied to winter wheat. One of the more common pesticides to which the map applies is the herbicide **Mecoprop**.

CONCLUSIONS

At the national/regional scale, simple mathematical models using soil, climate and pesticide characteristic data can be linked to spatial soil and climate datasets to produce maps showing quantitative assessments of the vulnerability of aquifers and surface waters to pesticide contamination. However, the maps need to be validated from national data on

Figure 3

AQUIFER VULNERABILITY ASSESSMENT FOR VERY MOBILE, SLIGHTLY PERSISTENT PESTICIDES

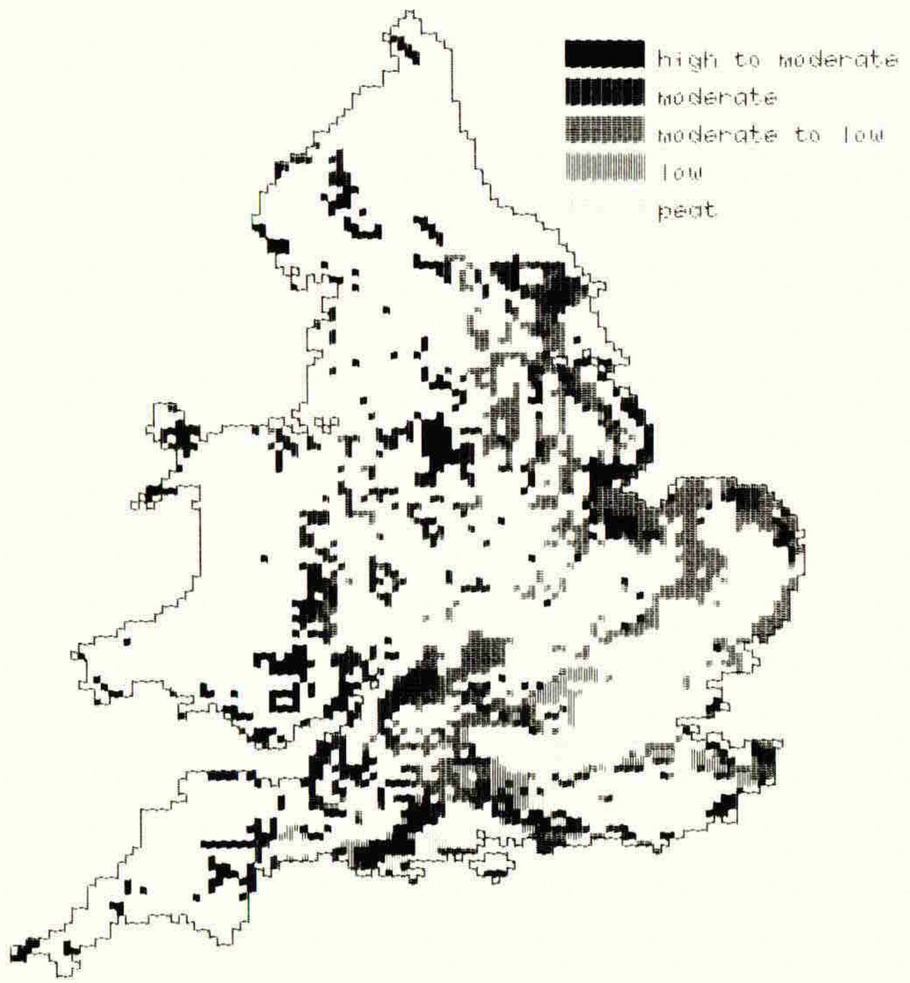
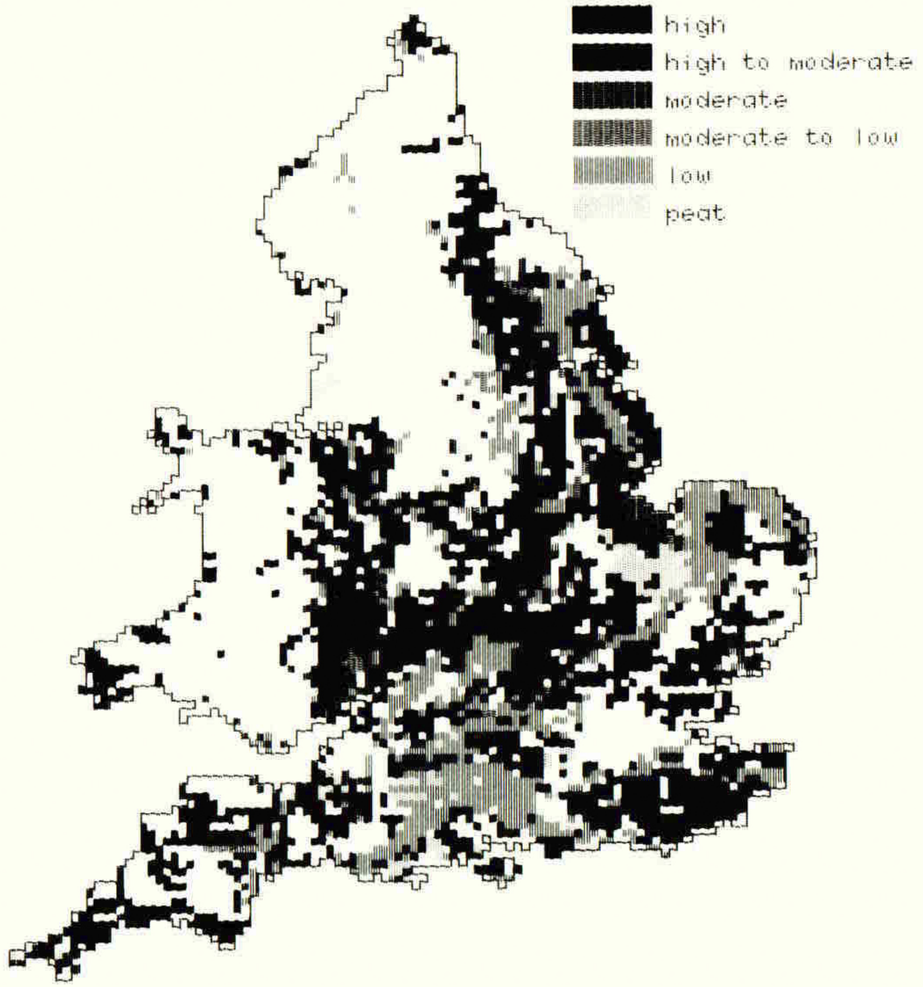


Figure 4

VULNERABILITY ASSESSMENT ON SURFACE WATERS FOR LAND WELL OR MODERATELY SUITABLE FOR WINTER WHEAT

(very mobile, slightly persistent pesticides)



pesticide concentrations in water sources. Some of the mechanisms of water movement incorporated into the models, particularly those for surface waters, also require validation.

ACKNOWLEDGEMENTS

I gratefully acknowledge the funding of research described in this paper by the MAFF. I would also like to thank Dr A Carter, Dr P Nicholls, Dr A Walker, Mr T Tooby, Mr P Marsden, Mr D Yon, Mr D Arnold and members of the BAA for their helpful advice, Ms A Saxby for processing the text, and Mr R I Bradley for producing the maps.

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THE POTENTIAL FOR ATRAZINE DEGRADATION IN AQUIFER SEDIMENTS

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ABSTRACT

The role of microorganisms in pesticide degradation in aquifer sediments has been examined. The herbicide atrazine was used because of its reported presence in groundwater and because little is known of its behaviour in these environments. When added and incubated with groundwater from five sites, in the London Basin, the DT50 value for atrazine was of the order of 15-20 weeks. When added and incubated with a mixture of groundwater and sediment from two boreholes, dissipation of atrazine also occurred but varied with lithostratigraphy. The relationship between these data and physical and microbiological properties of the materials is discussed.

INTRODUCTION

In Britain 30% of the potable water supplies are derived from groundwater. There is therefore a need to protect this valuable resource in order that the major aquifers may continue to be used as a source of wholesome water. Both agricultural and industrial practices may affect groundwater quality; the concern over this in Europe is reflected in a Directive from the Council of European Communities (1980) which defines the Maximum Admissable Concentration (MAC) of one or more pesticides in water for human consumption. There is evidence of the presence of 1,3,5-triazines (for example atrazine) at concentrations near to the MAC in groundwater, although the quantitative reliability is uncertain (Hance, 1987).

Little is known about the persistence of pesticides in groundwater. The bacterial population in groundwater can vary between 0 and 10^6 cfu/ml (Bitton and Gerba, 1984), and there is limited evidence of diverse microbial populations in deep aquifer sediments in the US (Kaiser and Bollag, 1990) and the UK (Parker and James, 1985). These organisms may play a role in the degradation of groundwater contaminants such as herbicides.

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Atrazine has been used widely around the world for 30 years. It is chemically stable at pH values between 5 and 11 (Armstrong *et al.*, 1967), therefore where atrazine is detected in chalk groundwater it is likely to persist unless degraded by microorganisms.

The aim of this study was to assess the potential for degradation of atrazine introduced into groundwater samples and sediment samples taken at depths down to 39 m from the London Basin.

MATERIALS AND METHODS

Atrazine determination

Atrazine was determined by high performance liquid chromatography using a 25 cm Zorbax C18 column, 85% methanol mobile phase at a flow rate of 0.65 ml/min, and detected at 215 nm. The limit of detection was approximately 10 µg/l.

Groundwater studies

Samples of groundwater were taken aseptically from 5 boreholes within the London Basin which had been pumped continuously for several months prior to sampling. The water level was measured at each borehole and immediately after sampling each groundwater sample was analysed for temperature, pH and Eh (Table 1). Triplicate 50 ml groundwater samples were incubated with 5 mg/l atrazine (99.6 ± 0.2 % purity supplied by Ciba-Geigy Ltd., Basle) in 100 ml Erlenmeyer flasks in an orbital incubator at 100 rev/min and 22 °C for 18 weeks. Samples were taken every 2 or 4 weeks and analysed for atrazine.

Sediment studies

General

Sediment was obtained by the British Geological Survey at two sites using a combination of U100 percussion and hollow stem continuous flight auger techniques. The boreholes (HL and CS) were 5 km apart. Undisturbed cored material was taken on the same day to a field laboratory and either sampled asceptically for microbiological studies immediately, or stored at 5 °C for up to 48 h before sampling. Uncontaminated samples of the sediment were used for the following experiments.

Adsorption experiment

Sediment from 32.8 and 34.5 m at borehole CS was sterilised by autoclaving at 121 °C for 15 min. Duplicate 2.5 g samples of sterile and non-sterile sediment were incubated with 10 ml 360 µg/l atrazine in groundwater in sterile Universal bottles at 25 °C. Immediately after adding the atrazine, and 1 and 7 days later samples of the groundwater were taken and analysed for atrazine.

Persistence experiment

Sediment was taken from 15.0-25.1 m at borehole HL, and 24.8-38.9 m at borehole CS. Triplicate (borehole HL) or duplicate (borehole CS) 5 g samples of sediment were incubated statically with 10 ml of a saturated solution of atrazine in groundwater (approximately 30 mg/l) in sterile Universal bottles at 25 °C for 10 weeks. After this time samples of the groundwater were taken and analysed for atrazine.

RESULTS

The geological sequence at the sites studied within the London Basin was London Clay overlying Lower London Tertiaries (Woolwich and Reading Beds and Thanet Beds) which rest upon Upper Chalk. At borehole HL and all the sites from which pumped groundwater samples were taken the water table was below the top of the Upper Chalk. At borehole CS the water table was above the Upper Chalk at 25 m. The pumped groundwater samples were similar in terms of temperature, pH and Eh (Table 1).

Table 1. Major characteristics of pumped groundwater samples used in this study taken from the Upper Chalk within the London Basin.

Groundwater site no.	Temperature (°C)	pH	Eh (mV)
1	12	7.2	102
2	12	7.5	94
3	12	7.4	96
4	12	7.45	84
5	13	7.4	75

Groundwater experiment

Data for atrazine persistence in the 5 pumped groundwater samples (Fig. 1) show that atrazine was dissipated during the 20 week incubation. Regression analysis of the original data and of the data following logarithmic transformation showed that the rate of removal of atrazine could in all cases by described by either zero order or first order kinetics (Table 2). The correlation coefficients were significant for both analyses and time taken for a 50% reduction in concentration (zero order) or half-life (first order) ranged from 16.3-17.6 weeks and 14.6-16.7 weeks respectively. Variability between samples was low and more frequent sampling intervals would be required to establish conclusively the order of reaction.

Table 2. Correlation coefficients (r) and rates of disappearance of atrazine (initial concentration approximately 5 mg/l) in groundwater from 5 sites in the London Basin based on changes in either concentration of atrazine or natural logarithm of concentration over a period of 18 weeks. Twenty one observations per site.

Groundwater site no.	No transformation		Ln transformation	
	r	DT-50 (weeks)	r	$t_{0.5}$ (weeks)
1	0.94	17.6	0.96	16.7
2	0.90	16.3	0.88	14.6
3	0.96	16.9	0.96	15.3
4	0.94	16.4	0.95	15.1
5	0.93	17.0	0.93	14.9

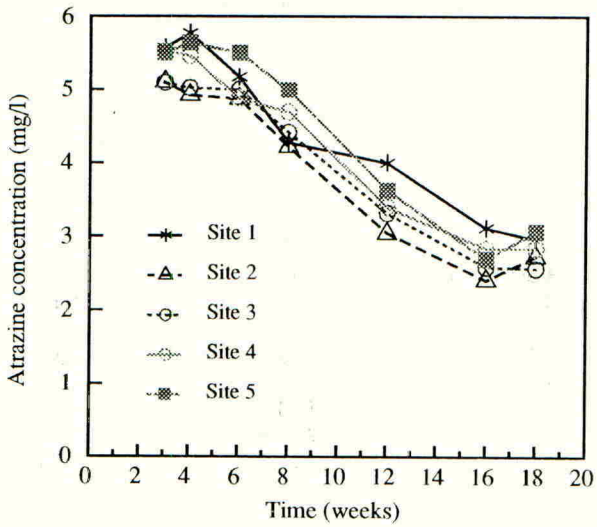

Figure 1 Concentration of atrazine remaining in groundwater from 5 sites in the London Basin incubated at 22°C. Three observation per mean.

Sediment experiments

Data from the adsorption experiment (Table 3) showed no significant adsorption of atrazine to the material from borehole CS. No atrazine was detected in the control to which no atrazine was added. The material taken from the Thanet Beds (Table 5) comprised uniform silty fine sand, which would have had only a very small cation exchange capacity. The atrazine persisted throughout the seven day experiment, and there was no clear difference between sterile and non-sterile treatments.

Table 3. Concentration of atrazine (µg/l) remaining in sterile (S) or non-sterile (NS) sediment material from borehole CS at different times after incubating with groundwater containing 360 µg/l atrazine. Two values per mean.

