Session 6D

Fate and Significance of Herbicide Residues in Soil and Water

Session Organisers	Mr S W BAILEY Dr N H STEPHEN
Posters	6D-1 to 6D-19

COMPARISON OF THE DISSIPATION CHARACTERISTICS OF CLOPYRALID AS DETERMINED BY LABORATORY, FIELD AND LYSIMETER STUDIES

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ABSTRACT

Laboratory soil degradation studies with the herbicide, clopyralid, gave DT50 (disappearance time for 50% of the initial concentration) values in the range 13-39 days indicating that the molecule would be considered moderately persistent. The physico-chemical properties of clopyralid suggest that this compound would leach to deeper soil horizons. Laboratory soil column leaching studies supported this hypothesis. However, field dissipation studies gave a more positive environmental picture with DT50 values in the range 8-14 days (classified as non-persistent) and low mobility. Lysimeter studies confirmed these findings and additionally demonstrated that under practical farming conditions, contamination of ground water in excess of the 0.1μg/L EC limit for drinking water is highly unlikely.

INTRODUCTION

Clopyralid (3,6-dichloropyridine-2-carboxylic acid) is the active ingredient of the herbicidal formulation LONTREL 100 (trademark of DowElanco) and shows systemic activity against the creeping thistle (Cirsium arvense). This molecule is characterised chemically by its acidity, high water solubility (approx. 9.0 g/L at 20°C) and its stability to hydrolysis and photolysis (Worthing and Hance, 1991). Such physical and chemical properties suggest that this molecule could readily leach to deeper soil horizons if no chemical or biological degradation occurred.

To investigate these characteristics experimentally, the environmental fate of clopyralid was studied in a three tiered approach starting with standardized laboratory experiments followed by field dissipation studies and finally lysimeter studies. The merits of the various laboratory and field studies in predicting the environmental fate of clopyralid will be discussed.

These studies were carried out using clopyralid labelled with carbon-14 at the 2,6-position of the pyridine ring (Figure 1) unless otherwise stated.

FIGURE 1. Structure of clopyralid showing positions of ^{14}C-label

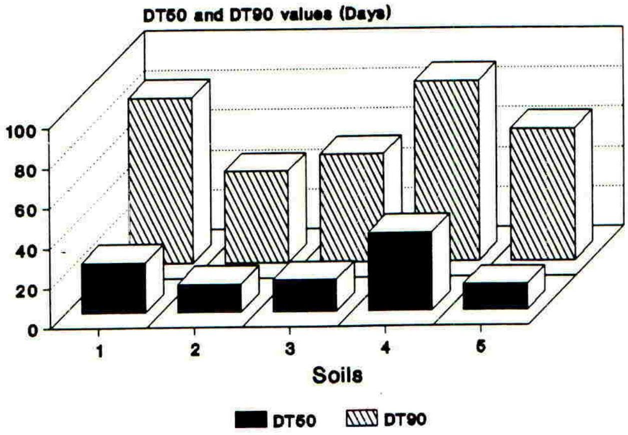
RESULTS AND DISCUSSION

Laboratory Soil Degradation Experiment

The degradation of clopyralid in soil (Baloch and Grant, 1991) was investigated in a laboratory study using five different soils: two standard German soils (2.1 sand and 2.2 loamy sand) and three agricultural soils (Parabraunerde silty loam; UK Marcham sandy clay loam and UK Castle Rising organic sandy loam). The soils were treated with ^{14}C-clopyralid giving a concentration of 0.3 mg/kg soil (approximating to field rate) and incubated at 40% moisture holding capacity (MHC) at 20°C for one year.

Under these conditions, clopyralid was degraded to give $^{14}CO_2$ as the sole radiolabelled metabolite. The calculated DT50 and DT90 values (disappearance time for 50% and 90% of the initial concentration were 13-39 days and 46-90 days respectively (Figure 2).

FIGURE 2. DT50 and DT90 values for clopyralid under laboratory conditions



Soils: 1 = Parabraunerde, 2 = Marcham, 3 = Castle Rising,
4 = Standard German 2.1, 5 = Standard German 2.2.

The effect of soil moisture and incubation temperature was also investigated. The rate of clopyralid degradation was markedly reduced at lower temperatures and soil moistures. These results would lead to the classification of clopyralid as moderately persistent and would trigger further investigation under field conditions.

Soil Column Leaching

The leaching behaviour of ^{14}C-clopyralid (Stork et al, 1990) was studied in accordance with BBA Guideline IV, 4-2 (BBA 1986). Clopyralid was applied to Parabraunerde soil at a concentration of 0.25 mg/kg (approx. field rate) and incubated at 20°C and 40% MHC for 121 days prior to leaching. A parallel leaching experiment was run with soils that were not aged. The columns were leached for 48 hours with approx. 400mL of water (equivalent to 200mm of rainfall) which corresponds to 25% of the average annual precipitation in Northern Germany.

After leaching, an average of 99% and 50% of the applied radioactivity (AR) was present in the leachates from non-aged and aged soils respectively. On the basis of this guideline laboratory study, clopyralid would be classified as highly mobile.

Field Dissipation

The field dissipation of clopyralid (Snel et al, 1986) was investigated at two sites in Westfalia, Germany: Benteler (loamy sand) and Lohne (degraded lõss). One half of each plot treated with non-radiolabelled clopyralid (as formulated product) was covered to determine whether dissipation of the herbicide could be attributed to either soil decomposition or leaching. In the covered parts of the plots, decomposition could take place without leaching. Soil samples were taken at regular intervals from 3 soil horizons (0-10, 10-20 and 20-40cm) up to 262 days after treatment (DAT).

At all sampling intervals, clopyralid was not detected (<10μg/kg) in the deeper soil horizons of 10-20 and 20-40cm. This applied not only to the covered plots, as expected, but also to the uncovered plots. In the open plots treated at field rate (120g AI/ha), clopyralid was not detected in the top 10cm of soil 28 and 49 DAT in the loamy sand and degraded lõss soil respectively.

The decomposition of clopyralid in the 0-10cm layer was much slower in the covered plots than the uncovered plots. In the covered plots, the DT50 values were found to be approx. 2 months in the loamy sand and 3 months in the lõss soil. This experiment demonstrated that dissipation of clopyralid could not be attributed to leaching since no clopyralid was detected in the lower soil horizons. The faster degradation observed in the uncovered plots was probably due to the availability of more soil moisture leading to more rapid degradation as indicated in the laboratory study.

These data show that, under normal field conditions, clopyralid is rapidly degraded and does not leach to deeper soil horizons which is contrary to the conclusions drawn from the laboratory studies. However, one doubt which remained from this study was that clopyralid could have been translocated rapidly downward into soil layers below 40cm which were not analysed. This possibility could be eliminated by conducting a lysimeter study where leachate samples are monitored.

Lysimeter Studies

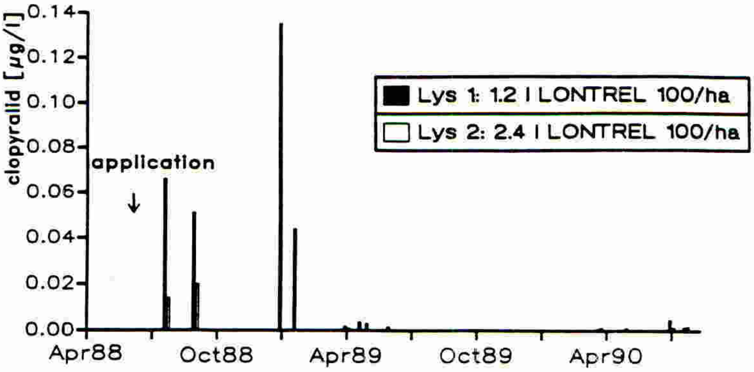
Lysimeter studies were conducted in Sweden (Bergström et al, 1991) and Germany (Brumhard et al, 1990 and 1991). The studies carried out in Germany are described here.

The fate of clopyralid in agricultural soil was investigated in several lysimeter studies at the Institute of Radioagronomy, KFA Forschungszentrum, Jülich. The first experiment was started in 1988 using two lysimeters filled with undisturbed Parabraunerde with a surface area of 1.0 m^2 and a depth of 110cm. Details of the study design, collection of leachate samples and soil type and soil profile used in this study are given by Führ and Steffens, (1985) whilst the soil characteristics are given by Brumhard et al, (1991). Clopyralid was applied to the lysimeters as a post emergence application to sugar beet. One of the lysimeters (lysimeter 1) was treated at field rate (120g AI/ha) and the other (lysimeter 2) at twice field rate. As rotational crop, winter wheat was planted in the autumn of 1988. Leachate samples were collected at regular intervals throughout the two year study. Soil samples were collected after the harvest of the sugar beet crop and at the end of the study (2 years after application).

At the time of the sugar beet harvest (131 DAT), 59.3 and 37.3% of AR was measured in the soil of lysimeter 1 and 2 respectively with the highest portion in the top 0-20cm layer. Extraction of soil with aqueous and organic media released only approx. 5% AR from each lysimeter approx. 50% of which was characterised as clopyralid by radio-TLC analysis. After the second growing season (August 1989), unchanged clopyralid was detected only in the fulvic acid fraction of the extractable soil organic matter and accounted for only 0.5 - 0.7% of AR.

Over the entire period of the study, a total of 0.45% and 0.66% of AR was found in the leachates from lysimeters 1 and 2 respectively and most of this was attributed to $^{14}CO_2$. Analysis of the leachate samples by radio-TLC revealed that the concentration of clopyralid ranged from 0.0005 - 0.14μg/L (Figure 3). The highest value (0.14μg/L) was only observed once, after a heavy rain storm shortly after application. The average concentration of clopyralid in the total leachate (180L) was 0.014μg/L.