Depth (m)	Sterile or Non-sterile	Time (days) 0	1	7
32.8	NS	349	338	359
32.8	S	349	380	372
34.5	NS	338	349	383
34.5	S	338	383	338

All sediment samples from both boreholes showed a reduction in atrazine concentration over 10–24 weeks (Table 4). The extent of removal of atrazine in the unconsolidated sand (Woolwich and Reading Beds and Thanet Beds) was at least 95%. The chalk samples from borehole CS (38.2–38.9 m) showed much lower rates of atrazine removal of 40–54%, and the sample taken from the interface of the Thanet Beds and Upper Chalk (38.0 m) showed an intermediate rate of removal.

Table 4. Concentration of atrazine remaining in sediment material (WRB Woolwich and Reading Beds, TB Thanet Beds, UC Upper Chalk) from boreholes HL and CS following incubation with a saturated solution of atrazine in groundwater (approximately 30 mg/l) for 10 weeks (borehole HL) or 24 weeks (borehole CS). Three observations per mean.

Depth (m)	Lithostratigraphic unit	Final concn (µg/l)	Overall reduction (%)
Borehole HL (10 weeks)			
15.0	WRB	1030	96.6
15.7	WRB	1060	96.5
20.6	WRB	180	99.4
22.9	WRB	220	99.3
25.1	WRB	600	98.0
Borehole CS (24 weeks)			
24.8	WRB	1064	96.5
25.9	WRB	1345	95.5
27.6	TB	1619	94.6
29.1	TB	1086	96.4
30.1	TB	345	98.9
32.8	TB	<100	>99.7
33.8	TB	206	99.3
34.5	TB	256	99.2
35.0	TB	115	99.6
38.0	TB/UC	3382	88.7
38.2	UC	13722	54.3
38.9	UC	17997	40.0

DISCUSSION

Differences between lithostratigraphic units

These data indicate a marked difference in the rate of dissipation of atrazine between the sands and the chalk, ie. between materials of very different texture. This difference does not appear to be related to the redox conditions. The Thanet Beds at borehole HL were dewatered and the presence of high concentrations of sulphate at approximately 21 m indicated oxidising conditions, whereas the Thanet Beds at borehole CS were saturated with water, and the presence of sulphate reducing bacteria indicated at least localised reducing conditions. The dissipation of atrazine in the groundwater experiment occurred under well-aerated conditions, although the rate of dissipation was slower than in the sediment system using sand which was initially aerobic. The slower rate of dissipation in chalk groundwater alone may reflect the lower potential of the source material to degrade atrazine (Table 4) and the lower population of microorganisms in the groundwater compared to the sediment material.

Table 5. Physical and biological properties of sediment material used in these studies. AHB aerobic heterotrophic bacteria, DNB denitrifying bacteria, SRB sulphate reducing bacteria, ND not determined.

Depth (m)	Texture	Metabolisable organic matter	Microorganisms present AHB	DNB	SRB
Borehole HL					
15.0	Fine sand	ND	+	–	–
15.7	Fine sand	ND	+	–	–
20.6	Coarse sand	ND	+	+	–
22.9	Coarse sand	ND	+	+	–
25.1	Medium sand	ND	+	–	–
Borehole CS					
24.8	Coarse sand	+	+	+	+
25.9	Silt clay/fine sand	+	+	+	+
27.6	Medium sand	–	+	+	–
29.1	Medium sand	–	+	+	–
30.1	Fine clayey sand	–	+	+	+
32.8	Fine clayey sand	–	+	+	–
33.8	Silty fine sand	+	+	+	–
34.5	Silty fine sand	–	+	+	–
35.0	Silty fine sand	–	+	+	–
38.0	Fine clayey sand	–	+	+	+
38.2	Putty chalk	+	+	+	+
38.9	Putty chalk	–	+	+	–

The difference in rates of dissipation of atrazine does not seem to be related to the general microbiological properties of the material, nor to the presence of metabolisable organic matter (Table 5). All sediment samples contained aerobic heterotrophic bacteria, and most samples

contained denitrifying bacteria. Sulphate reducing bacteria were absent from the material from borehole HL but were present in the chalk samples from borehole CS. It is likely that one or more specific organisms are responsible for the dissipation of atrazine, and these organisms would not necessarily fall into one of the broad groups tested for in this study.

Chemical or microbiological dissipation?

The dissipation of atrazine from the groundwater could have been due to either chemical hydrolysis or microbiological degradation. In addition, atrazine could have been adsorbed to sediment material.

The adsorption experiment demonstrated that no absorption occurred with the samples of material taken from 32.8 and 34.5 m at borehole CS, a fine clayey sand and silty fine sand respectively. It seems therefore that adsorption was not responsible for the observed dissipation, particularly as many of the samples did not contain any appreciable amounts of clay (Table 5).

Atrazine is chemically stable in the range pH 5-11 (Armstrong *et al.*, 1967). The pH of the groundwater used in these studies was around 7.5 (Table 1), so chemical hydrolysis was not responsible for the observed dissipation. The absence of any rapid reduction in the concentration of atrazine in the adsorption experiment confirms this.

The evidence therefore indicates that the dissipation was due to microbiological degradation. The apparent stability of atrazine during the seven days of the adsorption experiment suggests that a lag phase may have occurred in the sediment. This may represent a period of adaptation and induction of enzyme systems by the indigenous microorganisms. In this respect the sediment systems seem to differ from surface soils for which adaptation to atrazine has not been reported. The groundwater and the sediment material contained a mixed bacterial population (Table 5) which included aerobic, facultative anaerobic (denitrifiers) and obligate anaerobes (sulphate reducing bacteria). A large number of microorganisms have the ability to degrade atrazine in pure culture, most of those reported being fungi, however, there are a few reports of bacteria (Kaufman and Kearney, 1970). These include *Arthrobacter sp.*, *Bacillus sp.*, and *Pseudomonas sp.*. Although the bacteria present in these sediment samples were not identified it is highly likely that these organisms would be present. *Pseudomonas sp.* were isolated from deep aquifer sediments in the US (Jimenez, 1990).

Oxidative dealkylation appears to be the major mechanism by which microorganisms degrade atrazine, but degradation has also been observed under anaerobic conditions (Kaufman and Kearney, 1970). In the groundwater experiments reported here the conditions were maintained aerobic throughout, but in the

sediment experiments although the conditions were initially aerobic, the restricted supply of oxygen may have led to a gradual reduction in redox potential of the saturated sediment. Accurate data on *in situ* redox conditions are difficult to obtain, but the data for pumped groundwater (Table 1) indicate that conditions are likely to be aerobic.

Conclusions

These data indicate that introduced atrazine may be dissipated from aquifer sediments due to microbial degradation. However, it is difficult to extrapolate from these data to likely rates of dissipation in the field. Rates are likely to be slower at the lower field temperature, and the concentration of atrazine will be several orders of magnitude lower than that added to the material here.

ACKNOWLEDGMENTS

The authors wish to thank Ciba-Geigy Ltd. for financial assistance with this work, Thames Water plc for allowing the use of material, M.J. Bird and I.N. Gale (British Geological Survey) for supplying the material, and R.T. Kimblin, J. Rae and A. Parker (Postgraduate Institute for Sedimentology, University of Reading) for providing lithostratigraphic data. The views expressed here are not necessarily those of Thames Water plc.

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THE OCCURRENCE OF SYNTHETIC PYRETHROID AND SELECTED ORGANOCHLORINE PESTICIDES IN RIVER SEDIMENTS

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ABSTRACT

The concentration of the pesticides α-BHC, γ-BHC, *p,p'*-DDE, dieldrin, endrin, *p,p'*-TDE, *p,p'*-DDT, *cis* and *trans*-permethrin, cypermethrin, fenvalerate and deltamethrin have been measured in several river sediments and waters at selected sites in streams in rural areas and an industrial area. The results illustrate varying levels of contamination of the sediments. Field partition coefficients for lindane, DDE, dieldrin and permethrin are estimated.

INTRODUCTION

This research was initiated to evaluate the occurrence of selected lipophilic pesticides in river sediments as an initial phase in the study of the interaction between pesticides and particles in freshwater habitats. Published information on the concentration of pesticides in natural sediments is very limited, partly because of the analytical difficulties associated with the analysis of trace amounts of pesticides in complex matrices and the view that sediments act as an infinite sink without any obvious effects on the sediment biota. Some suspended particles and sediments effectivly scavenge pesticides from the water and so improve water quality and at the same time enhance the degradation of the pesticides in biofilms associated with natural particles. However, it is important to evaluate the ecological implications of the distribution of pesticide mixtures in sediments, particularly on benthic animals and microfauna. It is also desirable to monitor sediments to assess any problems caused by persistence in the sorbed state in particular sediment conditions.

The results presented are an attempt to examine selected river sites for a range of organochlorine and synthetic pyrethroid insecticides. The sites were chosen because of questions arising about the diversity of invertebrate fauna or where known discharges from agricultural or industrial origin occur.

EXPERIMENTAL

Materials

All the pesticides used to prepare standard solutions 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'-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% 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 *cis* and *trans* isomers of permethrin correspond to 3-phenoxybenzyl-(*1RS*)-3- (2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate stereoisomers. Cypermethrin and fenvalerate were only available as racemic mixtures which separated on glc as four and two components respectively. All solvents were pesticide research grade (BDH, Poole).

TABLE 1. Location of the river sites studied together with the organic matter content and total pesticide concentration in the sediment. Standard deviation of duplicates in brackets.

Sample code	National grid reference	Organic matter, OM, content/ % by mass	Total pesticide concentration /μg kg^{-1} (dry weight)
A	TL555701	23.3 (0.8)	2
B	TL548691	20.8 (0.6)	30
C	SY858923	1.6 (2.8)	4
D	SY858923	11.4 (2.5)	11
E	SO555478	8.2 (0.1)	123
F	SO555478	11.4 (0.2)	133
G	SO555478	9.2 (0.2)	87
H	SO822715	0.89 (0.04)	18
I	SO822715	0.71 (0.03)	19

Sample collection and preparation

The sites chosen for sampling are listed in Table 1. In brief:

Samples A and B were taken on 13.6.90 from drainage channels, Wicken Lode and Reach Lode respectively, on the River Cam in Cambridgeshire. These were selected because of differences in the invertebrate communities at the sites.

Samples C and D were taken on 20.3.90 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.

Samples E, F and G were taken on 12.7.90 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 advantages that records of the use of pesticides on the farm are available.

Samples H and I were obtained on 12.9.88 and 13.9.89, respectively, from the River Stour near Stourport in Worcestershire. This was the only site chosen in a predominantly industrial area.

Surface sediments were collected using either a stainless steel scoop or in large agglomerates using a pond net (1 mm mesh). If necessary the sediments were transferred on site through a 5 mm screen into a wide-necked glass jars with tops lined with aluminium foil. The sediments were immediately transported back to the laboratory, further sieved through 1 mm mesh brass sieve 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). Separate experiments were also performed 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 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 within 2 days after collection.

Analytical methods

The sediments were analysed using a new extraction and isolation procedure developed initially for the analysis of permethrin, but later extended to include the pesticides listed above. This involved a two-stage extraction with acetone, followed by a two-stage isolation procedure using solid-phase extraction with magnesium silicate, Florisil. The details and performance of the method have been discussed by House et al (1990). The method has been found to be suitable for the analysis of complex natural sediments but for the most accurate quantitative work does necessitate the use of recovery trials on individual sediments using different loadings of a pesticide standard mixture. This is a time consuming procedure and is not necessary in semi-quantitative applications eg screening sediments for specific compounds. The results reported here have not been adjusted for losses during analysis. Experiments with sediment I, which was spiked with a multi-pesticide standard to a concentration of 20 $\mu g\ kg^{-1}$, gave recoveries of between 67 and 97% for the synthetic pyrethroids and between 39 and 82% for the organochlorine pesticides. The lowest recoveries of 39% was obtained for *p,p'*-DDT and *p,p'*-DDE (House et al, 1990). In all the extractions a blank was determined alongside the sediment extraction and isolation. For samples H, E, F and G the blanks were prepared using a sample which had been pre-extracted with acetone and for the other samples, the blank extract was prepared following the procedure for the sediment analysis but without any sediment in the extraction phase.

The samples were analysed in the following groups : A,B; C,D; E,F,G; H; I. A blank extract was included in each group. Samples H and I were analysed in triplicate and duplicate respectively and the other samples were

analysed without replication. The limits of determination were generally : ca 0.1 $\mu g\ kg^{-1}$ for the organochlorine pesticides and 1.0 $\mu g\ kg^{-1}$ for the synthetic pyrethroid pesticides. In instances when a pesticide occurred in the blank sample, the determination limit was taken as double the concentration in the blank sample.

The one litre water samples were analysed by a two-stage hexane extraction followed by drying the extract with sodium sulphate (heated to 110°C for a minimum of four hours) and Kurdena-Danish concentration to a volume of 2 ml. Recoveries were determined by the addition of a multi-pesticide standard to a concentration in the aqueous phase of 0.2 $\mu g\ dm^{-3}$ in each pesticide. The percentage recoveries were determined as α-BHC, 86%; γ-BHC, 94%; heptachlor, 101%; aldrin, 90%; DDE, 93%; dieldrin, 103%; endrin, 160%; TDE, 100%; DDE, 119%; *cis*-permethrin, 123%; *trans*-permethrin, 107%; cypermethrin, 89% and fenvalerate, 103%. A 1 litre sample of distilled water was analysed with each batch of freshwater samples and the results showed that in general the organochlorines were either not detected or only detected in trace amounts ie < 1 ng dm^{-3}. These levels are similar to the limits observed for carry-over from injections following the calibration. Two of the pyrethroids, permethrin and cypermethrin, were detected at concentrations < 7 ng dm^{-3} in the blanks but this varied slightly between extractions and glc determinations. The determination limits were 1 ng dm^{-3} for the organochlorines and 10 ng dm^{-3} for the pyrethroids.

The glc analysis of the extracts was performed using a Perkin-Elmer 8700 instrument with split-splitless injector, an electron-capture detector, ecd, and fused silica capillary with 5 % phenyl-methyl silicone stationary phase (House et al, 1990). Peak assignments were based on the relative retention times (RRT) with respect to the internal standard, aldrin, and these were confirmed when necessary by mass-spectroscopy using a Hewlett-Packard 5971A glc with a mass-selective detector (MSD). For the assignment of peaks to specific pesticides the RRT's of the organochlorine and pyrethroid pesticides had to be within ±0.001 and ±0.002 of the corresponding calibration values respectively. The calibration was done using a multi-pesticide standard to give a nominal concentration in each pesticide of 0.05 $\mu g\ ml^{-1}$. The linearity of the ecd response was verified over a concentration range of 0.02-0.1 $\mu g\ ml^{-1}$. Prior to every sample analysis the RRT's and response factors were calibrated by an injection of the 0.05 $\mu g\ ml^{-1}$ multi-standard followed by a second injection for confirmation and then a solvent injection to measure any trace carry-over of pesticides from the injector followed by the replica samples. This sequence was repeated for each sample.

RESULTS AND DISCUSSION

Water samples

The results of the analysis are shown in Table 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.

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 determination 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 determination 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 determination. 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 colloidial content in the individual samples. It is significant that better reproducibility between samples was obtained for α-BHC and γ-BHC (Table 2) which are more soluble in water then 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.

TABLE 2. Concentration of 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
Diel'	-	-	-	-	-	*9(0.2)C	8(0.1)C	6(1)C
Endr'	-	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	-	-	-	-
total	54	24	19	19	13	620	722	355

*: pesticides also found in sediment samples

Sediment samples

The results of the analysis of samples A,B and C,D are shown in Table 3. The results for sample A indicate negligible amounts of the pesticides, with the concentration either similar to that in the blank or close to the limits of determination 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 content of the sediment (Table 1) and is not reflected in the pesticide concentrations in the associated waters at the time of sampling. An example of a chromatogram obtained for sample B is shown in Figure 1.

The concentration of pesticides in sample C and D are also low with sample D having higher levels of all the pesticides. *Cis*-permethrin, although detected in the water (Table 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 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. 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 total organic content. Both DDT and DDE decrease in concentration downstream whilst the concentration of TDE was less 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 RRT's 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, significant concentrations of dieldrin and α-BHC were also detected in some of the samples.

TABLE 3. Concentration of pesticides in the river sediments for samples A-D / $\mu g\ kg^{-1}$.† :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
Diel'	1.0	1.0C	2.0C	0.7	-	-
Endr'	0.3	-	-	-	-	-
TDE	-	-	2.0C	-	-	0.9C
DDT	-	-	-	0.2	0.6	7.6C
c-per'	1.0	-	-	-	<1	-
t-per'	0.3	-	18†	-	-	-
cyp'	-	-	2.7	-	-	-
fen'	0.3	0.6	1.0C	-	2.2	-

FIGURE 1. Example of a chromatogram obtained for sample B with ecd.

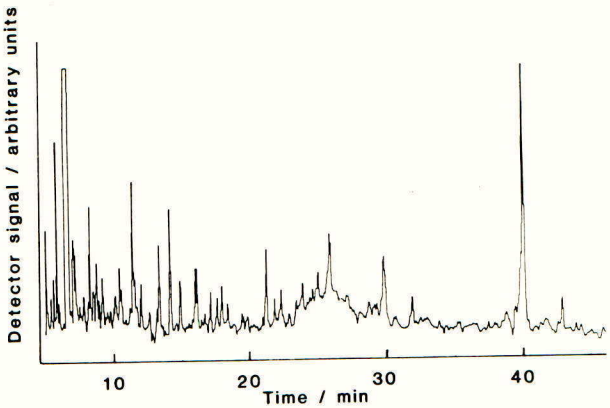

TABLE 4. Concentration of pesticides in river sediments for samples E-G /μg kg^{-1}. Values in brackets are the standard deviations of glc duplicates. Endrin, *trans*-permethrin and cypermethrin were not detected. C indicates confirmation by MSD.

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
Diel'	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-per'	0.6 (0.1)	-	-	-
fen'	-	-	3.6 (0.8)	2.6 (1.3)
del'	-	1.9 (0.4)	14.0 (0.8)	37.5 (2.0)

The results for the two samples H and I are shown in Table 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 use in the carpet manufacturing industry in the area. There 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.

The results of the water and sediment analysis can be used to calculate a Henry's law adsorption constant or field distribution coefficient, K_f, in units of $dm^3\ kg^{-1}$ ie the concentration of pesticide in the sediment ($\mu g\ kg^{-1}$ dry weight) divided by the concentration in solution ($\mu g\ dm^{-3}$). 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 content of the sediments to calculate K_{om} values where $K_{om} = 100\ K_f / OM$ with OM values given in Table 1. This has been done for those pesticides that were detected in both the water and sediment samples (see Table 2).

γ-BHC was in five of the samples and gave log K_{om} 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_{om} values are in reasonable agreement with those predicted from the Collander relationship (Briggs, 1981) :

$$\log K_{om} = 0.52 \log K_{ow} + 0.62 \quad (1)$$

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).

The results for DDE show more variation with values of log K_{om} of 5.1 and 3.1 for samples E and H respectively compared with calculated values from eq(1) 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_{om} 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 2 leads 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 (1) predicts a result of between 3.3 and 3.8 depending on the choice of 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.

TABLE 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)	-	-
Diel'	<0.2	1.0(0.2)C	-	2.0(0.3)C
c-per'	-	9.5(1.6)C	-	11.1(2.3)C
t-per'	1.0	6.8(2.2)C	1.0	4.0(0.3)C
cyp'	1.0	-	-	<1
fen'	-	-	-	1.5(0.2)

CONCLUSION

Several pesticides have been determined in different river sediments and their associated waters. In most instances the concentration of organochlorine compounds is low with the notable exception of samples E-G in which DDT and its metabolites were found. Pyrethroids have been measured in many of the sediments and some waters. These include permethrin in samples B,H and I, deltamethrin in samples E-G and *cis* permethrin in water samples A,B,C/D and H. Further work is needed to evaluate the ecological implications of particle bound pesticide mixtures and to establish criteria for the assessment of sediment contamination.

The results have also enabled a tentative estimate of field distribution coefficients for γ-BHC, DDE, dieldrin and permethrin. The findings appear to be consistent with existing information on the partition behaviour and Collander relationship.

ACKNOWLEDGEMENTS

The authors thank the Natural Environmental Research Council and the Department of the Environment, contract No.PECD/7/7/329, for supporting this work. We also thank colleagues at the Eastern Rivers Group of the Institute of Freshwater Ecology, Dr Clive Pinder and Jon Bass, and at the Institute of Hydrology, Dr Paul Whitehead and Richard Williams, for their encouragement and help in field sampling. One of us, Z. Ou, wish to thank The Royal Society for their fellowship.

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PESTICIDES IN A CHALK CATCHMENT: INPUTS AND AQUATIC RESIDUES.

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ABSTRACT

Complementary studies of land-use, agricultural pesticide application and pesticide concentrations in rain, river water and groundwater were carried out in the Granta catchment in Cambridgeshire. Cropping patterns are discussed and related to pesticide usage. The concentrations of agricultural pesticides in environmental waters are viewed in the context of the land-use within the catchment.

Certain anomalies in pesticide occurrence were identified, particularly the prevalence of the triazines in groundwaters in excess of the concentrations expected from their agricultural usage.

INTRODUCTION

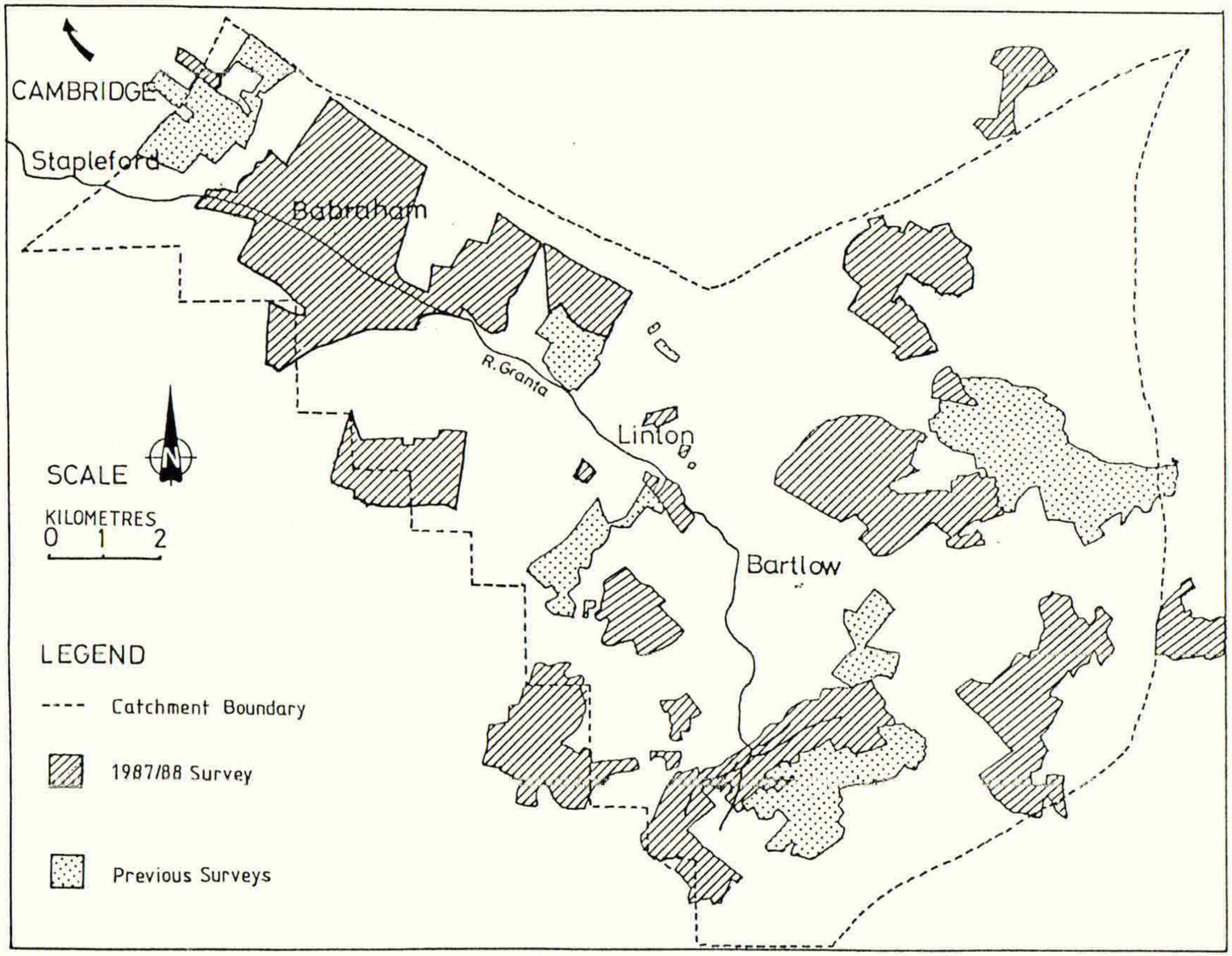
The River Granta catchment, Cambridgeshire, covers approximately 16,000 ha, with about 230 ha built up, 620 ha of woodland and 15,200ha devoted to agriculture. The agricultural land overlays both impermeable clays and permeable chalk, and farming practices within the area are considered typical for the south and east of England. The catchment also offers existing facilities for the monitoring of hydrological resources (boreholes, river flow-gauging stations, models).

Hunting Land and Environmental Ltd. (formerly Land Capability Consultants Ltd.) were commissioned by WRc to carry out a survey of pesticide use in the Granta catchment over three growing seasons (1985/86, 1986/87, 1987/88). The survey formed part of a research programme into pesticide concentrations in ground and surface water being carried out by WRc and the Anglian Water Authority. This programme has continued, after privatisation of the water industry, with funding by the National Rivers Authority.

The aim of the survey was to estimate the areas devoted to major crop types within the river catchment and the quantities of pesticides applied between the 1st September and 31st August of each growing season. Baxter (1986) estimated the mass of pesticides used in England and Wales and found that cereal-applied herbicides were predominant, because the area under cereals was much larger than that under other arable crops and cereal herbicides were applied at a rate of 10-100 times that of fungicides and insecticides. Eastern England was found to have received the highest applications of cereal-applied herbicides and fungicides. Insecticide application was also highest in this region. The present survey was designed to give a more precise, localised perspective on this pesticide use data.

Analytical methods were used to gather information on the distribution of pesticides within the aquifer and surface waters of the chalk catchment, in line with the EEC directive (EEC/80/778) on the quality of water intended for human consumption. This stipulates a maximum admissable concentration of 0.1 $\mu g\ l^{-1}$ and 0.5 $\mu g\ l^{-1}$ for an individual pesticide and the total of all pesticides present, respectively.

FIGURE 1. Map of the River Granta catchment showing the areas involved in the land-use surveys. The areas incorporated in the 1987/88 survey are indicated, along with those surveyed in the previous two seasons but not used in 1987/88.



METHODS

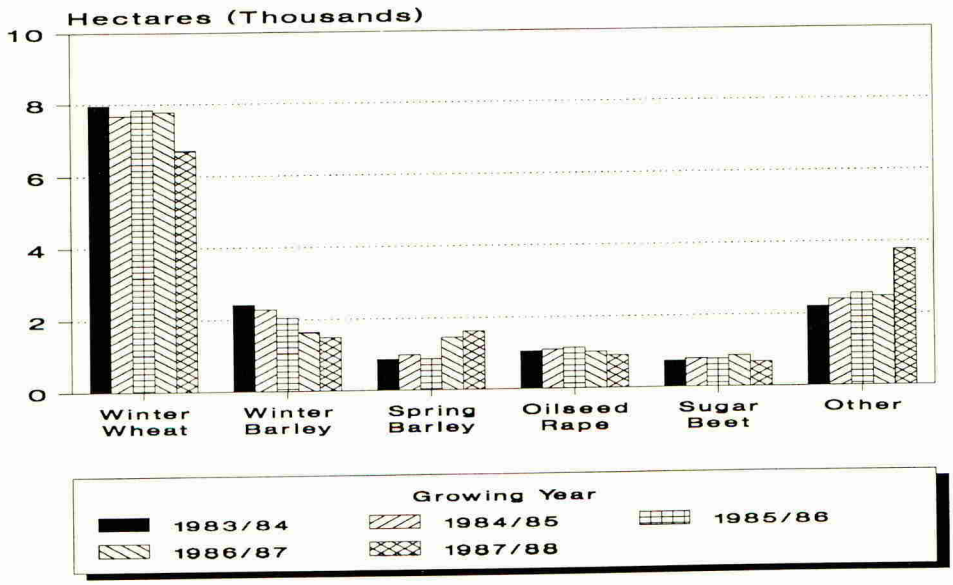
A sample of agricultural holdings within the survey area (sufficient to provide 25% of the total agricultural area within the catchment) were engaged for the 1985/86, 1986/87 and 1987/88 growing seasons. Some of these holdings crossed the catchment area boundary or were adjacent to it. Since the soils and cropping of these holdings did not differ significantly from land within the catchment, the information was considered to be valid. Figure 1 shows the land included in the surveys.

The land-use survey was carried out by questionnaires. Two basic types of information were obtained:

- The total area of the holding, the crops grown and the area under each crop during the growing season.
- The mass of active ingredient in herbicides, desiccants, growth regulators, fungicides, insecticides, nematocides, molluscicides, soil sterilants and fumigants used on each crop during the growing season. Adjuvants, surfactants, wetting agents, micronutrient feeds, elemental sulphur and sulphuric acid were not included.

For the analytical survey, water samples were obtained from rainwater collectors, three river sites, four public supply boreholes and a number of observation boreholes and analysed for 20 'target' pesticides (chosen on the basis of annual loading and trends in usage in the MAFF Eastern Region). The sampling was carried out from March 1987 onwards.

FIGURE 2. Cropping areas of the major crops in the Granta catchment from the 1983/84 to 1987/88 growing seasons.