FIGURE 3. Concentration of ^{14}C-clopyralid (μg/L) in leachates of two lysimeters in Jülich, Germany after application to sugar beet.



In this study, clopyralid appeared to be rapidly degraded and showed very little mobility through the soil profile. Similar results have been obtained in two other lysimeter studies conducted at the same location. In these two studies, a sandy soil with low organic carbon was used in the lysimeters. In one of the studies, the first crop was oilseed rape rather than sugar beet. Changing the soil or the crop appeared to have no significant effect on the results which consistently showed clopyralid to degrade rapidly with minimal tendency for leaching. Based on these data, it seems highly unlikely that, under German conditions, clopyralid will move far enough down the soil profile to contaminate ground water above the EC limit for drinking water of 0.1μg/L (80/778/EEC).

CONCLUDING DISCUSSION

Although the physical and chemical characteristics of clopyralid cannot predict that it will be persistent in the environment, they do suggest that clopyralid has a high potential to leach. This prediction was confirmed by the standardized laboratory soil column leaching studies which showed clopyralid to be highly mobile in soil. The laboratory soil degradation experiments showed that the herbicide could be moderately persistent in soil which was also indicated by the "aged" leaching study. However, the evidence gathered from field and lysimeter studies shows that under field conditions, clopyralid is rapidly decomposed irrespective of soil type, crops and weather conditions. Vertical movement of clopyralid to deeper soil layers was not demonstrated under the more realistic conditions used in these studies.

This obvious difference in the behaviour of clopyralid under conditions which are similar to actual farming practices compared with standardized laboratory conditions illustrates how results from laboratory studies can give a very unfavourable picture of the environmental behaviour of an agrochemical. It raises the issue of how much useful data can be gained from standardized laboratory experiments. Although laboratory experiments are useful for obtaining a preliminary profile of the environmental behaviour of a molecule, these experiments by the nature of their design, have limitations. Parameters which should be considered include soil photolysis, application rate and timing, temperature, soil moisture and soil microbial biomass. All these parameters can be best considered interactively in either field or lysimeter studies.

With the increasing use of computer models, which use input data generated from standardized laboratory studies, for predicting the environmental behaviour of agrochemicals, the possibility of obtaining a false environmental fate profile cannot be ruled out. Therefore, field or lysimeter studies may provide more realistic data for those compounds for which the physico-chemical properties and laboratory studies predict the possibility of persistence or high leaching potential. In such cases, the need for extensive laboratory testing could be reduced and it may be sufficient to conduct shorter and more simplified laboratory studies.

The example given in this paper, where different results are obtained in laboratory and field situations will certainly not apply to every agrochemical. However, it highlights the need to use the most appropriate experiments for each molecule in order to obtain a realistic environmental assessment rather than a standardized approach to cover all agrochemicals.

ACKNOWLEDGEMENT

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REFERENCES

Baloch, R.I.; Grant, R.K. (1991). The investigation of degradation and metabolism of clopyralid in two standard and three agricultural soils. BCPC Monograph No. 47, Pesticides in Soil and Water.

Bergström, L.; McGibbon, A.; Day, S.; Snel, M. (1990). Leaching potential and decomposition of clopyralid in Swedish soils under field conditions. Environmental Toxicology and Chemistry, **10**, 563-571.

BBA (1986). Richtlinien für die amtliche Prüfung von Pflanzen schutzmitteln. Teil, IV 4-2. Versickerungsverhalten von Pflanzenschutzmitteln. BBA, Braunschweig, Germany.

Brumhard, B.; Bergström, L.F.; Snel, M.; Führ, F.; Baloch, R.I.; Trozelli, H. (1991). Dissipation of clopyralid in soil under field conditions: lysimeter studies in Germany and Sweden. Med. Fac. Landbouww. Rijksuniv. Gent, **56/3a**, 887-900.

Brumhard, B.; Führ, F. (1990). Lysimeter studies on long-term fate of pesticides: leaching of clopyralid in a degraded loess soil after post-emergence application to sugar beet. Seventh Int. Congress of Pesticide Chem. Book of Abstracts, Vol. **III**, Hamburg: 91.

Führ, F.; Steffens, W. (1985). Transport und Bilanzierung von Umweltchemikalien in Agrarökosystemausschnitten. Bonner Universitätsblätter 1985, 25-28.

Snel, M.; Almond, R.; Scorer, D.J. (1986).Dissipation of clopyralid in German soils under field conditions. Med. Fac. LandBouww. Rijksuniv. Gent. **51(2A)**, 227-234.

Stork, A.; Brumhard, B.; Führ, F. (1990). Standardized laboratory experiments on degradation and leaching of clopyralid in a degraded loess soil. Seventh Int. Congress of Pesticide Chem. Book of Abstracts, Vol. **III**, Hamburg, 80.

Worthing, C.R.; Hance, R.J. (Eds.) (1991). The World Pesticide Manual, 9th Edition, Thornton Heath, 181-182.

A NEW INSTRUMENT FOR MEASUREMENT OF pK_a VALUES AND PARTITION COEFFICIENTS (logP)

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ABSTRACT

Values of pK_a are of fundamental significance in solution chemistry, while octanol/water partition coefficients (quoted as logP values) are useful indicators of the biological activity and environmental properties of molecules. Standard techniques of pK_a and logP measurement are tedious, and provide limited information for molecules with unusual properties.

A powerful new instrument is described which automates pK_a and logP measurement, and which has been successfully used for compounds with multiple overlapping pK_as and logP values as high as 5 and above, and also for poorly water-soluble compounds. Examples are shown of pK_a and logP measurement for a variety of compounds including a series of alkoxyphenols with increasing logP values, glyphosate and carbendazim.

This instrumental technique can be used to generate data for meeting EPA and OECD approvals for registration of new materials.

THE INSTRUMENT

Known as the Sirius PCA101, the instrument contains a pH sensing circuit, semi-micro combination pH electrode (Orion ROSS), temperature probe, overhead stirrer, precision dispenser and valve for distributing reagents and titrants (0.5M HCl, 0.5M KOH, 0.1M KNO3, octanol, methanol, surfactant solution). The 0.1M KNO3 is referred to below as "ionic-strength adjusted water". A polyimide-clad quartz capillary (ID 0.5mm) serves as a dispenser tip. The instrument moves the electrode/stirrer/dispenser tip assembly in and out of the sample, buffer and wash solutions. The user need only supply a weighed sample (1-10 mg); the diluent and all the other reagents are added automatically.

Real-time graphics are displayed on the VDU during analysis. All the functions of the instrument are controlled by an on-board computer which is operated via a 19-button keypad on the front panel. An optional PC-type keyboard can be plugged into the rear panel for alphanumeric input of sample information. A built-in ink-jet printer prints the contents of any screen display on demand.

Assay of a sample to determine pK_a and logP is in two stages; data collection, followed by a "supervised" computerized calculation. Reagents and the pH electrode must be standardized before use.

USING THE INSTRUMENT

Standardization

Before a sample can be analyzed, the pH electrode must be standardized, first by recording the mV in a pH7 buffer solution (the "anchor point"), followed by an acid-base "blank titration". The experimental titration curve is compared with a calculated, theoretical curve and the data are fitted to a four-parameter equation of the following form:

$$pH = \alpha + sp[H^+] + j_H[H^+] + j_{OH}K_w/[H^+]$$

$\alpha = -\log f_H \approx 0.08$ at 25°C & 0.1M ionic strength

(f_H = activity coefficient of H^+)

$s \approx 0.99 - 1.01$ (slope factor) takes account of slight departures from theoretical Nernst value assumed in "anchor point" calibration

j coefficients take into account non-linear electrode effects in the extreme regions of pH ($pH<2.5$ and $pH>11.5$), related to junction and asymmetry potentials

This procedure corrects for non-ideal response of the pH electrode at low and high pH and the effect of dissolved CO_2 in the base titrant and water, and enables a "true" pH reading to be obtained (Avdeef & Bucher, 1978). The quality of this standardization is such that pK_a values can be determined between pH 1.8 and 12.2, values that are outside the normal range of potentiometric pK_a determination. Standardization using a weighed standard is a built-in feature of the instrument.

Data Collection

In a typical pK_a measurement, a sample of pure substance (1-10mg) is weighed into a vial and placed on the instrument, which then adds ionic-strength adjusted water, followed by acid (or base) to move the pH outside the range of possible pK_a values. It then titrates with base (or acid) until the region of "pK_a interest" has been passed. The pK_a is subsequently calculated.

To measure logP, the pK_a must be known (or determined as above). Octanol (or other water-immiscible partition solvent) is added to a solution of the sample in ionic-strength adjusted water and the sample is titrated as above. Experimentally, the logP titration can follow on directly from the pK_a titration, with solvent added at the end of the first titration, or it can be done as a separate titration with the sample starting out in solution in the partition solvent. The "apparent pK_a" (p_oK_a) of the sample in the water/solvent mixture is different to the aqueous pK_a; logP is calculated from this difference using a relationship of the form below: (for simple monoprotic substances)

$$\log P = \log[10^{|pKa - poKa|} + \log[v_{water}/v_{solvent}] \quad (v = \text{volume})$$

A typical curve of a titration to determine pK_a is shown in Figure 1. Titration on the instrument is fully automated, and takes 20-30 minutes for each forward or reverse stage.