RESULTS

Land-Use Survey

Cropping Areas

Figure 2 shows the trends in major crops over the course of the survey. Winter wheat and winter barley followed regional and national trends with a reduction in the area on which they were grown. The area of spring barley, on the other hand, increased during this period, again following regional and national patterns. Land under oilseed rape peaked in the 1985/86 season, though UK and Eastern Counties areas peaked the following year. Sugar beet was grown on similar areas each year (about 700-800 ha), reflecting widespread national stability.

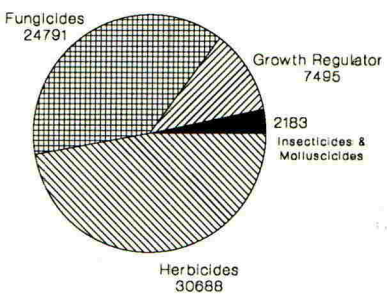
Other crops grown in the study region were spring wheat, oats, linseed, beans, peas, potatoes, mixed roots, onions, maize and grass. Some increase in the areas devoted to these crops was seen in 1987/88, after a drop the previous year. Protected crops were also surveyed, though it was estimated that only 10 ha were devoted to these crops (lettuce, celery, tomatoes, peppers and ornamentals) over the entire catchment. It should be noted, however, that the protected area under lettuce produces about five or six crops a year.

Pesticide Usage

Taking the 1987/88 growing season as an example, it is possible to view the major patterns in agricultural pesticide applications. Figure 3 shows estimated pesticide applications for the Granta catchment survey area in 1987/88, categorised into four main groups: herbicides, fungicides, growth regulators and insecticides/molluscicides. Of the 65,257 kg applied in the 1987/88 growing season, herbicides accounted for 30,688 kg, or 47%. Herbicides were mainly applied to cereals, with most of the remainder used on oilseed rape, sugar beet, beans and peas.

Approximately 38% of the pesticide loading, 24,791 kg, was in the form of fungicide, with about half of this directed at winter wheat. The remainder was applied to other cereals, oilseed rape, beans, peas and potatoes.

FIGURE 3. The estimated mass (kg) of each main pesticide group applied in the entire Granta catchment for the 1987/88 growing season.



7,495 kg of growth regulators were applied almost exclusively to cereals (onions received a small application of 30 kg).

Finally, 2,183 kg of insecticides and molluscicides were applied in the survey area, winter wheat attracting the majority with spring wheat, oilseed rape, sugar beet, beans and peas responsible for the rest.

TABLE 1. Estimated application of pesticide active ingredient in the entire Granta catchment for the 20 'target' pesticides and ten other major pesticides. The values given represent the means of three growing seasons (1985/86, 1986/87 and 1987/88). The presence of the target pesticides in rainwater, river water and groundwater is indicated (•), along with their detection limits.

Pesticides	3-Season Average kg/ha	Detected in: Rainwater	Riverwater	Groundwater	Detection Limits $\mu g\ l^{-1}$
'Target' Pesticides					
Mecoprop	0.717	•	•		0.03
Isoproturon	0.693	•	•	•	0.06
Chlorotoluron	0.209		•	•	0.13
Triallate	0.171	•	•		0.02
Captofol	0.113				0.30
Chlorothalonil	0.084	•			0.05
Bromoxynil	0.068				0.03
Ioxynil	0.066				0.06
Dimethoate	0.054	•			0.05
Simazine	0.037		•	•	0.04
Carbetamide	0.034				0.11
MCPA	0.033				0.04
Propyzamide	0.024		•		0.03
Lindane (Gamma-HCH)	0.014	•			0.03
Triademefon	0.012				0.10
Atrazine	0.004	•	•	•	0.05
Dichlorprop	0.003				0.02
MCPB	0.003				0.03
2,4-D	0.001				0.05
2,4-DB	0.001				0.04
Non-'target' Pesticides					
Maneb	0.437	-	-	-	-
Chloromequat	0.435	-	-	-	-
Carbendazim	0.184	-	-	-	-
Mancozeb	0.155	-	-	-	-
Prochloraz	0.124	-	-	-	-
Fenpropimorph	0.114	-	-	-	-
Glyphosphate	0.066	-	-	-	-
Propiconazole	0.046	-	-	-	-
Metamitron	0.038	-	-	-	-
Fenpropidin	0.035	-	-	-	-

Analytical Results

Clark *et al.* (in press) provide a detailed account of analyses carried out in the Granta catchment.

Table 1 summarises the information gathered in the land-use and analytical surveys. It is believed that the water feeding the river of relatively constant pesticide composition throughout its length. The maximum number and concentration of pesticides in the river water were detected in winter and early spring, when the river stage is high. A correlation was observed for certain pesticides (isoproturon, propyzamide and chlortoluron) between high river flow and high concentration. Filtration of water samples suggested that the greater part of the pesticide load was carried dissolved in the water.

Of the four public supply boreholes, one contained no detectable pesticides, while the others contained only atrazine and simazine at low concentrations. Similar patterns were recorded at the observation boreholes with atrazine and simazine present.

Rainwater samples were found to contain pesticides, though problems with this method did not allow their concentrations to be fully quantified.

In river water, groundwater and rainwater, individual and joint concentrations of pesticides occasionally exceed the stipulated EC directives for water quality for human consumption.

DISCUSSION

The usage of pesticides depends on seasonal weed and pest incidence, the prevailing weather and ground conditions during the season and the management system employed on each holding. The 1987/88 growing season demonstrates these factors well.

The poor spraying conditions in the wet autumn of 1987 were a factor in the 30% reduction in herbicide usage compared with the previous season. Although conditions were more favourable in the spring of 1988, those sprays missed in the autumn were not fully recovered. Herbicide applications in the spring also reflected the advanced stages of both weeds and crops, some herbicide types being favoured for this reason.

The difficult autumn made weed control in oilseed rape problematical. Desiccant use was down, possibly a result of increased windrowing to ripen the crop.

The cropping of sugar beet showed no large changes in chemical use. The increase in the area of beans was echoed in the marked increase in the use of simazine and other triazine herbicides. However, applications of the two triazines commonly found in groundwater supplies (atrazine and simazine) were only a fraction of the total mass of pesticides used in agriculture, representing about 1% of the total pesticide input during 1987/88.

The widespread practice of soil sterilization with methyl bromide for protected crops rendered the use of herbicides largely unnecessary in these areas. However, growing several crops per season in protected areas requires repeated applications of other pesticides. Thus, inputs of pesticides in protected environments may be more significant than area alone would suggest.

Growth regulators, used only on cereals and onions, have shown an increase in use on spring crops. Over the three years of the survey, the use of growth regulators has risen steadily, up 16% over the period.

The damp conditions of the summer of 1988 encouraged the incidence of disease, whilst reducing the number of fungicide spraying opportunities. Most fungicide was applied to winter wheat to combat mildews, rusts and *Septoria.* Fungicide use was also high in protected crop areas (with as many as 26 applications of fungicide within a season). Blight in potatoes was also a problem.

Substantial quantities of organophosphates were widely applied to combat wheat bulb fly. Synthetic pyrethroids were used increasingly to control pest species.

The land-use survey only covered pesticides applied for agriculture and horticulture, where uniform application of pesticides on field crops at recommended rates of application provides opportunity for adsorption and breakdown. There is no information here regarding applications at high concentrations to point sources, which could arise from spillage or incorrect disposal. Industrial, municipal and domestic uses were also outside the scope of this survey, though it is evident that many such practices utilise high concentrations of pesticides which may be applied to hard surfaces which shed water directly into drainage systems.

The findings from the surface water samples, showing peak concentrations during heavy rain preceeding flood, may be due to rapid transport of pesticides from hard surfaces or areas adjacent to the river. The presence of major agricultural pesticides during river flood are believed to represent inputs from less rapid transport paths, via field drains in agricultural areas. The proportion of pesticides leaving the catchment in river water has been calculated at less than 0.1% annually.

Analyses of water from public supply boreholes showed the presence of only simazine and/or atrazine, which are only minor agricultural pesticides in the Granta catchment. There was no sign of major agricultural pesticides and the two most rural boreholes showed least contamination with the triazines. Non-agricultural sources of contamination must be suspected for the presence of some pesticide residues in public supply boreholes.

Almost all the observation boreholes contained only atrazine and simazine. These two triazines appear to be dominant pesticides in groundwater.

CONCLUSIONS

It is clear from this study that the inputs of pesticides do not match concurrent outputs detected in the water. There are four possible explanations for this:

- Historical land-use and pesticide usage patterns may be showing up in the water samples today. A time lag of several years between surface application and appearance in the groundwater is possible. It is suggested that 20-30 years of usage data is required.
- Spatial and temporal variation in pesticide concentrations in groundwater is almost unknown.
- Pesticide data from the unsaturated zone of the aquifer is not available. This is the place where most pesticide attenuation will take place.
- Pesticides in water samples may be of non-agricultural origin.

ACKNOWLEDGEMENT

The authors would like to express their gratitude to the farmers who took part in the surveys. The work was undertaken in co-operation with the Anglian Water Authority and has continued with funding by the National Rivers Authority. The technical and financial contributions of these organisations are acknowledged and the NRA thanked for their permission to publish this paper.

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6.
Residues in Water: Occurrence and Risk

Session Organiser and Chairman:
MR DAVID ARNOLD

PESTICIDES IN GROUNDWATER: SOME PRELIMINARY OBSERVATIONS ON BEHAVIOUR AND TRANSPORT

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ABSTRACT

Over the past 10-15 years, considerable attention has been given to the leaching of nitrate from agricultural soils to the underlying groundwater. More recently, concern has been growing at the possibility of contamination of groundwater supplies by pesticides. Pesticide usage has increased considerably since the 1960s and 1970s, most rapidly in the case of herbicides and fungicides applied to winter-sown cereals. There has also been increasing non-agricultural use of triazine compounds for general defoliation.

All pesticide compounds potentially pose an environmental health hazard as they are chemically-tailored to be toxic. The stringent EC directive maximum admissable concentration of 0.1 µg/l has been exceeded in some British water supply boreholes, although concentrations above 1.0 µg/l have very rarely been recorded. The compounds most frequently detected are the herbicides atrazine, simazine, mecoprop and isoproturon. The first of these, together with soil insecticides of the carbamate and chloropropane groups, have been detected at concentrations exceeding 1 µg/l in shallow aquifers elsewhere in Europe and in the USA.

Groundwater systems are generally characterised by relatively slow rates of groundwater flow. The response time of deep water supply boreholes to surface inputs of pollutants is of the order of decades, as has been clearly demonstrated by the study of nitrate pollution of groundwater from agricultural practices. This slow response means that pesticide determinations on pumped samples from such boreholes provide an inadequate indication of water quality in the groundwater system as a whole. To properly evaluate the current situation, data are needed on the three-dimensional subsurface distribution of pesticides, especially in the unsaturated zone of aquifers.

A preliminary assessment of the probable transport of pesticides in groundwater systems has been made, based on the physicochemical properties of the pesticides themselves and on knowledge of groundwater flow and pollutant transport in British aquifers gained from previous research. The aim of this assessment is primarily to guide field investigations which are just commencing, by addressing three fundamental questions:

(a) Which pesticide compounds are most likely to be transported to groundwater?

(b) What are the most probable transport routes?

(c) Are pesticide concentrations currently detected in supply boreholes likely to be approaching equilibrium?

Factors affecting the leaching of pesticides from the soil include rates and methods of application, water solubility, mobility in soil solution and degradability. Mobility can be expressed as the partition coefficient for the compound with respect to organic carbon, and degradability by the soil half-life. Information on both of these can be obtained from the literature for many compounds, but are generally related to a fertile, organic, clayey soil. Mobility and persistence may be much greater beneath the soil in aquifer materials, which contain a much smaller proportion of clay minerals and organic matter and reduced populations of indigenous bacteria.

Retardation factors have been estimated for a range of pesticide compounds and for the three principal British aquifers, making a number of simplifying assumptions which are explained. This approach is considered to provide an indication of the likely maximum retardation of pesticides in the unsaturated zone with respect to a mobile, conservative, non-reactive solute.

Transport of such a solute through the unsaturated matrix of British aquifers is known to occur at rates of 0.5 to 1.5 m/a. Thus, since most compounds have been in general use for less than 10 to 20 years, most pesticides leached from agricultural soils would be expected to be still in the unsaturated zone, except in areas of shallow water table. However, because of the consolidated and fractured nature of the principal British aquifers, their hydraulic characteristics imply a high probability of preferential flow in macropores or fissures, bypassing the matrix. Preferential flow is difficult to prove and to quantify but, if present, would permit more rapid pollutant transport and less opportunity for retardation by adsorption, chemical reaction and degradation.

Sampling of preferential flow presents major difficulties. The investigation of pesticides in the unsaturated zone presents additional sampling and analytical problems because of the wide range of compounds in common agricultural use, the difficulty of obtaining adequate sample volumes to reach the analytical detection limits implied by the EC directive, and the care required to avoid sample modification or loss.

PESTICIDE RESIDUES IN WATER - IMAGINARY THREAT OR IMMINENT DISASTER

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INTRODUCTION

Many man-made chemicals can be found as environmental contaminants but few generate as much controversy and public fear as pesticides. They are considered to be a special case because they are deliberately introduced into the environment and they are, by their very nature, intended to kill or injure some form of life.

In an ideal world pesticides would be wholly specific for the target species. Unfortunately this is not yet the case and the majority of pesticides are capable of affecting a wide range of non-target species. In fact much of the public fear of pesticides and their environmental residues derives from the discovery in the 1960s that persistent organochlorine insecticides such as DDT and more particularly the "drins" were causing damage to non-target species such as birds of prey. These compounds are highly bioaccumulated in the fatty tissues with consequent magnification of environmental concentrations through the food chain. In addition, they were found in significant quantities in humans and, particularly emotive, in breast milk.

They have been largely replaced by less persistent compounds which are more short-lived in the environment but there are many more different pesticides in use. Public understanding has not been enhanced by an almost obsessive secrecy with regard to safety and environmental data on the part of some manufacturers and a past unwillingness for the authorities to adequately investigate pesticide incidents involving the general public.

Public perception of drinking water is a special case and there is considerable concern about the "contamination" of drinking water by chemicals resulting from man's activities. When those contaminants are pesticides, no matter how small the concentrations, the public response is often exaggerated. This situation has been made more difficult by the rapid improvement in the sensitivity and specificity of analytical techniques which make it possible to identify and quantify tiny amounts of a wide range of pesticides in natural and drinking waters. However, the major cause of this concern is the European wide standard of 0.1 $\mu g\ l^{-1}$ for any pesticide in drinking water.

HOW DO PESTICIDES REACH WATER

Pesticides can reach the aquatic environment in three main ways. Firstly, spills in which large quantities of pesticide, sometimes in very high concentrations, enter surface water causing a major incident. Secondly, contamination which refers to acute problems caused by the careless use of pesticides such as overspraying water courses or drainage ditches, direct run-off from sprayed and treated areas and careless disposal of empty container or washings from equipment. Levels of pesticides in the immediate

receiving waters can be quite high, but are generally attenuated by dilution. Problems in both of these categories are avoidable by careful use of pesticides.