"Supervised" computerized calculation

The first stage of calculation is to set up an "ionization model" and to determine approximate values for pK_a and logP. The ionization model indicates the state of ionization of the sample substance; (the charge on the fully deprotonated species, number of pK_as and charge on the substance in the form introduced at the start of the experiment). A Difference curve (Avdeef *etal.*, 1982) is then calculated, from which approximate pK_a values may be read as the pH values equivalent to the half-integral values of $\bar{n}_H$ (the number of bound protons). Figure 2 shows a difference curve for glyphosate; approximate values for the three higher pK_as are clearly apparent, while the lowest pK_a is obtained by extrapolation. Figure 3 shows Difference curves for carbendazim. The Difference curve represents the difference between the full titration curve and the contribution from the blank titration (i.e. the water and the acid/base background), and it corresponds to the signal from the sample substance only.

The final stage of calculation is the refined solution, in which approximate pK_a and logP values are refined using least-squares fitting. Figure 4 shows a typical screen display from the final stage of refinement. The low value for the "Goodness of Fit" (GOF) indicates the high quality of the refinement. Figure 5 shows the Lipophilicity Profile for carbendazim, which is calculated following the refined solution. The plot shows how the effective partition coefficient (logD) changes with pH. The logD distribution parameter is derived simply from logP and pK_a of the substance.

TYPICAL RESULTS

The results in Table 1 show pK_a and logP of benzoic acid and benzylimidazole (two reference substances) and a series of alkoxyphenols with increasing logP values. Results are also shown for glyphosate and carbendazim.

DISCUSSION

Carbon dioxide correction

Unless extreme precautions are taken, carbon dioxide may be present in the ionic-strength adjusted water and the base titrant. It will also be absorbed by sample solutions at high pH. As an alternative to rigorous reagent purging and working under inert gas, the instrument will undertake "carbon dioxide correction", in which the effect of carbon dioxide on the data is calculated during the refined solution. For this purpose the pK_as and logP of carbon dioxide are stored in memory as a function of ionic strength and temperature, and they are entered as fixed values. The process of correction is iterative, in that values for carbon dioxide concentration are proposed and the resulting GOF is noted, with the minimum GOF value suggesting the most likely carbon dioxide value. Carbon dioxide concentrations down to 0.00001M can be determined by this technique.

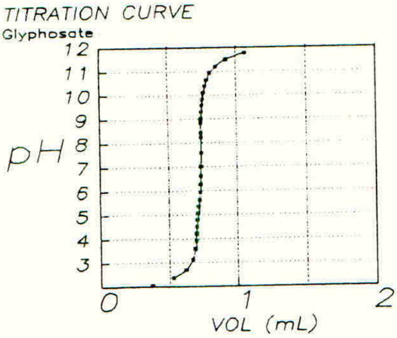


Figure 1

Titration curve. 0.003M glyphosate, pH adjusted to 2 with HCl, titrated with KOH

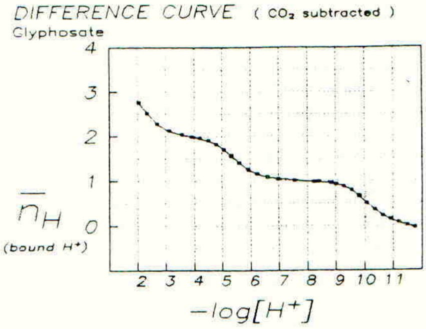


Figure 2

Difference curve for glyphosate calculated from titration curve by subtracting acid/base background

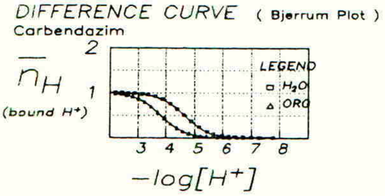
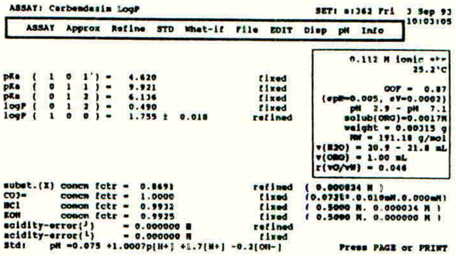


Figure 3

Difference curves for carbendazim based on two titrations (first one in aqueous solution, second in water/octanol (ORG)



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                                                                        10:03:05
   ASSAY  Approx  Refine  STD  What-if  File  EDIT  Disp  pH  Info

                                                              0.112 M ionic str
                                                                        25.2'C
pKa  (  1  0  1')  =   4.620                      fixed
pKa  (  0  1  1 )  =   9.921                      fixed              GOF =  0.87
pKa  (  0  1  2 )  =   6.136                      fixed    (epH=0.005, eV=0.0002)
logP (  0  1  2 )  =   0.490                      fixed         pH  2.9 - pH  7.1
logP (  1  0  0 )  =   1.755 ±  0.018           refined      solub(ORG)=0.0017M
                                                             weight = 0.00315 g
                                                                MW = 191.18 g/mol
                                                         v(H2O) = 20.9 - 21.8 mL
                                                         v(ORG) = 1.00 mL
                                                         r(vO/vW) = 0.046

subst.(X) concn fctr =  0.8691                  refined  ( 0.000824 M )
CO3=      concn fctr =  1.0000                    fixed  (0.072%*.0.010mM.0.000mM)
HCl       concn fctr =  0.9932                    fixed  ( 0.5000 M. 0.000034 M )
KOH       concn fctr =  0.9925                    fixed  ( 0.5000 M. 0.000000 M )
acidity-error(J)      = 0.000000 M              refined
acidity-error(L)      = 0.000000 M                fixed
Std:     pH =0.075 +1.0007p[H+] +1.7(H+) -0.2(OH-)               Press PAGE or PRINT
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Figure 4

Typical summary of results

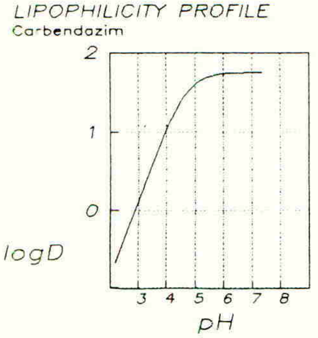

Figure 5

Lipophilicity profile for carbendazim. Plot shows that carbendazim is most lipophilic at high pH, where molecule is unionised

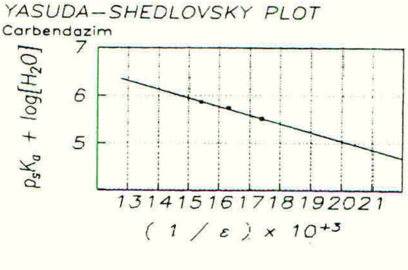

Figure 6

Yasuda-Shedlovsky extrapolation for carbendazim. Each point represents the p_sK_a (apparent pK_a determined from a titration in water/methanol solution) + the concentration of water in the mixture, plotted against the inverse of the dielectric constant of the mixture. Aqueous pK_a is equal to the p_sK_a value at zero methanol concentration

TABLE 1. pK_a and logP; weighted mean values

Substance	pK_a	logP octanol/ water	ionic strength/ temp	n	Lit. value
Benzoic acid	4.08 ±.01		0.1M 25°C	5	4.04[1]
		1.90 ±.04	0.1M 25°C	5	1.97[1]
1-benzylimidazole	6.70 ±.03		0.1M 26°C	10	
		1.60 ±.04	0.1M 26°C	5	
p-methoxyphenol	10.05±.01		0.1M 23°C	4	
		1.41 ±.03	0.1M 23°C	4	1.34[2]
p-ethoxyphenol	10.03±.01		0.1M 24°C	4	
		1.81 ±.02	0.1M 24°C	4	1.81[2]
p-propoxyphenol	10.05±.01		0.1M 26°C	5	
		2.31 ±.03	0.1M 26°C	5	2.33[2]
p-butoxyphenol	10.04±.08		0.1M 20°C	3	
		2.87 ±.08	0.1M 20°C	3	2.90[2]
glyphosate	10.09±.02 5.43 ±.01 2.16 ±.05 1.60 ±.15		0.12M 25°C	2	
		<-1			
carbendazim	4.62**		0.1M 25°C		4.48[3]
		1.75±.004	0.1M 25°C	2	

* 0.15M ionic strength

** result by Yasuda-Shedlovsky extrapolation from 3 p_sK_as measured in water/methanol solution (Figure 6: see below).

[1] Clarke & Cahoon, 1987

[2] Pomona College Medicinal Chemistry Project Data Base

[3] Merck Index, 1989

Solubility

Some samples do not dissolve in aqueous solution over all or part of the pH range, leading to difficulties in pK_a determination. Sometimes the free acid or base is insoluble in aqueous solution while the ionized species is soluble. In this case the pK_a titration is started at a pH where the ion is in solution. Often sufficient data can be collected before the onset of precipitation to estimate the aqueous pK_a.

If samples are very insoluble in water, "apparent pK_a" (p_sK_a) can be calculated from titration of a solution in a mixture of water with a water-miscible co-solvent such as methanol (after the electrode has been standardized by a blank titration at the same water/co-solvent ratio). If several p_sK_a values are measured at different water/co-solvent ratios, they can be related to aqueous pK_a using graphical methods. One such method is the Yasuda-Shedlovsky (Y-S) extrapolation (Benet & Goyan, 1967), in which (p_sK_a + $\log[H_2O]$) is plotted as a function of $1/\varepsilon$ (ε = the dielectric constant of the water/co-solvent mixture). Figure 6 shows the Y-S extrapolation used to calculate the aqueous pK_a of carbendazim.

REFERENCES

Avdeef, A.; Bucher J.J. (1978) Accurate measurements of the concentration of hydrogen ions with a glass electrode: calibrations using the Prideaux and other universal buffer solutions and a computer-controlled automatic titrator. *Analytical Chemistry,* **50,** 2137-2142.