The third route into water, both surface and groundwater, is by leaching which can be considered to be the washout of pesticides and their degradation products over a long period of time. The levels of pesticides contributed by leaching are generally low but they can be sufficient, in certain circumstances, to concentrations in derived drinking water which exceed the statutory limits.

With the improvements in analytical techniques increasing numbers of pesticides have been found in water.

Triazine herbicides, in particular atrazine, have been widely found in ground, surface and drinking waters. It is thought that the majority of the input of triazines is derived from non-agricultural use such as weed control by railway and local authorities.

The chlorophenoxy acid herbicides, such as MCPA, mecoprop and dicamba have also been found in many surface, ground and drinking waters and isoproturon has been found in many surface waters.

Surface waters usually contain the greatest diversity of pesticides and in addition to herbicides, fungicides such as carbendazim and insecticides such as cypermethrin have been detected. Following storm wash-off "events" then the number of pesticides reaching surface water in a significant concentration is greater.

The concentrations of individual pesticides typically found in water samples are very low and rarely exceed ten parts per billion on a regular basis. Levels in drinking and groundwater are generally lower than those in untreated surface waters. It must be emphasised that conventional drinking water treatment is poor at removing many pesticides, particularly the more water soluble herbicides, since it was not specifically designed for this purpose.

Although the concentrations found are generally very low they are high enough in certain instances to exceed drinking water standards.

TOXICOLOGICAL CONSIDERATIONS

Toxicity is the intrinsic capacity of a chemical to cause injury. Hazard is the capacity of that chemical to cause injury under the circumstances of exposure. It must be remembered that the presence of a toxic substance in the environment does not necessarily constitute a hazard. Toxicity is dependent on both the magnitude of the dose and the duration of the period of exposure so if the dose is sufficiently small and/or the period of exposure is sufficiently short, then no injury will result.

MAMMALIAN TOXICITY

Pesticides found in drinking water are unlikely to be present in sufficient concentration to cause acute toxicity. The exception to this

would be in the case of a chemical spill where a large quantity of a compound enters water, usually surface water, over a short period of time, for example the Sandoz disaster on the river Rhine. The major concern with pesticides as contaminants in water is exposure to low concentrations for long periods of time. The worst case is probably contamination of groundwater since many compounds once they have reached groundwater are unlikely to degrade at a significant rate and will therefore, without treatment, be present continuously in derived drinking water. Supplies derived from surface waters, in particular rivers, will show a somewhat different pattern of contamination. As a consequence of seasonal use in agriculture there will usually be greater variation in the concentration of pesticides present and exposure to a particular pesticide is likely to be intermittent.

Therefore, the potential for chronic toxicity will be of most importance to man, but pesticides vary widely in both chemical structure and toxicity. This is reflected in the acceptable Daily Intakes for pesticides in food calculated by the joint World Health Organization/UN Food and Agriculture Organization (WHO/FAO) expert committees who are drawn from all over the world. These are the quantities which are considered to be sufficiently low to cause no ill effects in individuals exposed to them over long periods of time, and vary by several orders of magnitude. For example, the ADI for the insecticide chlordimeform is 0.0001 mg/kg bodyweight and that for the herbicide glyphosate is 0.3 mg/kg bodyweight. In general the pesticides most toxic to man, and therefore with the lowest ADIs, are to be found among the insecticides while the least toxic are to be found among the herbicides which consequently have higher ADIs.

The diversity of chemical types among pesticides and their widely varying toxicity precludes generalisations about what concentrations in drinking water would pose a hazard to health. The determination of such a level can only be established by evaluating the toxicity of individual compounds, or particular mixtures of compounds if that is what is present.

TOXICITY TO AQUATIC LIFE

In discussing the impact of pesticides in water it is inappropriate not to consider the effect on aquatic life. The major problem in this case is that many of the species are closely related to insects and some are indeed insects which will be particularly susceptible to the insecticides so that compounds such as the pyrethroids which are of very low toxicity to mammals can have a devastating impact on the aquatic environment under the right circumstances. However, there are also many pesticides which will have no effect whatsoever on the aquatic biota until relatively massive concentrations, usually only achieved in a spill, are reached.

STANDARDS FOR PESTICIDES IN DRINKING WATER

The standard for pesticides in drinking water in the EEC, which is also incorporated in UK law, is 0.1 $\mu g\ l^{-1}$ for individual pesticides and 0.5 $\mu g\ l^{-1}$ for total pesticides. This is not a figure based on protection of public health, but a political statement that pesticides should not be present in drinking water and reflects the detection limit for organochlorines at the time this parameter was proposed. It is difficult to

argue with the view that pesticides in drinking water are undesirable but there are a number of practical problems which arise as a consequence of a very stringent standard. The most important of these is what to do when the standard is exceeded. Clearly the first priority is protection of public health and some guidance can be found in the guideline values for individual pesticides in drinking water published by the World Health Organization. These guidelines which are based on toxicological data and intended to give protection over a lifetime of exposure, are currently under revision and the list of compounds will be extended.

Assuming there is no risk to public health then the decisions are whether to treat the drinking water, which can be very costly, and/or to control contamination at source, which will necessitate changes in farming practice in particular areas.

DISCUSSION

Pesticides, particularly some herbicides, are found in drinking water and drinking water sources as a consequence of agricultural and non-agricultural uses which are quite legitimate and do not breach present good practice. However, pesticides have a bad public image and their presence in drinking water, even in very small quantities, is considered to be unnecessary and undesirable. They are pollutants which are present as a consequence of activities which are of no benefit to water supply.

To pretend there is any great hazard to health at the concentrations found or to imply that any concentrations in excess of the 0.1 $\mu g\ l^{-1}$ standard for drinking water will cause damage to health is irresponsible and dishonest.

Perhaps the compromise is to maintain the current standard for drinking water but to allow the fall back position that if pesticides are found in drinking water, providing there is no threat to health, supply may continue with suitable monitoring while action is taken to prevent the contamination at source. Such a compromise will be the most cost effective way of dealing with such problems, accepting the consumer's right to have drinking water free from pesticide pollution.

However, it can only work if the manufacturers and users are prepared to play their role in seeking ways to reduce contamination and the media and pressure groups are prepared not to claim disaster at the first sign of a drinking water containing a pesticide above the present standard.

The alternative is a destructive conflict which will result in damage to all sides and be of no benefit whatsoever to the consumer.

PESTICIDES IN WATER - AN ENVIRONMENTALIST'S PERSPECTIVE

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Environmental pressure groups have always taken a special interest in pesticides. The intrinsic toxicity of pesticides and their wide and deliberate dissemination in the environment has meant that they have proved a fertile ground for debate between environmentalists and industry for decades.

This protracted debate has often been heated and already some of the early participants, such as Rachel Carson, have become minor legends within certain sections of society, although probably less venerated elsewhere. It has also been a healthy debate since there does appear to have been progress - no one believes that environmental campaigners want to return society to the stone age any more than people believe that the agrochemical industry is cynically setting out to poison the globe.

However, progress is one thing, consensus is another. Despite the intensive and wide-ranging debate there are still a number of questions that we must address over the fate of pesticides in the environment, questions that the public have a right to ask and manufacturers and users have a moral duty to answer.

Such questions focus on the level of contamination in the environment and the harm that may be associated with such pollution. The public also want to know just how good our methods are for detecting pesticides and whether the legal limits we set on the levels of contamination are satisfactory. The public also want to know who pays for the mess if things go wrong.

These questions, at least to the layman, appear straightforward but of course nothing in life is as simple as it seems. If we examine the data generated by an experimental farm belonging to the Ministry of Agriculture, Fisheries and Food we see that the results of routine monitoring for pesticides entering an adjacent stream was in the region of 0.1-0.3 ug/l, . However, if we examine the results during rain storms we see that these levels rise to over five hundred times these values. Given these findings, can we be sure that our present monitoring strategy is actually giving us the whole picture?.

If we examine a river in the West Midlands we see a variety of different moth-proofing agents present in the water with the Environmental Quality Standards (EQSs) frequently breached. However, the monitoring equipment used by the regulatory agency for one of the target pesticides has a limit of detection many times higher than the EQS. Are we really serious about enforcing such limits?

It is often said that pesticide contamination of rivers usually occurs at very low levels but it is a fact that pesticides account for 25% of fish kills in the Anglian National Rivers Authority Region. Are we using and storing pesticides in a way that respects their toxicity and what can manufacturers and users do to improve the situation?

Fish in a river in Cornwall are contaminated by a persistent pesticide which has now been withdrawn. The manufacturer of the pesticide does not believe that it has a responsibility to clean up the source of contamination even though the product was used by farmers according to label instructions. Will the taxpayer pick up the bill?

These concerns are not without context. Low level contamination of pesticides is now widespread and it would be a mistake to imagine that concern over this state of affairs is simply this years fad for the obsessively health-concious. The public will reasonably ask why it is that we find ourselves in this situation and what benefits were derived from the use of herbicides that now end up in our drinking water. They will also ask, quite reasonably, how we can be sure that the situation will not deteriorate and what Government and industry will do to arrest the situation.

The challenge to industry is to answer these questions in a way that the public will both understand and find convincing.

7.
Posters

HERBICIDES MOVEMENT AND PERSISTENCE IN SOIL: COMPARISON BETWEEN EXPERIMENTAL DATA AND PREDICTIONS OF A MATHEMATICAL MODEL.

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ABSTRACT

To predict the mobility and persistence of maize herbicides such as atrazine, butylate and alachlor, a field test was carried out on a silty soil of the Po Valley (Italy). The decrease of herbicide concentration in the soil was studied for about 120 days at three different soil depths: 0-10, 20-30 and 45-60 cm. Results were compared with outputs of the LEACHM forecasting program. The three herbicides behaved differently in the soil. Their half-life times were 17, 14 and 12 days in the 0-10 cm soil layer and 18, 18.5 and 38 days in the 20-30 cm layer for atrazine, alachlor and butylate, respectively. The forecasting model predictions were in reasonable agreement with the field data, mainly for the top soil.

INTRODUCTION

Butylate, atrazine and alachlor are herbicides used for maize cultivation. In Italy the use of butylate has increased lately because of its effectiveness to control grass weeds such as *Sorghum halepense* Pers.. The opposite happened for atrazine; in fact its use was forbidden by the Government after it was found in groundwater. Alachlor is still widely used in maize, especially in association with triazines, although its use is somewhat limited by the Italian law.

There are few data about the fate of these herbicides under field conditions in Italy. The aim of this work was to verify the mobility and persistence in soil. The work was carried out in a Po valley area on silty-loam soil and the data obtained were compared with predictions from the LEACHM model (Wagenet and Hutson, 1989).

MATERIALS AND METHODS

Field studies

On 25 April 1988 at Lardera (Milano) 6 plots of 10x25 m were delimited along both the field length and the tillage direction. Soil characteristics for each plot are shown in Table 1.

Three plots were treated with alachlor and atrazine, and the other three plots with butylate. Herbicides were used as commercial formulations: butylate as Sutar 85 E, 85.5% active ingredient (a.i.), alachlor as Lasso, 43.2% a.i. and atrazine as Maizina L, 44.5% a.i.. Butylate was applied at 6.43 kg a.i. ha^{-1}, atrazine at 1.02 kg a.i. ha^{-1} and alachlor at 2.83 kg a.i. ha^{-1}.

TABLE 1. Soil characteristics

Depth (cm)	Sand (%)	Clay (%)	Silt (%)	O.M. (%)	pH
0-30	20	18	62	3.1	5.8
30-50	14	24.5	61.5	1.2	6.5

All treatments were made with a tractor mounted sprayer calibrated to give 400 L/ha of water. Butylate was sprayed before seeding on 26.04.88 and immediately incorporated into soil by disk harrowing. Atrazine and alachlor were sprayed pre-emergence on 28.04.88. It did not rain for 24 hours after treatments. The cumulative rainfall at the end of the experiment (30.10.88) was 420 mm.

Soil samples were taken at different times (Table 3) using a 5 cm diameter motor-driven core sampler. Seven cores per plot were taken; each core was cut in three segments (0-10 cm, 20-30 cm and 45-60 cm) and soil samples were mixed, sieved to 5 mm and frozen at -20 °C until required. Moisture contents of the samples were determined before analysis.

Sample preparation and analysis

After extraction with acetone, the herbicide residues were measured by gas chromatography following the Ambrus procedure (Ambrus et al., 1981), as modified in our laboratory.

Sample extraction

Add 50 ml acetone containing 2 ml 2 N ammonium acetate and 40 g of soil into a glass jar and shake for 30 minutes. Filter extract through Buchner funnel. Add other 50 ml acetone and shake. Filter extract through Buchner funnel and rinse jar and residual soil with 30 ml acetone. Combine acetone solutions. Transfer extract and rinses to 0.5 l separatory funnel. Add 200 ml water containing 4 % sodium sulphate. Extract with 200, 50, and 50 ml portions of dichloromethane and filter extracts through column with 30 g sodium sulphate. Rinse column with 20 ml methylene chloride. Reduce volume of combined dichloromethane extracts to about 2 ml in a vacuum rotary evaporator at 30 °C. Add 10 ml acetone and evaporate to 2-3 ml; repeat this step twice. Transfer concentrate with Pasteur pipette to conical glass test tube, rinse flask with two 2 ml portions of acetone, evaporate excess solvent, and adjust final volume to 2 ml. Remove exactly 1 ml for direct GLC determination.

Gas chromatography

A Dani model 3800 gas chromatograph, equipped with an NPD detector and a PTV injector, was used with autosampler set to inject 2 µl. A Supelco (cat. N° 2-5322) Sup-Herb *wide bore* capillary column, 15 m x 0.53 mm ID 0.5 µm film, was used with the following temperature programmes:

a) for atrazine and alachlor:
60 °C for 1 min, then to 280 °C at 16 °C/min and hold 2 min.
b) for butylate:
65 °C for 1 min, then to 250 °C at 16 °C/min and hold 4 min.

Carrier gas: helium, flow rate 5 ml/min. Detection limits: alachlor 0.05 ng, atrazine 0.04 ng and butylate 0.3 ng. Recoveries of herbicides were determined by the extraction of untreated soil fortified at 50 and 200 µg/kg. Mean recoveries of alachor were 95%, of atrazine 98% and of butylate 90%.

Kinetics studies

Approximate values of the apparent first-order rate constants (K) were derived from the best fit of logarithm of residue concentration against time, under the assumption that first-order kinetics would apply. At the bottom layer, residue concentrations are near the detection limit and the rate was not calculated. After 100 days, residue levels were very low and processes other than degradation did prevail; the data were excluded from the calculations.

Rate constants calculated from top soil (0-10 cm) and from middle layer (20-30 cm) data are similar for atrazine and for alachlor (Table 4). Half-lives (HL) have been calculated from the apparent rate constants (Table 4). The calculated half-lives understimate true (i.e. degradation dependent) half-lives.