Avdeef, A.; Kearney, D.L.; Brown, J.A.; Chemotti, A.R. (1982) Bjerrum plots for the determination of systematic concentration errors in titration data. *Analytical Chemistry,* **54,** 2322-2326.

Clarke, F.H.; Cahoon, N.M. (1987) Ionization constants by curve fitting: determination of partition and distribution coefficients of acids and bases and their ions. *Journal of Pharmaceutical Sciences,* **76,** 611-619.

Pomona College Medicinal Chemistry Project Data Base, MEDCHEM Vol. 33, Clairemont CA(USA).

Benet, L.Z., Goyan, J.E.(1967) Potentiometric determination of dissociation constants *Journal of Pharmaceutical Sciences* **56,** 665-680 (see particularly pp. 667-668).

DISSIPATION OF ACETANILIDE AND TRIAZINE HERBICIDES IN ITALIAN SOILS. FIELD DATA SETS

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ABSTRACT

Trials were carried out in Italy in 1988 to measure the dissipation in soil of terbuthylazine and atrazine applied pre-emergence to maize and of alachlor and metolachlor applied pre-emergence to soyabean. Dissipation and mobility in soil were investigated at different sites and at three depths, (0-10, 20-30 and 45-60 cm), by means of scheduled sampling during the 190-day period after herbicide application. Data sets collected provide information on herbicide behaviour in soil under Italian conditions.

INTRODUCTION

Few studies on herbicide dissipation have been published in Italy. In the data base ResPest-I (Natali *et al.*, 1989), which reports all pesticide residue data available in Italy since 1978, only 50 out of more than 600 abstracted papers reported data on pesticide dissipation in soil. In almost all cases pedological and climatic data needed to run mathematical models were not given.

In this paper we report data sets on triazine and acetalide dissipation obtained in field trials representative of north Italian agriculture in the Po Valley. The data sets contain most of the climatic, pedological and agronomic data needed to run models. Some of the results are reported in Trevisan *et al.* (1993), Trevisan *et al.* (1991), Capri (1992) and Del Re *et al.* (1991).

MATERIALS AND METHODS

Experimental fields

In 1988 a number of representative farms were selected in the Po Valley (Table 1). At each farm, three 250 m^2 sampling plots were delineated within a large experimental field (2500-4000 m^{2}). Soyabean and maize were grown following the standard field practice used at each farm. Soil properties are reported in Table 1, herbicide rates in Table 2. Herbicide mixtures were applied overall by using a tractor-mounted sprayer calibrated to distribute 400-800 l/ha of water. Alachlor was applied as Lasso ® (43.2 % AI); atrazine as Fogard ® (45 % AI); terbuthylazine as Gardoprim ® (50 % AI); metolachlor as Duals ® (68.5 % AI). A more detailed description of the trials is reported elsewhere in Capri (1992).

Sampling was carried out with a cylindrical corer (internal diameter of 5.8 cm), fitted to an electrical hollow-stem auger column. The cores were cut into three sections, corresponding to 0-10, 20-30, 45-60 cm depth. Three replicate cores for each plot were mixed, sieved through a 5-mm mesh sieve and immediately frozen at -20 °C until analysis. The moisture content was determined before analysis. Soil sampling was carried out over the period from sowing to harvest, i.e. April to November.

Weather data (maximum and minimum air temperature, rainfall) were recorded for each experimental site. Rainfall for all fields was between 400 and 600 mm over the study period. Most of the fields were irrigated twice with 200 mm of water on each occasion.

Residues data

Soil samples were analyzed by the Del Re procedure (Del Re *et al.*, 1991). Mean recoveries from untreated soil samples fortified at 0.050 and 0.200 mg/kg were 100±5 % for alachlor, atrazine, and metolachlor, and 88±5 % for terbuthylazine. Detection limits were 0.005, 0.007, 0.002 and 0.004 mg/kg of air-dried soil for terbuthylazine, alachlor, atrazine, and metolachlor respectively.

TABLE 1. Physical and chemical properties of the soils used.

	SITE											
	Palazzina		**Lardera**		**Tencara**		**S.Giorgio**		**C. Mora**		**Crocina**	
Latitude (°)	(45.06 N)		(45.05 N)		(45.10 N)		(45.07 N)		(45.07 N)		(45.29 N)	
Altitude (m)	(20 asl)		(45 asl)		(46 asl)		(99 asl)		(99 asl)		(117 asl)	
Depth §	**T**	**S**	**T**	**S**	**T**	**S**	**T**	**S**	**T**	**S**	**T**	**S**
pH	7.8	7.9	5.8	6.5	7.9	7.9	5.1	5.7	6.0	6.1	5.8	6.0
Organic matter (%)	2.0	1.6	3.0	1.4	2.2	1.9	1.7	1.1	1.8	1.3	2.0	1.5
Sand (%)	13	10	21	14	61	22	47	44	35	42	43	44
Silt (%)	46	46	61	62	46	47	42	46	50	48	46	42
Clay (%)	41	44	18	24	31	31	11	10	15	10	11	14
Textural Class *	SC	SC	SL	SL	CL	CL	L	L	L	L	L	L

§ **T** is top soil (0-30 cm), **S** is sub-soil (30-50 cm).
* SC = Silty Clay; SL = Silty Loam; CL = Clay Loam; L = Loam as defined by Soil Science Society of America.

TABLE 2. Herbicides used.

FARM	CROP	HERBICIDE (AI)	RATE (kg AI/ha)	APPLICATION DATE
Palazzina	SOYABEAN	alachlor	2.16	3 May
		metolachlor	1.71	3 May
Lardera	MAIZE	alachlor + atrazine	2.83 + 1.02	26 April
		terbuthylazine *	0.80	27 April
Tencara	MAIZE	terbuthylazine *	0.80	3 May
		terbuthylazine + metolachlor	0.84 + 1.67	4 May
San Giorgio	MAIZE	alachlor + atrazine	2.40 + 0.90	20 April
		terbuthylazine + metolachlor	1.14 + 2.28	20 April
Mora	SOYABEAN	alachlor	2.88	20 April
		metolachlor	1.57	20 April
Crocina	MAIZE	metolachlor	1.50	23 April
		alachlor + atrazine	2.40+0.80	24 April

* Herbicide incorporated to 10 cm depth.

Calculation of DT50

Dissipation times and rate constants were calculated by regression analysis of the logarithm of residue concentration against sampling time (days). First-order kinetics were assumed only when the regression was significant (P >0.001).

RESULTS AND DISCUSSION

Assuming first order kinetics, values of DT50 may be used to compare herbicide persistence. Although the application rates were different, the persistence was characteristic of each herbicide and could be ranked in the order alachlor < atrazine < metolachlor < terbuthylazine.

Alachlor had the lowest DT50, 8.2-13.5 days for the topsoil (0-10 cm) and 7.2-21.3 days for the sub-soil (20-30 cm) (Table 3). About 180 days after herbicide application, the residues were 0.011-0.05 mg/kg in the topsoil (1.2-3.0 % of applied dose).

Metolachlor had a DT50 of 11.8-22.8 days in the 0-10 cm layer and of 14.1-20.3 in the 20-30 cm layer (Table 4). At the last sampling date metolachlor was not detected at Palazzina and Tencara but was present at 0.012-0.028 mg/kg in topsoil at Mora and Crocina respectively (1.2-2.9 % of applied dose).

Atrazine had DT50 values in the range of 9.2-17.7 and 12.2-17.8 days for the 0-10 and 20-30 cm layers respectively (Table 5). About 194 days after application the residues were 0.010 mg/kg (1.4-1.8 % of applied dose) in the topsoil (0-10 cm).

The effects of soil incorporation were evident for terbuthylazine which was more persistent when incorporated than when surface applied.When applied to the soil surface its DT50 value was 19.0-26.2 days in the 0-10 cm layer but 27.2-37.1 days when incorporated (Table 6). These differences declined with time: about 190 days after application, terbuthylazine residues were 0.026 mg/kg at Tencara and 0.021 mg/kg at Lardera (3.9-5.1 % of applied dose).

This work shows that under normal agricultural practices in the north Italian climate the herbicides studied showed lower persistence than values usually reported in the literature. For example Wauchope *et al.* (1992) report the following data on dissipation times: 15 days for alachlor, 60 days for atrazine, 90 days for metolachlor. This is not surprising since the hot and dry climate, associated with few but heavy rainfall and irrigation events, would enhance the dissipation of herbicides in soil.

The small differences between experimental sites for the same AI mainly appear to be due to the effects of soil type, because meteorological parameters are only slightly different: e.g. herbicide persistence was greater at Palazzina than Crocina. The Palazzina soil has a higher clay content, yet the climate is almost the same.

All the herbicides appeared rapidly in the deeper soil layers. This behaviour is not consistent with the literature; the most reasonable hypothesis is that there were systematic errors associated with the type of sampler used. The data set for the upper layers appears however to be suitable for use with simulation models, as shown by previous research reported by Del Re *et al.* (1991) and Trevisan *et al.* (1993).

TABLE 3. Alachlor residues in soil at different sampling times.