TABLE 2. Model inputs

Pesticides properties

	Application (kg/ha)	Solubility (mg/L)	Vapor Density (mg/dm3)	Koc (L/kg)	K * (day^{-1})
alachlor	2.83	242	3.1E-06	190	0.0433
atrazine	1.02	30	7.5E-06	160	0.0108°
butylate	6.43	46	1.5E-04	540	0.0433

*degradation rate decreasing below 30 cm following Jury (Jury et al., 1987)
°or 0.0414 (see text).

Profile details
Depth 110 cm, thickness of each segment 10 cm
Free-draining profile with unit hydraulic gradient at the lowest node.
Molecular diffusion coefficient (mm^2/d): 6.7
Diffusion coefficient (mm^2/d): 6.7×10^5

Crop data: maize
Wilting point: -1500 kPa; min water potential: -3000 kPa
Plant and root growing.
Plant uptake option activated for atrazine only

Soil properties
Bulk soil density (kg/dm^3): 1.5
Satured hydraulic conductivity (mm/d): 276

The model

The model used to predict herbicide redistribution in soil was LEACHM of Wagenet, version 2 (Wagenet and Hutson, 1989). The model inputs are shown

in Table 2. Rate constants were selected from literature data (Del Re *et al.*, 1990). For atrazine only, predictions were compared with predictions made using the apparent value calculated from the measured data.

RESULTS AND DISCUSSION

Field experiments

Experimental residues are shown in Table 3. Atrazine was slightly more persistent in the top soil than alachlor, with half-lifes of 17 and 14 days, respectively; in the middle layer their persistence was nearly the same. Butylate half-life was 12 days in the top soil and 38 days in the middle layer. It may appear to be more persistent because the data were near the detection limit.

As reported in previous studies, persistence data from this experiment for the various chemicals seem representative of values reported for similar soil and climatic condition. The mobility ranking for the pesticides were atrazine ≥ alachlor > butylate.

TABLE 3. Residues of alachlor, atrazine and butylate. Mean (and standard deviation) of three observations

Days from	---alachlor (mg/kg)---			---atrazine (mg/kg)---			-----butylate (mg/kg)---		
treatment*	0-10	20-30	45-60	0-10	20-30	45-60	0-10	20-30	45-60
-20,-21	0.008 (0.003)	0.002 (0.002)	ND	0.003 (0.000)	0.002 (0.000)	0.001 (0.000)	0.002 (0.001)	0.002 (0.001)	ND
2,1	2.572 (0.635)	0.423 (0.132)	0.113 (0.45)	0.965 (0.362)	0.164 (0.035)	0.041 (0.038)	1.618 (0.482)	0.038 (0.024)	0.046 (0.022)
8,10	1.126 (0.479)	0.191 (0.128)	0.074 (0.053)	0.318 (0.072)	0.056 (0.042)	0.029 (0.020)	2.38 (0.005)	0.025 (0.005)	0.029 (0.018)
29,31	0.591 (0.04)	0.129 (0.062)	0.039 (0.009)	0.304 (0.047)	0.050 (0.012)	0.025 (0.003)	1.393 (0.345)	0.074 (0.006)	ND
71,73	0.108 (0.026)	0.041 (0.008)	ND	0.082 (0.011)	0.044 (0.013)	0.005 (0.002)	0.333 (0.007)	0.009 (0.005)	ND
97,99	0.011 (0.004)	0.005 (0.001)	ND	0.008 (0.001)	0.003 (0.000)	ND	0.013 (0.003)	ND	ND
194,196	0.011 (0.000)	ND	ND	0.010 (0.002)	0.003 (0.000)	ND	0.011 (0.003)	ND	ND

* first figure: atrazine and alachlor, second one: butylate.
§ ND not detectable. Detection limits: 0.002 mg/kg for atrazine, 0.002 mg/kg for alachlor, and 0.007 mg/kg for butylate.

Prediction of persistence and mobility

Simulation outputs are shown in Figures 1 and 2 and are in good agreement with experimental data for all herbicides in the 0-10 cm layer, in accordance with other findings (Priesack, 1990; Teutsch et al., 1990). Simulated

Figure 1 Predicted and observed residues of alachlor, atrazine, and butylate in the t op soil layer. Boxes with error bar: experimental data, dotted line: simulation data. Thick line (atrazine): simulation with degradation rate costant 0.0108 days^{-1}

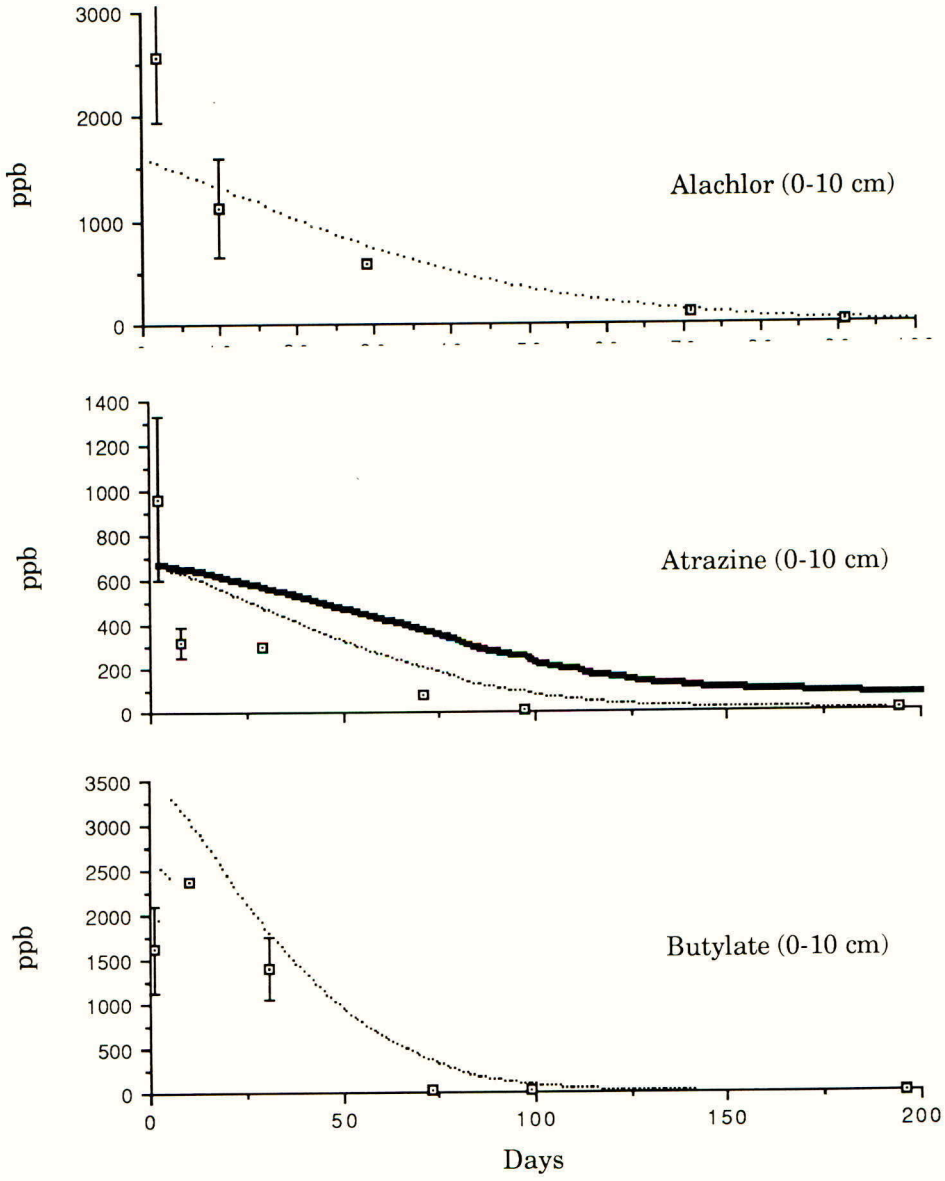
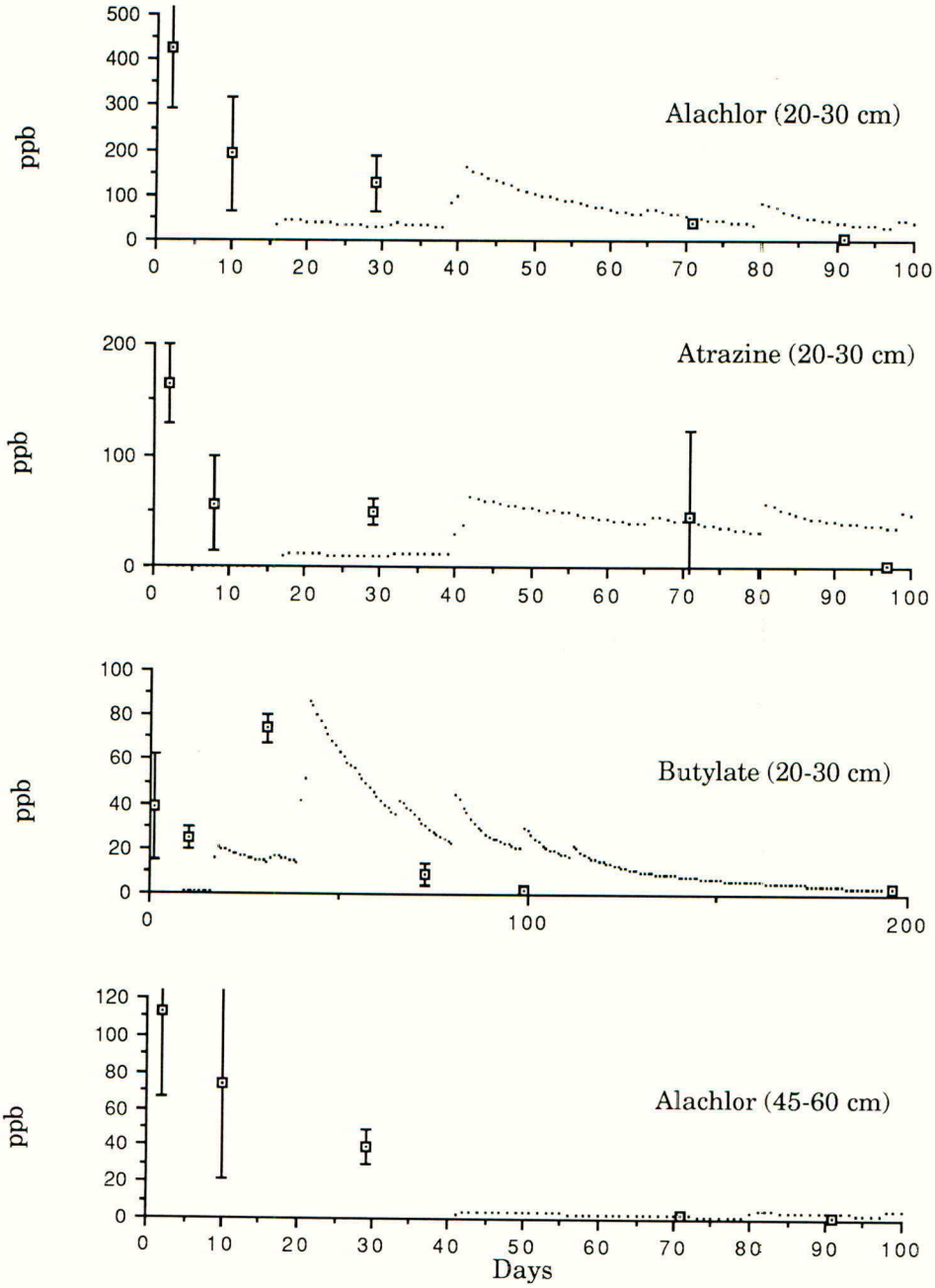


Figure 2 Predicted and observed residues of alachlor, atrazine, and butylate in the 20-30 layer and in the 45-60 one (alachlor only). Boxes with error bar: experimental data, dotted line: simulation data.



data confirm the somewhat unexpect trend of butylate levels in the top soil.

For deeper layers (Figure 2) the variability of field data due to soil and sampling variability, together with low residue levels near detection limits, hinders any significant comparison between measured and simulated data. Trends are in qualitative agreement for long times; predictions for the initial weeks were not accurate.

TABLE 4. Degradation rate constants (K), correlation coefficients (r), and half-lives (HL) of alachlor, atrazine and butylate in soil.

Active ingredient	Depth (cm)	r	K (day^{-1})	HL (days)
alachlor	0-10	0.97	0.0509	14
	20-30	0.94	0.0388	18
atrazine	0-10	0.95	0.0414	17
	20-30	0.91	0.0375	18_5
butylate	0-10	0.97	0.0583	12
	20-30	0.72	0.0182	38

Clearly the rate constant obtained from the literature for atrazine is not suitable for the soil of the tested field. A better fit was obtained by using the apparent rate calculated from the data of this same experiment.

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PHOTOCHEMICAL STUDIES ON PESTICIDES

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ABSTRACT

Some examples of u.v. photochemical studies on pesticides (fluazifop-methyl, quinalphos and acifluorfen) involving several types of reaction pathways are reported. The effect of the medium on the course of the photodegradation reactions and the methods used to investigate the respective mechanisms are described.

INTRODUCTION

Photolysis is an important transformation process for pesticides in the environment. In order to undergo photoreaction, a compound has to absorb light either directly or indirectly. Since the ozone layer in the upper atmosphere removes practically all the sun's emitted radiation below 290 nm, compounds which have no ultraviolet absorption above 290 nm should not undergo photochemical breakdown. However, photosensitisers present naturally or, for instance, added into the formulation can transfer them the necessary energy. Therefore the photochemistry of xenobiotic compounds induced by sunlight has rapidly become an integrated part of studies on the environmental transformation of pollutants. Such studies have often been criticized since most of them were performed on laboratory model systems. On the other hand, the identification of the photoproducts and the determination of the degradation rates by laboratory methods serve as guidelines for environmental testing (Choudry & Webster, 1985).

Following our interest in the environmental fate of pesticides (Frigerio et al., 1987; Pusino et al., 1989; Pusino & Gessa, 1990), we report here some examples of our photochemical studies on model systems together with reaction rate determination and photoproduct identification.

EXPERIMENTAL METHODS

Chemicals

Fluazifop-methyl, quinalphos and acifluorfen were supplied by ICI Solplant, Sandoz and Rhone-Poulenc, respectively, as active ingredients with pure grade. They were purified further by column chromatography.

Analytical methods

Fluazifop-methyl and its photoproduct were analysed by glc using a Perkin-Elmer 3920 B chromatograph, equipped with a stainless column (2 m x 3.2 mm) containing 3% SE 30 on Chromosorb W (80-100 mesh) and a flame ionization detector. The temperature was programmed from 230 to 280°C at 8°C min^{-1}; the carrier gas was nitrogen at a flow-rate of 30 ml min^{-1}.