Field	Depth (cm)	Concentrations (mg/kg)°						DT50 (d)	rate constant K (d-1)	r
		Time after application								
		1 day	*13 days*	*30 days*			*161 days*			
Palazzina	0-10	2.930±1.213	1.178±0.177	0.550±0.161			0.034±0.019	12.5	0.0556	0.91
	20-30	0.554±0.489	0.211±0.132	0.025±0.026			ND	7.2	0.0968	0.82
	45-60	0.033±0.010	0.041±0.022	0.005±0.002			0.004±0.004	-	-	-
		2 days	*8 days*	*29 days*	*71 days*	*97 days*	*194 days*			
Landera	0-10	2.572±0.635	1.126±0.479	0.591±0.044	0.108±0.026	0.011±0.005	0.011±0.000	13.5	0.0515	0.97
	20-30	0.423±0.132	0.191±0.128	0.129±0.062	0.041±0.008	0.005±0.001	ND	19.0	0.0364	0.94
	45-60	0.113±0.045	0.074±0.053	0.039±0.010	0.002±0.000	ND	ND	-	-	-
		1 day	*13 days*	*33 days*	*77 days*	*97 days*	*192 days*			
San Giorgio	0-10	1.670±0.954	1.359±1.003	0.457±0.326	0.038±0.019	ND	0.022±0.005	13.3	0.0523	0.97
	20-30	0.790±0.594	0.178±0.129	0.131±0.058	0.008±0.011	0.013±0.001	0.016±0.002	21.3	0.0326	0.87
	45-60	0.552±0.366	0.205±0.138	0.127±0.054	ND	ND	0.040±0.015	-	-	-
		2 days	*13 days*	*33 days*			*168 days*			
Mora	0-10	1.055±0.346	0.881±0.118	0.174±0.051			0.054±0.011	11.4	0.0608	0.93
	20-30	0.322±0.112	0.205±0.115	0.065±0.044			ND	13.1	0.0527	0.87
	45-60	0.047±0.015	ND	ND			ND	-	-	-
		1 day	*10 days*	*23 days*	*60 days*		*161 days*			
Crocina	0-10	1.340±0.386	0.860±0.353	0.254±0.169	ND		0.019±0.013	8.2	0.0843	0.98
	20-30	0.259±0.039	0.062±0.033	0.030±0.009	ND		0.013±0.011	15.4	0.0449	0.87
	45-60	0.146±0.062	0.075±0.028	0.019±0.002	ND		ND	-	-	-

ND - none detected
° mean of three replicates

TABLE 4. Metolachlor residues in soil at different sampling times.

Field	Depth (cm)	Concentrations (mg/kg)°						DT50 (d)	rate constant K (d-1)	r
		Time after application								
		1 day	*13 days*	*30 days*			*161 days*			
Palazzina	0-10	0.732±0.167	0.536±0.207	0.313±0.013			ND	22.8	0.0304	0.77
	20-30	0.131±0.044	0.121±0.039	0.011±0.009			ND	-	-	
	45-60	0.027±0.018	0.033±0.031	0.029±0.050			ND	-	-	
		2 days	*9 days*	*29 days*	*65 days*	*90 days*	*187 days*			
Tencara	0-10	0.716±0.165	0.352±0.119	0.290±0.045	0.048±0.018	0.009±0.008	ND	14.9	0.0164	0.94
	20-30	0.035±0.006	0.110±0.162	0.014±0.002	0.036±0.063	ND	ND	20.3	0.0341	0.84
	45-60	0.018±0.008	0.079±0.106	0.011±0.003	ND	ND	ND	-	-	
		1 day	*10 days*	*23 days*	*60 days*		*161 days*			
Crocina	0-10	0.970±0.095	0.724±0.205	0.432±0.203	0.035±0.013		0.028±0.020	11.8	0.0588	0.97
	20-30	0.628±0.126	0.077±0.026	0.037±0.011	0.018±0.002		0.014±0.010	14.1	0.0490	0.82
	45-60	0.118±0.012	0.049±0.021	0.031±0.013	0.009±0.007		0.004±0.002	-	-	
		2 days	*13 days*	*33 days*			*168 days*			
Mora	0-10	0.452±0.055	0.242±0.031	0.130±0.011			0.012±0.012	18.2	0.0381	0.97
	20-30	0.105±0.059	0.095±0.033	0.053±0.012			0.008±0.007	-	-	
	45-60	0.064±0.050	0.053±0.047	0.012±0.010			ND	-	-	

ND - none detected
° mean of three replicates

TABLE 5. Atrazine residues in soil at different sampling times.

Field	Depth (cm)	Concentrations (mg/kg)°						DT50 (d)	Rate constant K (d-1)	r
		Time after application								
		2 days	*8 days*	*29 days*	*71 days*	*97 days*	*194 days*			
Lardera	0-10	0.966±0.362	0.319±0.072	0.304±0.047	0.082±0.012	0.008±0.001	0.010±0.002	16.5	0.0421	0.95
	20-30	0.165±0.035	0.056±0.042	0.050±0.012	0.014±0.011	0.003±0.001	0.003±0.000	17.8	0.0390	0.88
	45-60	0.041±0.038	0.029±0.020	0.026±0.003	0.005±0.002	0.002±0.000	ND	-	-	
		1 day	*13 days*	*33 days*	*77 days*	*97 days*	*192 days*			
San Giorgio	0-10	0.692±0.376	0.578±0.401	0.256±0.136	0.074±0.018	0.011±0.003	0.011±0.003	17.7	0.0391	0.93
	20-30	0.326±0.247	0.131±0.107	0.074±0.018	0.018±0.014	0.006±0.002	0.006±0.002	17.8	0.0389	0.92
	45-60	0.236±0.171	0.086±0.053	0.063±0.015	0.006±0.002	ND	0.004±0.002	-	-	
		1 day	*10 days*	*23 days*	*60 days*		*161 days*			
Crocina	0-10	0.566±0.086	0.477±0.136	0.234±0.118	0.008±0.002		0.008±0.002	9.2	0.0757	0.98
	20-30	0.130±0.007	0.039±0.024	0.029±0.012	0.004±0.001		ND	12.2	0.0578	0.95
	45-60	0.069±0.029	0.044±0.019	0.013±0.002	ND		ND	-	-	

ND - none detected
° mean of three replicates

TABLE 6. Terbuthylazine residues in soil at different sampling times.

Field	Depth (cm)	Concentrations (mg/kg)°						DT50 (d)	rate constant K (d-1)	r
		Time after application								
		2 days	*8 days*	*29 days*	*71 days*	*97 days*	*194 days*			
Lardera *	0-10	0.332±0.089	0.576±0.203	0.305±0.105	0.120±0.048	0.032±0.009	0.021±0.010	27.2	0.0255	0.91
	20-30	0.036±0.023	0.008±0.001	0.027±0.012	0.021±0.005	0.018±0.026	ND	-	-	
	45-60	0.016±0.006	0.014±0.009	0.006±0.006	0.006±0.002	ND	ND	-	-	
		2 days	*9 ddys*	*29 days*	*65 days*	*90 days*	*187 days*			
Tencara *	0-10	0.644±0.181	0.303±0.093	0.417±0.083	0.164±0.083	0.043±0.014	0.026±0.003	37.1	0.0187	0.92
	20-30	0.042±0.016	0.096±0.114	0.025±0.005	0.013±0.008	0.019±0.013	0.006±0.003	-	-	-
	45-60	0.017±0.008	0.067±0.088	0.013±0.003	0.004±0.004	0.009±0.006	0.002±0.002	-	-	-
		2 days	*9 days*	*29 days*	*65 days*	*90 days*	*187 days*			
Tencara	0-10	0.379±0.135	0.425±0.069	0.362±0.022	0.159±0.032	0.074±0.009	0.028±0.009	26.2	0.0265	0.89
	20-30	0.053±0.028	0.028±0.022	0.051±0.015	0.019±0.018	0.027±0.016	0.009±0.003	-	-	-
	45-60	0.010±0.007	0.015±0.012	0.006±0.005	0.006±0.007	0.012±0.001	ND	-	-	-
		1 day	*13 days*	*33 days*	*77 days*	*97 days*	*192 days*			
San Giorgio	0-10	0.548±0.127	0.332±0.127	0.131±0.038	0.054±0.056	0.025±0.028	0.008±0.001	19.0	0.0364	0.89
	20-30	0.195±0.087	0.076±0.094	0.018±0.010	0.007±0.004	0.005±0.004	ND	29.7	0.0233	0.86
	45-60	0.087±0.075	0.048±0.049	0.006±0.002	0.008±0.002	0.002±0.001	ND	-	-	

ND - none detected
° mean of three replicates
* incorporated to 10 cm

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REFERENCES

Capri, E. (1992) Persistenza dei diserbanti nel terreno. *Tesi di Dottorato*, Biblioteche nazionali di Firenze e Roma, 144 pp.

Del Re, A.A.M.; Capri, E.; Bergamaschi, E.; Trevisan, M. (1991) Herbicide movement and persistence in soil: comparison between experimental data and predictions of a mathematical model. In: *Pesticides in soil and water - current perspectives*, A. Walker (Ed.), *BCPC Mono. No. 47*, BCPC Publications, pp. 213-220.

Natali, P.; Trevisan, M.; Del Re, A.A.M. (1989) L'archivio ResPest-I. In: *VII° Simposio Chimica degli Antiparassitari, Agricoltura ed Informatica*, A.A.M. Del Re (Ed), Lucca: Biagini Edizioni, pp. 111-132.

Trevisan, M.; Capri, E.; Ghebbioni, C.; Del Re, A.A.M. (1991) Field persistence of alachlor in soil and its residues in maize. *Brighton Crop Protection Conference - Weeds* , **2**, 529-536.

Trevisan, M.; Capri, E.; Del Re, A.A.M. (1993) Pesticide soil transport models: model comparisons and field evaluation. *Toxicological and Environmental Chemistry*, in press.

Wauchope, R.D.; Buttler, T.M.; Hornsby, A.G.; Augustijn-Beckers, P.W.M.; Burt, J.P. (1992) The SCS/ARS/CES pesticide properties database for environmental decision-making. *Reviews of Environmental Contamination and Toxicology*, **123**, 1-164.

TABLE 3. Alachlor residues in soil at different sampling times.

Field	Depth (cm)	Concentrations (mg/kg) °						DT50 (d)	rate constant K (d-1)	r
		Time after application								
		1 day	*13 days*	*30 days*			*161 days*			
Palazzina	0-10	2.930±1.213	1.178±0.177	0.550±0.161			0.034±0.019	12.5	0.0556	**0.91**
	20-30	0.554±0.489	0.211±0.132	0.025±0.026			ND	7.2	0.0968	**0.82**
	45-60	0.033±0.010	0.041±0.022	0.005±0.002			0.004±0.004	-	-	-
		2 days	*8 days*	*29 days*	*71 days*	*97 days*	*194 days*			
Lardera	0-10	2.572±0.635	1.126±0.479	0.591±0.044	0.108±0.026	0.011±0.005	0.011±0.000	13.5	0.0515	**0.97**
	20-30	0.423±0.132	0.191±0.128	0.129±0.062	0.041±0.008	0.005±0.001	ND	19.0	0.0364	**0.94**
	45-60	0.113±0.045	0.074±0.053	0.039±0.010	0.002±0.000	ND	ND	-	-	-
		1 day	*13 days*	*33 days*	*77 days*	*97 days*	*192 days*			
San Giorgio	0-10	1.670±0.954	1.359±1.003	0.457±0.326	0.038±0.019	ND	0.022±0.005	13.3	0.0523	**0.97**
	20-30	0.790±0.594	0.178±0.129	0.131±0.058	0.008±0.011	0.013±0.001	0.016±0.002	21.3	0.0326	**0.87**
	45-60	0.552±0.366	0.205±0.138	0.127±0.054	ND	ND	0.040±0.015	-	-	-
		2 days	*13 days*	*33 days*			*168 days*			
Mora	0-10	1.055±0.346	0.881±0.118	0.174±0.051			0.054±0.011	11.4	0.0608	0.93
	20-30	0.322±0.112	0.205±0.115	0.065±0.044			ND	13.1	0.0527	0.87
	45-60	0.047±0.015	ND	ND			ND	-	-	-
		1 day	*10 days*	*23 days*	*60 days*		*161 days*			
Crocina	0-10	1.340±0.386	0.860±0.353	0.254±0.169	ND		0.019±0.013	8.2	0.0843	0.98
	20-30	0.259±0.039	0.062±0.033	0.030±0.009	ND		0.013±0.011	15.4	0.0449	0.87
	45-60	0.146±0.062	0.075±0.028	0.019±0.002	ND		ND	-	-	-

ND - none detected
° mean of three replicates

TABLE 4. Metolachlor residues in soil at different sampling times.

Field	Depth (cm)	Concentrations (mg/kg) °						DT50 (d)	rate constant K (d-1)	r
		Time after application								
		1 day	*13 days*	*30 days*			*161 days*			
Palazzina	0-10	0.732±0.167	0.536±0.207	0.313±0.013			ND	22.8	0.0304	0.77
	20-30	0.131±0.044	0.121±0.039	0.011±0.009			ND	-	-	-
	45-60	0.027±0.018	0.033±0.031	0.029±0.050			ND	-	-	-
		2 days	*9 days*	*29 days*	*65 days*	*90 days*	*187 days*			
Tencara	0-10	0.716±0.165	0.352±0.119	0.290±0.045	0.048±0.018	0.009±0.008	ND	14.9	0.0464	0.94
	20-30	0.035±0.006	0.110±0.162	0.014±0.002	0.036±0.063	ND	ND	20.3	0.0341	0.84
	45-60	0.018±0.008	0.079±0.106	0.011±0.003	ND	ND	ND	-	-	-
		1 day	*10 days*	*23 days*	*60 days*		*161 days*			
Crocina	0-10	0.970±0.095	0.724±0.205	0.432±0.203	0.035±0.013		0.028±0.020	11.8	0.0588	0.97
	20-30	0.628±0.126	0.077±0.026	0.037±0.011	0.018±0.002		0.014±0.010	14.1	0.0490	0.82
	45-60	0.118±0.012	0.049±0.021	0.031±0.013	0.009±0.007		0.004±0.002	-	-	
		2 days	*13 days*	*33 days*			*168 days*			
Mora	0-10	0.452±0.055	0.242±0.031	0.130±0.011			0.012±0.012	18.2	0.0381	0.97
	20-30	0.105±0.059	0.095±0.033	0.053±0.012			0.008±0.007	-	-	
	45-60	0.064±0.050	0.053±0.047	0.012±0.010			ND	-	-	

ND - none detected
° mean of three replicates

TABLE 5. Atrazine residues in soil at different sampling times.

Field	**Depth** (cm)	**Concentrations (mg/kg) °**						**DT50** (d)	**Rate constant K** (d-1)	**r**
		Time after application								
		2 days	*8 days*	*29 days*	*71 days*	*97 days*	*194 days*			
Lardera	0-10	0.966±0.362	0.319±0.072	0.304±0.047	0.082±0.012	0.008±0.001	0.010±0.002	16.5	0.0421	0.95
	20-30	0.165±0.035	0.056±0.042	0.050±0.012	0.014±0.011	0.003±0.001	0.003±0.000	17.8	0.0390	0.88
	45-60	0.041±0.038	0.029±0.020	0.026±0.003	0.005±0.002	0.002±0.000	ND	-	-	-
		1 day	*13 days*	*33 days*	*77 days*	*97 days*	*192 days*			
San Giorgio	0-10	0.692±0.376	0.578±0.401	0.256±0.136	0.074±0.018	0.011±0.003	0.011±0.003	17.7	0.0391	0.93
	20-30	0.326±0.247	0.131±0.107	0.074±0.018	0.018±0.014	0.006±0.002	0.006±0.002	17.8	0.0389	0.92
	45-60	0.236±0.171	0.086±0.053	0.063±0.015	0.006±0.002	ND	0.004±0.002	-	-	-
		1 day	*10 days*	*23 days*	*60 days*		*161 days*			
Crocina	0-10	0.566±0.086	0.477±0.136	0.234±0.118	0.008±0.002		0.008±0.002	9.2	0.0757	0.98
	20-30	0.130±0.007	0.039±0.024	0.029±0.012	0.004±0.001		ND	12.2	0.0578	0.95
	45-60	0.069±0.029	0.044±0.019	0.013±0.002	ND		ND	-	-	

ND - none detected
° mean of three replicates

TABLE 6. Terbuthylazine residues in soil at different sampling times.

Field	**Depth** (cm)	**Concentrations (mg/kg) °**						**DT50** (d)	**rate constant K** (d-1)	**r**
		Time after application								
		2 days	*8 days*	*29 days*	*71 days*	*97 days*	*194 days*			
Lardera *	0-10	0.332±0.089	0.576±0.203	0.305±0.105	0.120±0.048	0.032±0.009	0.021±0.010	27.2	0.0255	0.91
	20-30	0.036±0.023	0.008±0.001	0.027±0.012	0.021±0.005	0.018±0.026	ND	-	-	
	45-60	0.016±0.006	0.014±0.009	0.006±0.006	0.006±0.002	ND	ND	-	-	
		2 days	*9 ddys*	*29 days*	*65 days*	*90 days*	*187 days*			
Tencara *	0-10	0.644±0.181	0.303±0.093	0.417±0.083	0.164±0.083	0.043±0.014	0.026±0.003	37.1	0.0187	0.92
	20-30	0.042±0.016	0.096±0.114	0.025±0.005	0.013±0.008	0.019±0.013	0.006±0.003	-	-	-
	45-60	0.017±0.008	0.067±0.088	0.013±0.003	0.004±0.004	0.009±0.006	0.002±0.002	-	-	-
		2 days	*9 days*	*29 days*	*65 days*	*90 days*	*187 days*			
Tencara	0-10	0.379±0.135	0.425±0.069	0.362±0.022	0.159±0.032	0.074±0.009	0.028±0.009	26.2	0.0265	0.89
	20-30	0.053±0.028	0.028±0.022	0.051±0.015	0.019±0.018	0.027±0.016	0.009±0.003	-	-	-
	45-60	0.010±0.007	0.015±0.012	0.006±0.005	0.006±0.007	0.012±0.001	ND	-	-	-
		1 day	*13 days*	*33 days*	*77 days*	*97 days*	*192 days*			
San Giorgio	0-10	0.548±0.127	0.332±0.127	0.131±0.038	0.054±0.056	0.025±0.028	0.008±0.001	19.0	0.0364	0.89
	20-30	0.195±0.087	0.076±0.094	0.018±0.010	0.007±0.004	0.005±0.004	ND	29.7	0.0233	0.86
	45-60	0.087±0.075	0.048±0.049	0.006±0.002	0.008±0.002	0.002±0.001	ND	-	-	

ND - none detected
° mean of three replicates
* incorporated to 10 cm

THE FIELD LEACHING BEHAVIOUR AND SOIL DISSIPATION OF DE-535

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ABSTRACT

Laboratory soil studies with haloxyfop-R methyl and racemic haloxyfop-methyl have shown that the ester hydrolyses rapidly to the acid, which then undergoes further degradation to 3-chloro-5-trifluoromethyl-2-pyridinol. The leaching behaviour and soil dissipation of haloxyfop-R methyl and both metabolites have been studied under field conditions in northern Germany. DE-535 (haloxyfop-R methyl) was applied in the autumn at normal field rate to bare sandy soil plots. Soil cores were taken to a depth of 2 metres at intervals up to 8 months after application. Cores were segmented prior to analysis. Soil residues of haloxyfop-methyl and both metabolites were determined using an analytical procedure validated to 0.5 and 0.1 μg/kg respectively. Study design and soil residue data are discussed, together with the results of subsequent computer modelling used to calculate concentrations of haloxyfop in soil and soil solution.