Quinalphos, acifluorfen and their photoproducts were analysed by hplc. A Waters 501 liquid chromatograph equipped with a 123 x 4 mm i.d. Lichrosorb RP 18, a 5 μm analytical column, a Waters 440 u.v. detector operating at 254 nm and a Waters 740 data modulus were used. The mobile phase (1 ml min^{-1}) was composed of methanol + water (10 + 30 by volume) in the case of quinalphos, and acetonitrile + water (70 + 30 by volume, pH 3.0) in the other cases. The photoproducts were identified by either comparison with authentic samples or spectroscopic (pmr, i.r. and u.v.) and m.s. analysis.

Melting points were determined with a digital Buchi apparatus. Microanalyses were obtained with a Perkin-Elmer 240 B elemental analyzer. I.r. spectra were recorded on potassium bromide pellets with a Perkin-Elmer 683 spectrophotometer. Pmr spectra were recorded a Bruker Wp 200 SY spectrometer in deuteriochloroform using tetramethylsilane as internal standard. Mass spectra were obtained using a VG-ZAB HF mass spectrometer. The samples were introduced via the direct inlet probe (source temperature: 200°C, ionization voltage 70 eV). Tlc was performed on Merck silica gel F_{254} plates. Column chromatography was conducted using silica gel (70-230 mesh) and glass chromatographic columns.

Photochemical procedures

The photoreactivity of pesticides was studied using a merry-go-round Rayonet reactor equipped with a battery of 12 (low-pressure, medium-pressure, or phosphor-coated) lamps. The appropriate battery of lamps was selected by taking into account the need of overlap between the emissiom and absorption spectra of the lamps and irradiated compound, respectively. Water-cooled vessels (of borosilicate for sunlight and quartz for u.v. light) were used for laboratory photolysis studies.

PHOTOTRANSFORMATION

Fluazifop-butyl

Fluazifop-butyl, butyl (RS)-2- 4-(5-trifluoromethyl-2-pyridyloxy)-phenoxy propionate (**Ia**), irradiated at 254 nm as a thin film on glass, was photo-rearranged to the isomeric compound **IIa**, butyl (RS)-2- 4-hydroxy-3-(5-trifluoromethyl-2-pyridyl)-phenoxy propionate. The photo-product was identified by spectroscopic data. About 49% of the pesticide was transformed after 11 days. The reaction followed first-order kinetics, with $k = 2.41 \times 10^{-3}$ and $t_{1/2} = 287$ h, as deduced from the linear semi-logarithmic plot of concentration versus time.

A mechanism that accounts for the formation of the isomer **IIa** is presented in Figure 1. Upon absorption of light, the ether molecule **Ia** dissociates into a pair of radicals. These two radicals remain in close proximity to each other for a time long enough to permit a large number of collisions between them. These conditions can lead either to a reversal of the dissociation reaction (reaction 2) or to the addition of the pyridyl radical to one of the ortho positions of the phenoxy radical (reaction 3). The latter mechanism results in the formation of an intermediate keto compound, which rearranges (reaction 4) to the final hydroxy-product **IIa**. This reaction is analogous to the so-called photo-Fries rearrangement of the phenolic esters (March, 1985).

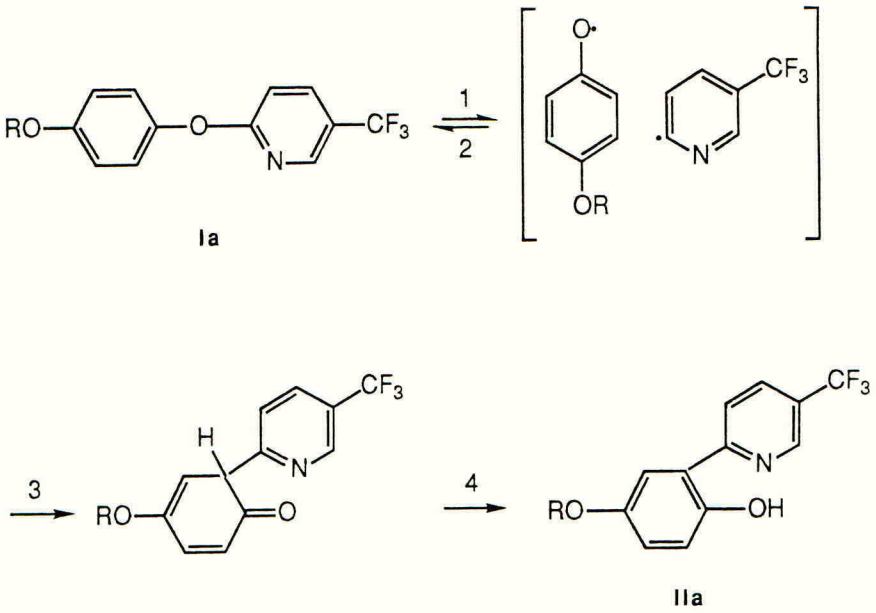

Figure 1. Proposed mechanism for the photoisomerization of fluazifop-butyl, R= $(CH_3)CHCO_2(CH_2)_3CH_3$.

Quinalphos

The photodegradation of quinalphos, 0,0-diethyl 0-(quinoxalin-2-yl) phosphorothioate (**Ib**) in ethanol was a relatively fast process with first-order kinetics ($k = 9.45 \times 10^{-2}\ h^{-1}$; $t_{1/2} = 7.33$ h). About 49% of the insecticide underwent the decomposition within 7 hours when irradiated by sunlight, yielding mainly **IIb**, 0,0-diethyl 0-(3-ethoxy-quinoxalin-2-yl) phosphorothioate, and **IIIb**, 0,0-diethyl 0-(3-(1-hydroxyethyl)-quinoxalin-2-yl) phosphorothioate, as minor and major products, respectively. Only traces of the phosphate analogue **IVb** were found in the reaction mixture.

The species **IVb** was identified by hplc and its structure was confirmed by comparison with an authentic sample supplied by Sandoz. The formation of photoproducts **IIb** and **IIIb** due to 0- or C- addition, respectively, from ethanol can proceed according to the mechanism shown in Figure 2. A photo-excited quinalphos molecule abstracts a hydrogen atom from the solvent molecule and a radical pair is formed. The coupling of these two radicals leads to the formation of 3,4-dihydro-quinalphos derivative, which aromatizes to the thermodynamically more stable hydroxyethylation product **IIIb**.

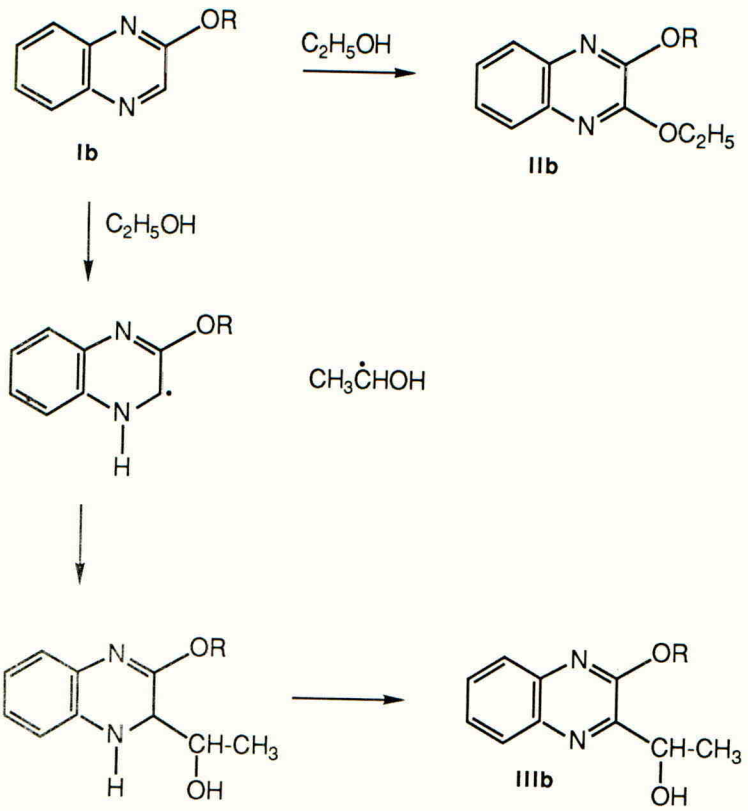

Figure 2. Proposed mechanism for the photodecomposition of quinalphos (**Ib**, R = $PS(OC_2H_5)_2$). The compound **IVb** has the same structure as **Ib** except that R = $PO(OC_2H_5)_2$.

The aromatization reaction is favoured by the presence of oxygen which acts as an oxidizing agent and is responsible for the traces of the phosphate analogue of quinalphos observed among the reaction products. The addition of ethoxide leading to product **IIb** is probably the result of a nucleophilic attack of ethanol to an electron deficient excited state of the quinoxalinic ring of quinalphos. Photo-ethoxylation and photo-hydroxyethylation are competitive processes, the latter being predominant (Furihata & Sugimori, 1975) at least at concentrations as low as that investigated here (about 7×10^{-3} M).

Acifluorfen

In distilled water the photodegradation of acifluorfen (**Ic**), sodium 5- 2-chloro-4-(trifluoromethyl)phenoxy -2-nitrobenzoate, exhibited first-order kinetics ($k = 1.05 \times 10^{-1}\ h^{-1}$). About 51% of the herbicide underwent decomposition within 7 hours, yielding **IIc**, 2-chloro-1-(4-nitrophenoxy)-4-trifluoromethylbenzene as the only product.

The reaction occurred much more rapidly under nitrogen. In fact, in the absence of oxygen the herbicide was totally degraded within 2 hours. Also in these conditions, **IIc** was the only product.

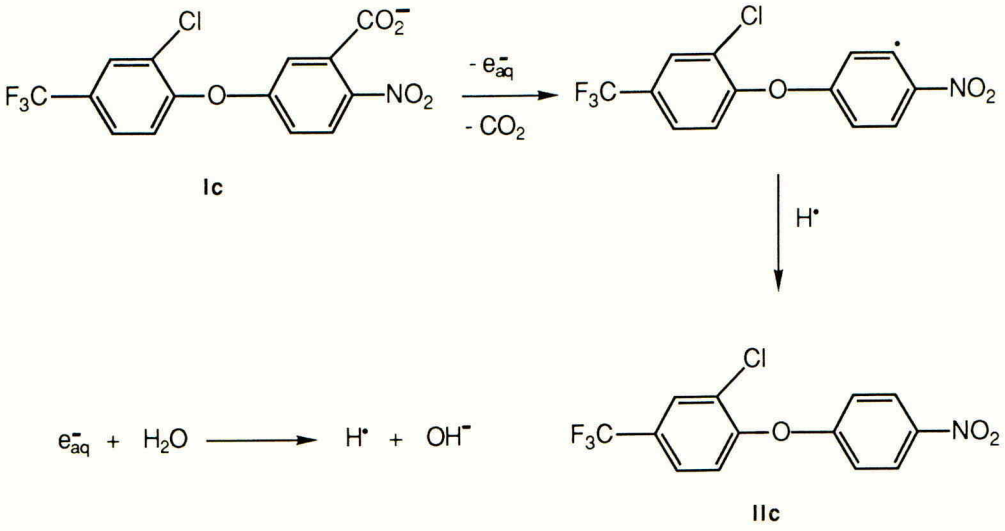

Figure 3. Proposed mechanism for the photodegradation of acifluorfen.

Depending on the characteristics of the solvent, the reaction rate varied. For instance, with an inefficient hydrogen donor such as acetonitrile, no detectable photodegradation was observed even after irradiation for 48 h.

The results suggest that the irradiation of **Ic** leads to photochemical decarboxylation. The mechanism for this reaction (Figure 3) implies that the herbicide gives rise to a phenyl radical by losing a hydrated electron and carbon dioxide. The phenyl radical can couple with the hydrogen atom, formed by reaction of the hydrated electron with water (Anbar, 1965). In the presence of oxygen the hydrated electrons are quickly quenched and this explains the greater rate of reaction observed under nitrogen.

ACKNOWLEDGEMENTS

The authors are grateful to S. Petretto for technical assistance.

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PRELIMINARY RESULTS OF AN EXPERIMENTAL SOIL CORE MICROCOSM AS A FLEXIBLE SCREENING METHOD

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ABSTRACT

A design for an experimental soil core microcosm is proposed as a flexible tool for preliminary and/or basic screening of pesticides. The system has the advantage of low cost, small scale, easy maintenance and wide application while still providing general but reliable characterisation of mobility and persistence.

INTRODUCTION

Soil core microcosms represent an attempt by researchers to maximise flexibility, accuracy and control in a simulated environment which is small in scale and cost, requires little maintenance and may be designed to run for several months (Mackay and Betts, 1991). Existing microcosms which approach these ideals are essentially hybrids of advantageous design features of small scale laboratory columns, box or tank models and larger lysimeters (Gile *et al.*, 1979; Van Voris *et al.*, 1985). The advantages of employing soil core microcosms as model ecosystems have been recognised by many researchers (Fredrickson, *et al.*, 1990; Van Voris, 1985; Gile *et al.*, 1979; Melancon *et al.*, 1986).

Previous test systems that have been developed or suggested are either over complex, bear little resemblance to an ecosystem or are too costly for simple testing procedures (Van Voris *et al.*, 1985). An attempt has been made to design an inexpensive and simple soil core microcosm which can be used for a variety of purposes. Its simplicity makes it an ideal preliminary screening tool for pesticides as it can provide scientifically sound general information yet conserve limited resources. The system can also be employed as a tool for obtaining basic persistence and mobility information which is required for pesticide registration (Anon, 1987). Also proposed is a method which allows researchers to sample the system throughout an investigation without seriously interfering with subsequent results. This dramatically reduces the number of soil cores required thus lowering the overall cost of a study. The fate of triallate in soil is currently being investigated using this microcosm and preliminary results are presented.

Design considerations

A soil microcosm can be defined as an enclosed and maintained portion of a terrestrial ecosystem which is subject to laboratory controls and can be used to investigate ecological processes as well as the environmental behaviour of chemicals. The microcosm must capture and incorporate key elements of that environment and allow for community interactions (Van Voris *et al.*, 1985). In designing a system which attempted to fulfill the conditions presented earlier a set of constraints or criteria were proposed and these are listed in Table 1.

MATERIALS AND METHODS

Construction of microcosm and sampling technique

The core sheaths were constructed from plastic (Osmatube; Barkston Industrial Plastics Ltd., Leeds). The extraction device was built in three parts (tip, shaft and plate) which were prefabricated from milled steel tubing and plate (Figure 1). The sheath was

TABLE 1. Design Consideration for Soil Core Microcosm

- Inexpensive deployment
- Portability
- Allows sampling and monitoring of soil within the core
- Low maintenance requirements
- Inexpensive storage
- Allows introduction of materials at the upper end under sterile conditions
- Allows circulation of air in the area immediately above the soil surface
- Allows assay of the volatilised fraction of chemicals applied to the soil and their degradation products
- Allows free drainage at the base while preventing contamination
- Allows assay of leachate for chemicals and their degradation products

rolled by Minster Engineers of York and the plate and tip were machined by the Department of Biology engineering workshops at the University of York.