INTRODUCTION

DE-535 is a post-emergence herbicide for use in broad-leaved crops to control annual and perennial grasses. The active ingredient is the resolved R-isomer of haloxyfop-methyl.

Laboratory and field studies on the transformation and persistence of aryloxyphenoxy propionic acid esters in soil show that the carboxylic acid forms rapidly under moist, aerobic conditions (Martens, 1978; Smith, 1985a; Smith, 1985b; Negre et al., 1986). Further hydrolysis occurs with the formation of a phenetole, phenol or, in the case of haloxyfop, a pyridinol metabolite (Swann and Hertel, 1984 and McGibbon, 1990).

The leaching behaviour and soil dissipation of haloxyfop-methyl, haloxyfop acid and 3-chloro-5-trifluoromethyl-2-pyridinol (pyridinol) have recently been studied under field conditions. The study was designed to establish the fate of these compounds under "worst case" conditions of autumn application, high rainfall and free-draining bare soil. Soil cores were taken to a depth of 2m using a contamination-free telescopic sampling device. Core segments were analysed using a procedure capable of detecting haloxyfop and pyridinol residues at or below 0.1 μg/kg and haloxyfop-methyl at 0.5 μg/kg. As part of a continuing modelling exercise, the Pesticide Root Zone Model was used to predict concentrations of haloxyfop through the soil profile. Measured soil properties, rainfall and half-life values obtained from the field experiment were used to predict the probability of residues occuring in soil and soil solution. These data were then compared with the observed soil residues.

EXPERIMENTAL

Field Trial

Three criteria were used for the selection of the trial site; a) soil type and uniformity of composition to 2m depth, b) a water table below 5m and c) rainfall at the upper limit for oilseed rape. An on-site Clima Thiess weather station was installed to continuously capture data on precipitation, air and soil temperatures. Trial details were as follows:

Location : Kolshorn, 10km East of Hannover in Germany.

Soil : 70 - 80% sand from 0 - 75cm then 85 - 90% sand to 2m. Clay content 5 - 10% and 1.1% organic matter from 0 - 38cm. pH 5.9.

Application : the soil was ploughed and rolled 3 days pre-application to provide a uniform surface. Replicated bare soil plots (4 x 2.5m x 60m) were sprayed at 0.5 l/ha with an EC formulation of DE-535 containing 108g AI/l haloxyfop-R methyl on October 1 1992. The herbicide was applied using an Agrartest plot sprayer, equipped with a 14l tank and mounted on a bicycle wheel. The 2.5m boom was fitted with five flat fan Lechler LU 120-05 nozzles, separated by a distance of 50cm.

Soil cores were taken to a depth of 2m at the following intervals; -1, 0, 7, 14 days and 1, 2, 3, 5, and 8 months after treatment. Five replicate soil cores were removed from each plot in successive 12cm increments (segments) at each interval. The 2m telescopic Humax corer (8cm dia.) used for sampling was fitted with acetate liners to protect the cores from contamination. Pre-tests with fluoroscein verified that the sampling procedure did not cause contamination of lower horizons. Soil cores were frozen on the day of sampling and maintained at or below -18°C prior to analysis.

Analytical

Core segments from the 0 - 100cm zone were allowed to thaw and the 20 replicates passed through a 2mm sieve before bulking together. The 1 - 2m portions of the cores were left undisturbed, pending analysis of the upper horizons. Duplicate portions of the homogenised field-moist samples were analysed using a multi-residue procedure, having lowest validated levels for haloxyfop-methyl, haloxyfop and pyridinol of 0.5, 0.1 and 0.1 μg/kg respectively. Samples were extracted with acidified acetone and extracts subjected to liquid-liquid and solid phase clean-up prior to analysis using gc/ms with mass selective or electron capture detection. The instrumental procedure utilises internal standards to compensate for detector response enhancement caused by the sample matrix.

Modelling

PRZM-2 (Mullins et al., 1992) was used to predict haloxyfop soil concentrations in increments through the soil profile. In the first run, specimen values for the soil half-life of haloxyfop and Koc provided the chemical inputs, taken together with measured soil properties and climatic data for the trial site. Koc values were allowed to vary within defined limits. For the second run, the measured soil half-life from the field study was input. A lower Koc value, typical of a sandy loam, was also input. In the third run, the soil properties and measured half-life were varied ±10%. In all cases, field capacity (FC), bulk density (BD) and wilting point (WP) inputs were calculated from the soil properties. FC, BD and organic carbon values were allowed ±10% variation in each run, while WP was kept constant. 1000 and 25000 simulations were conducted for runs 1 and 3 respectively, while a single simulation was performed for run 2 to allow comparison with the measured data. The modelled data were analysed with a Monte Carlo shell to give the probability distribution of dissolved herbicide concentration at 1m depth. Chemical inputs used in each run are summarised in Table 1. No estimates were attempted for the pyridinol metabolite.

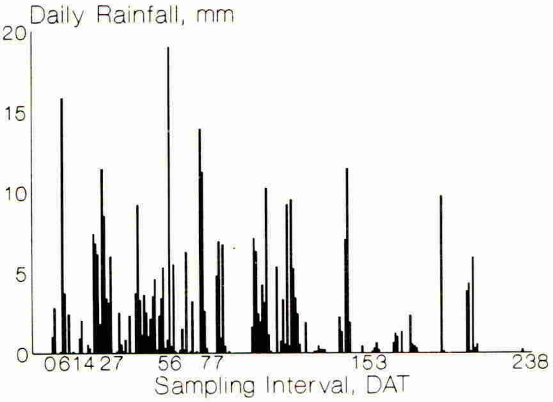
TABLE 1. Chemical values used for PRZM-2 modelling

	Half-life values for each horizon, days				
Run No.	0 - 38	38 - 112	112 - 176	176 - 200,cm	K_{oc} (range)
1	50	100	150	150	180 (10-350)
2	7.6	12	18	18	30 (10-30)
3	7.6	12	18	18	30 (10-30)

RESULTS AND DISCUSSION

Average monthly rainfall for the 4 month period following application was 76mm. This value is 27% above the Hamburg 30-year average for the autumn period. The late winter and spring periods were much drier than average. The daily rainfall pattern is shown in Figure 1.

Figure 1. Kolshorn site rainfall



Analysis of the 0-12cm and 12-25cm soil horizons showed that haloxyfop-R methyl hydrolysed very rapidly, such that 83% conversion to the acid form was observed in the day 0 soil. Haloxyfop also dissipated rapidly in these horizons (Table 2), following first order kinetics, with a calculated half-life of 7.6 days ($r^2 = 0.936$). The DT90 value was 84 days. Pyridinol residues in the upper two horizons increased to a maximum of approximately 4 µg/kg five months after application (Table 3).

TABLE 2. Residue profile of haloxyfop in loamy sand

Soil Horizon, cm	Haloxyfop Residues, ug/kg									
	-1	0	6	14	27	56	77	152	236	DAT
0 - 12	0.30	25.50	13.00	6.00	3.60	1.25	1.55	0.75	0.84	
12 - 25	0.36	0.42	1.22	0.56	1.65	1.20	0.84	0.48	0.72	
25 - 38	0.27	N.a	0.39	N.a	0.48	0.35	0.53	0.28	0.52	
38 - 50	<0.1	N.a	<0.1	N.a	<0.1	<0.1	<0.1	<0.1	<0.1	
50 - 62	<0.1	N.a	<0.1	N.a	<0.1	<0.1	<0.1	<0.1	<0.1	

TABLE 3. Residue profile of pyridinol in loamy sand

Soil Horizon, cm	Pyridinol Residues, ug/kg									
	-1	0	6	14	27	56	77	152	236	DAT
0 - 12	1.05	0.90	1.85	3.00	3.10	3.80	3.40	3.50	2.57	
12 - 25	0.57	0.92	0.85	0.94	1.90	2.40	2.10	4.05	2.37	
25 - 38	0.98	N.a	0.98	N.a	0.80	0.84	0.82	1.80	0.87	
38 - 50	0.26	N.a	0.21	N.a	0.18	0.22	0.18	0.20	0.24	
50 - 62	0.11	N.a	<0.1	N.a	<0.1	0.10	0.10	0.10	0.10	
62 - 75	<0.1	N.a	<0.1	N.a	<0.1	<0.1	<0.1	N.D	<0.1	

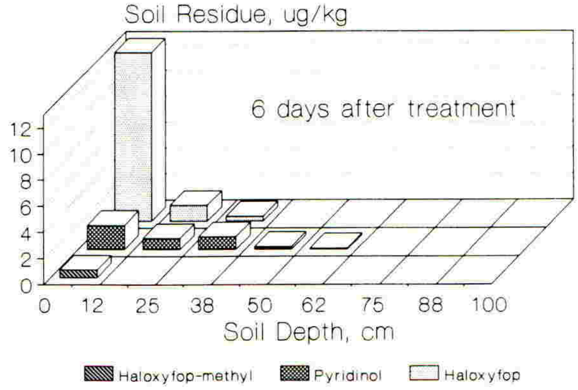
N.D Not detected
N.a Not analysed

<u>Note</u>. Haloxyfop residues in the three horizons analysed between 62cm and 100cm were always below the validated limit of 0.1 µg/kg. No pyridinol residues (N.D) were detected below 75cm in the soil profile at any time.