The extraction device was designed to allow removal of an intact core and consisted of a steel pipe in which the core sheath rested as it was driven into the ground. This was 70 cm tall and fitted with a strengthened, tapered bit on the base (Fig. 1). The taper was such that the outer diameter reduced from 21 cm to 19 cm at the tip. The tip itself was 20 cm long and the core sheath rested on a ledge created by the taper in the bit. There was a gap of 0.65 cm within the device on which the core sheath sat. The sheath was held in place by a cross bar pushed through two opposing holes 1 cm from the top of the extraction device. This bar also served as a means of pulling the extraction device out of the ground and the two holes were later used as the vapour ports discussed later. A strengthened metal plate machined to fit in the head of the device provided a firm surface onto which pressure could be applied when driving the core assembly into the ground.

Prior to sampling the core sheaths were soaked in Pyroneg (Diversey Ltd., Northampton) for 24 hours to clean and sterilise their surfaces. A small quantity of lubricating gel was used to coat the outer face of each sheath to facilitate subsequent separation from the extraction device. The assemblies were removed from the ground by digging around the cores. After cleaning the extractors could be reused.

Collection of the soil core microcosms

Intact core samples were obtained using 25 cm core sheath segments from a field site provided by the High Mowthorpe MAFF Experimental Husbandry Farm (Duggleby, Yorkshire).

The soil used for this study was a Panholes series silty clay loam soil. The soil field capacity was 34.2 % and the wilting point was 18.8 %. (Anon, 1990). Sampling took place 30 days after application and incorporation of triallate (S-2,2,3 trichloroallyl di-iso-propylthiolcarbamate). The compound was applied in good weather conditions as an emulsion at 1.5 kg/ha AI using a backpack precision sprayer with subsequent soil incorporation by harrowing.

Operation of the microcosm

After collection the cores were stored in a controlled temperature room at 15 °C for a period of six months. They were placed upon raised drainage dishes filled with washed and sterilised fine gravel. Three hundred millilitres of standard reference rainfall solution (Lee and Weber, 1976) was sprayed from overhead onto the surface of each core at intervals of one week. No further addition of materials was necessary during this study.

Sampling ports at appropriate horizontal and vertical intervals were produced by drilling holes (2.0-2.5 cm diameter) in the plastic shell. Measurement of various parameters could be taken either by inserting an electrode into the port or by removing a sample of soil.

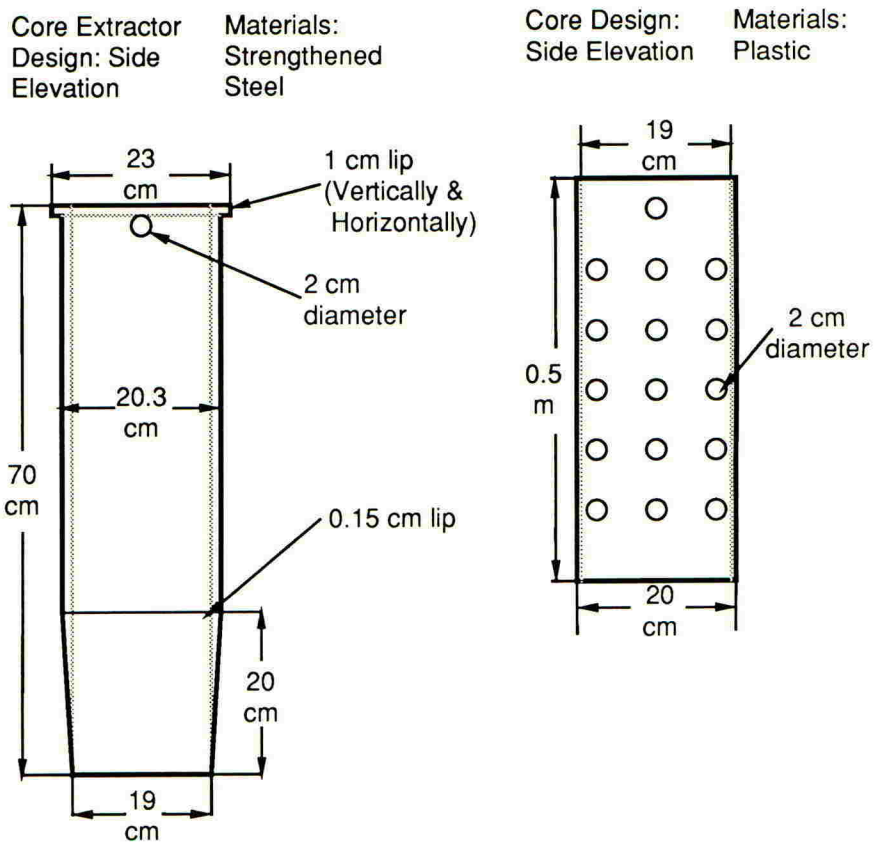


Figure 1. Soil Core and Core Extracter Design

for assay. Initially an inert plug was fitted to fill the void created by sampling. The sampled soil was analysed and replacement soil samples from a nearby site were made up to the appropriate residue concentrations so that, they blended in with the surrounding soil physically, biologically and chemically. Following sampling and soil replacement the sampling ports were then sealed with plastic caps.

The upper end of the core was capped with a plastic shield to prevent biological and chemical contamination. To imitate and monitor the volatilisation of chemicals within the closed chamber three sealable ports were included. A small volume pump was connected to one of the ports permitting constant flushing of the chamber with air to simulate air movement immediately above the soil surface. Another port could then either be left open or fitted with a vapour trap for quantitative assessment of volatilisation and/or transformation to carbon dioxide. A third, overhead port could be used for the introduction of simulated rainfall solution or other materials. The base was placed directly upon fine gravel filling a leachate capture tray.

Pesticide and soil analysis

Portions of frozen samples (approximately 10 g) from the cores were analysed by extraction with an equivalent weight of 2.5% (vol/vol) acetic acid in methanol solution. Extraction was carried out in 250 ml centrifuge tubes on an orbital shaker for 18 hours.

The mixture was then separated by centrifugation at 3,000 rpm for 10 minutes. Aliquots (2 µl) of the extract were then injected onto a gas chromatography apparatus fitted with an electron capture detector (Pye Unicam Series 104) and an 10% OV-1 column. The gas chromatography conditions were as follows: Carrier gas; nitrogen (80 ml/min), column temperature; 150° C, detector oven temperature; 250° C, detector current; 11, Range; 128. Separate portions from the same core sample were also subjected to moisture and organic matter content determinations by heating at 100° C for 24 hours and 900° C for 24 hours respectively. This allowed reference of the triallate residue content of the soil samples to µg/g sampled soil dry weight.

RESULTS

Levels of triallate residues throughout the core depth profile have been obtained for two cores sampled 49 and 151 days after triallate application. Fig. 2 and 3 demonstrate that

Figure 2. Residue Depth Profile: Core 1

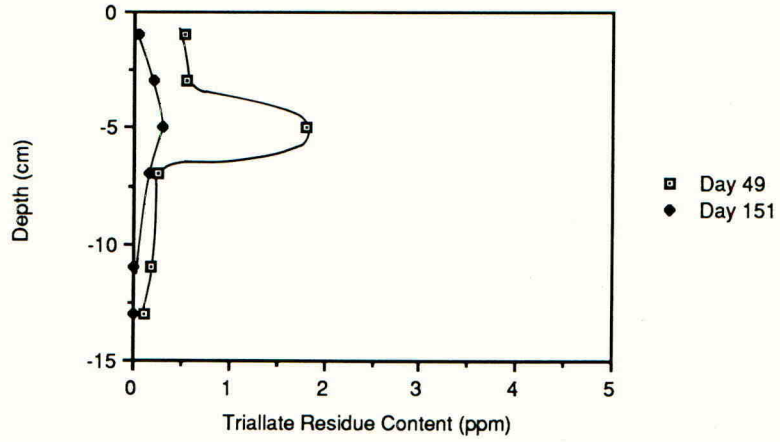
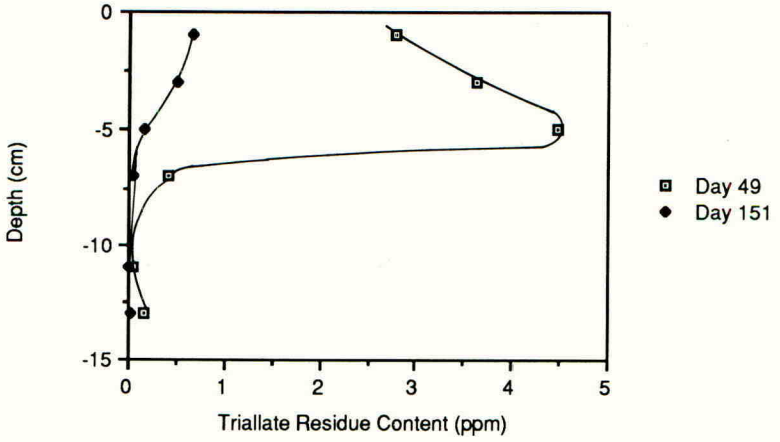


Figure 3. Residue Depth Profile: Core 2



there is a wide variation in the residue content between individual cores and, therefore individual sampling sites. Nonetheless, the changes in the residue depth profile indicate that degradation and some leaching took place. Variation from site to site is quite natural and in order to obtain a representative average a larger number of cores must be taken.

The moisture content profile for the cores (shown in Fig. 4) demonstrates the efficient maintenance of the cores through the regime described earlier. The scale of the soil moisture content axes in Fig. 4 runs approximately between the soil wilting point and field capacity. The organic matter content profiles of the cores (Fig. 5) emphasises the importance of taking intact cores since this important partitioning characteristic can fall quite quickly with depth.

Figure 4: Moisture Content Profile

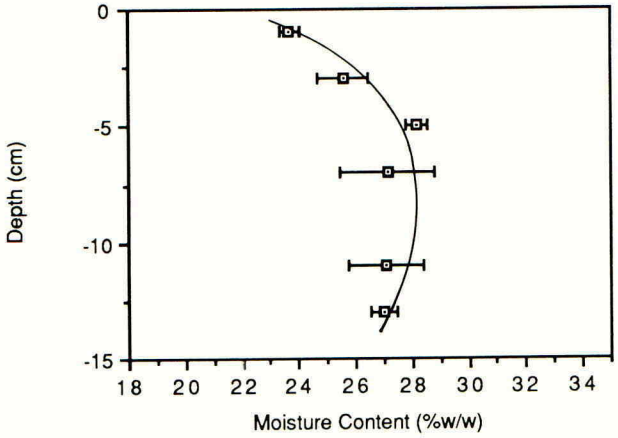
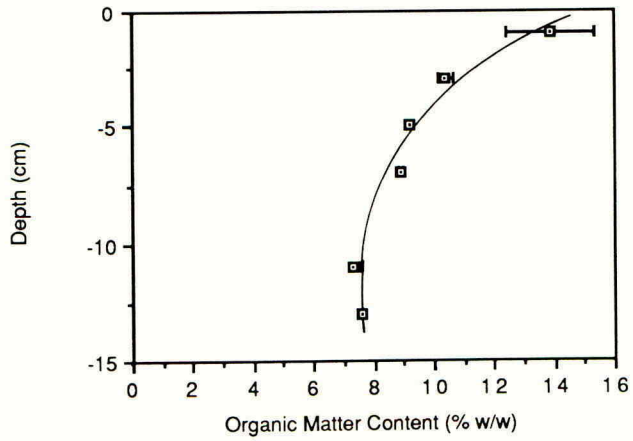


Figure 5: Organic Matter Profile



DISCUSSION

The prime motive to develop this type of system was to increase accessibility to otherwise expensive and complicated screening tests. Van Voris and co-workers (1985) compared a similar soil core microcosm to two alternative systems - a representative simple laboratory scale system ("Flower Pot System") and a field plot system. This comparison (Table 2) has been expanded to include the microcosm discussed in this paper.

TABLE 2. Comparison of Experimental Unit Capabilities and Characteristics

CHARACTERISTICS OF EXPERIMENTAL UNIT	EXPERIMENTAL UNIT			
	FLOWER POT	YORK MICROCOSM	VAN VORIS MICROCOSM	FIELD PLOT
Typical Surface Area	324-507 cm^2	283.5 cm^2	240.5 cm^2	10-100 cm^2
Soil Depth	20-25 cm	25-50 cm	60 cm	1-4 m
Reliable Experimental Period	3-6 months	6 months - 1 year	2-4 years	decades
Reliable Research Cost Factor [a]	3	4	5	9
Control of Individual Environmental Factors	Yes	Yes	Yes	No
Quality of Prediction Compared to Field [b]	2	5	7	10
Soil Temperature Gradient Deviation from Field	Major	Minor	Minor	None

[a] Relative cost for units and monitoring on a scale from 1 (least expensive) to 10 (most expensive)

[b] Reliability of obtained results on a scale from 1 (least reliable) to 10 (most reliable)

The systems described in Table 2 are diverse not only in physical and temporal scale and reliability, but also expense. In terms of cost the microcosm described in this paper (York Microcosm) lies between the simple, inexpensive laboratory study and the more complex, expensive microcosm system. By directly comparing the present system with the Van Voris microcosm we find that the former is much cheaper. Current (1990) materials and set-up costs for 24 units of the Van Voris microcosm are estimated at $(US)5700 compared to approximately $(US)3650 for the present system, a difference of over 30%. Financial comparison has been accomplished by updating the cost benefit analysis data of Van Voris *et al.* (1985) allowing for an average seven percent inflation per year since 1983.

Not surprisingly one would expect the system to fit between the small scale laboratory system ("Flower Pot system") and the more complex and expensive microcosm in terms of reliability and quality of results. In order to test the reliability of the system and the results obtained, it is necessary to compare it to the imitated environment. However, because the microcosm is so highly controlled (precipitation, temperature of storage etc) in contrast to the natural environment, a direct comparison is impossible. An effective method for testing microcosms such as these is to compare them directly with recognised computer models. Preliminary work with an experimental fugacity based

computer model has shown promising results but, further and more rigourous testing on published computer models is required.

A direct comparison between the microcosm described here and other microcosms should be possible. However, microcosms have been developed for a variety of purposes and not only for transport and persistence screening. Because of this there is very little directly analogous data. This "problem" highlights the diversity of tasks to which soil core microcosms can be put.

With small modifications to the design such as construction, methods of storage, sampling etc. it is quite likely that the microcosm described can be applied to the study of such diverse phenomenon as phytotoxicity, plant productivity, soil respiration, chemical transport in plants, chemical transport in soils, nutrient loss in soils, chemical persistence, and chemical volatility (Van Voris *et al.*, 1985). In addition, soil core microcosms have, in the past, been used for the examination and testing of computerised chemical fate models (Melancon *et al.*, 1986) and the effects of genetically engineered microorganisms on soil (Fredrickson *et al.*, 1990).

ACKNOWLEDGEMENTS

The authors wish to thank Monsanto Agrochemicals plc for sponsoring this research, High Mowthorpe MAFF Experimental Farm for kindly providing field facilities, and SSLRC staff at York for advice and information.

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