No haloxyfop-methyl or haloxyfop residues exceeding 0.1 μg/kg were found in any horizon sampled below 38cm at any time. Pyridinol residues in the range 1.0 - 0.1 μg/kg were found in the horizons between 38 and 62cm, although these values are similar to background levels found in pre-application samples. No pyridinol residues were detected between 75 and 100cm. Since two residue-free horizons were found below 75cm, samples obtained below 1m were not analysed.

Soil cores taken 6 DAT were sampled within 24 hours of 16mm rainfall. The vertical distribution of residues found in the soil profile following this event is shown in Figure 2, which illustrates the lack of downward mobility of parent compond or metabolites, even under these severe conditions.

Figure 2. Residues in loamy sand profile



Results of the preliminary modelling calculation, using a half-life of 50 days, (run 1) indicated that there would be a 15% chance of dissolved concentrations exceeding 0.1 μg/l at 1m depth. When the measured half-life value of 7.6 days was input (runs 2 and 3) the probability fell to 6%. Comparison of the measured and calculated soil residue data showed a good match, indicating that PRZM-2 was adequately predicting the behaviour of haloxyfop residues. Mean daily dissolved concentrations in the soil profile were calculated from the maximum and minimum values obtained in the 25000 Monte Carlo simulations. The mean haloxyfop concentration at 100cm depth was 0.018 μg/l (standard deviation 0.05, range 0.00 - 0.61 μg/l).

Interpretation of the modelling data should be tempered with a degree of caution. Firstly, the hydrology of the field site during the trial period was not measured and therefore could not be compared with that calculated by the model. Secondly, the PRZM model assumes a constant rate of degradation throughout the simulation, with no correction for variations in soil temperature and moisture. This results in removal of material from the system which would otherwise be available for leaching.

CONCLUSIONS

The mobility of haloxyfop-R methyl, haloxyfop and its pyridinol metabolite was studied under "worst case" leaching conditions, ie. application of DE-535 to bare sandy soil, followed by autumn rainfall in excess of the Hamburg 30-year average. Despite these severe conditions, neither haloxyfop nor its pyridinol metabolite were found below 38cm and 62cm respectively in the soil profile at concentrations above the validated limit of determination of 0.1 μg/kg.

Using measured rainfall, half-life value and soil properties of the loamy sand, probability modelling predicted that the likelihood of haloxyfop exceeding a soil solution concentration of 0.1 μg/l at a depth of 1m is extremely low. The modelling to date represents only a first attempt to interprete the field study data and efforts will continue, with the aim of obtaining a realistic estimate of likely groundwater concentrations following normal agricultural use of DE-535.

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REFERENCES

Martens, R. (1978) Degradation of the herbicide [^{14}C]-diclofop-methyl in soil under different conditions. Pesticide Science, **9**, 127-134.

Mullins, J.A.; Carsels, R.F.; Scarborough, J.E.: Ivery, A.M. (1992) PRZM-2 User Manual, Version 1.0, Environmental Research Laboratory., Office R&D., USEPA.

Negre, M.; Gennari, M.; Cignetti, A.; Zanini, E. (1988) Degradation of fluazifop-butyl in soil and aqueous systems. Journal of Agricultural and Food Chemistry, **36**, 1319-1322.

Smith, A.E. (1985a) Transformation and persistence of the herbicide [^{14}C] haloxyfop-methyl in soil under laboratory conditions. Journal of Agricultural and Food Chemistry, **33**, 972-976.

Smith, A.E. (1985b) Persistence and transformtion of the herbicides [^{14}C] fenoxaprop-ethyl and [^{14}C] fenthiaprop-ethyl in two prairie soils under laboratory and field conditions. Journal of Agricultural and Food Chemistry, **33**, 483-488.

Swann, R.L.; Hertel, J.A. (1984) Aerobic soil degradation of haloxyfop-methyl ester. McGibbon, A. (1990) The soil column leaching characteristics of haloxyfop-R methyl ester. Unpublished research reports. DowElanco Europe, Letcombe Regis, Oxfordshire, OX12 9JT.

SULFONYLUREAS AND QUINCLORAC DEGRADATION IN WATER

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ABSTRACT

Using a tomato seedling bioassay, several sulfonylureas (bensulfuron, chlorsulfuron, cinosulfuron, primisulfuron, triasulfuron and tribenuron) and quinclorac can be detected at µg/l levels in water. Tap water , a proprietary mineral water , and Albufera Lake water were used to study herbicide persistence under three environmental storage conditions (open air, growth chamber at 25°C, and a cold room at 4°C).

Sulfonylureas and quinclorac were shown to persist in water, at the bioassay detection levels,for periods exceeding four months depending on the storage condition.

INTRODUCTION

The sulfonylureas are a very highly active group of chemicals (application rates 10-100 g AI/ha). Several sulfonylureas including chlorsulfuron, tribenuron and triasulfuron, are used in cereal crops in temperate regions.

The rice fields in the Valencia region are linked to the Albufera Lake, which serves for irrigation and drainage purposes. The sulfonylureas bensulfuron and cinosulfuron and the quinolinecarboxylic acid quinclorac are three new herbicides for rice growing areas. The herbicide treatments in rice are conducted over a very short period of time. Consequently concentrations in the surface water canals are very variable and high during certain periods.

The use of this water has caused phytotoxicity in vegetable crops, particularly tomatoes, in adjacent areas, (Gómez de Barreda et al., 1993). It is considered that quinclorac is the product most responsible for damage and a local law bans the use of this chemical in the rice fields of Valencia.

The vapour pressure of many sulfonylureas is very low, particularly bensulfuron and cinosulfuron, which are in the order of 10^{-14} mm Hg at 25°C. Quinclorac is greater, in the order of 10^{-7} mm Hg. Therefore, it is possible that differences in volatilisation between sulfonylureas and quinclorac lead to different pathways of dissipation.

Several authors (Kashibuchi et al., 1990; Yuyma et al., 1988)have cited that the persistence of bensulfuron, cinosulfuron and quinclorac in soil is very low, in the order of weeks, particularly in humid rice field soils. The purpose of the work reported here was to study the persistence of biological activity of sulfonylureas and quinclorac in water.

MATERIALS AND METHODS

Biological activity of herbicides in water was measured using a slight modification of the procedure described by Gómez de Barreda and Lorenzo (1991). Ten tomato seeds were placed in paraffin film-wrapped Petri dishes containing 10 ml of herbicide solution previously stored under various conditions. After 7 to 8 days in a growth chamber, the seedling main root length was measured to the nearest mm. The results were always calculated using three replicate dishes of 10 seedlings per treatment.

Herbicide persistence was measured using three types of water: tap, proprietary mineral and Albufera Lake water. The first two can be considered to have low microbiological activity. The Albufera water was sampled long before the rice herbicide treatment period.

Herbicide solutions were stored in glass bottles under the following environmental conditions:

open air: water situated outside a laboratory window, orientated towards the sun. Some bottles were wrapped with aluminium foil, to prevent photodecomposition;bottles were also stored both open and closed.

chamber at 25°C: the average temperature of the Albufera Lake during the main herbicide application period in July and August. The chamber characteristics were: 100 $\mu Em^{-2}s^{-1}$, 16/8h light/dark.

cold room in the dark, at 5°C: to simulate temperature conditions that can be reached in the cereal belt.

RESULTS

In previous non reported work it was observed that the bioassay with propietary mineral water produced more precise results than with the tap water for different dates.Also the response (length of the tomato seedling main root) with the mineral water was closer to the Albufera water than to the tap water.Therefore the propietary mineral water was used in many of the experiments,particularly in those with the Albufera water, as a control source. A trial with the three sources of water without herbicide, seven days in the growth chamber, gave the following data: 85.9 ± 8.0 (propietary mineral), 80.5 ± 9.9 (Albufera Lake water) and 69.6 ± 8.4 (Moncada tap water). The values are averages in mm, (mean of 3 petri dishes ± standard deviation).

Results are represented in Tables 1-5.

TABLE 1. Length of main root as % of control, (tap water)

–	bensulfuron		cinosulfuron		quinclorac	
	DAS					
	8	120	8	120	8	120
Cold room 5°C	16	15	19	15	20	19
Gr.chamber 25°C	17	14	19	14	24	16
Open air	18	74	18	68	23	91

DAS = days after start.

Table 1 shows the effect of storage conditions on herbicide activity in tap water with an initial concentration of 100 μg/l. Herbicide degradation in open air conditions was very limited by eight days after start (DAS), but was extensive after 120 days. In the other two storage treatments (cold room and growth chamber) the herbicide activity remained very high, even after 120 DAS. These results were confirmed, following storage for one year (Table 2).

TABLE 2. Length of main root as % of control one year after start,(tap water).

	bensulfuron	cinosulfuron	quinclorac
Cold room 5°C	20	24	21
Growth chamber 25°C	17	24	23

Table 3 shows degradation with time in the Albufera water, treated with three chemicals at 100 μg/l and stored under four regimes. After 44 days all the chemicals remained active under the four regimes but after 212 days the results were very different between herbicides and storage conditions. In the open air without the aluminium foil wrapping, cinosulfuron was degraded faster than either bensulfuron or quinclorac. The response to temperature was very important for bensulfuron and cinosulfuron, but not for quinclorac.

TABLE 3. Length of main root as % of control, (Albufera Lake water).

	bensulfuron		cinosulfuron		quinclorac	
	DAS					
	44	212	44	212	44	212
Cold room 5°C	18	13	24	18	51	53
Gr. chamber 25°C	18	73	26	69	47	18
Open air with alum.foil	20	16	21	21	48	27
Open air without alum.foil	22	32	24	83	45	54

DAS = days after start

Table 4 shows results after five months storage under sunlit conditions for open and closed bottles initially containing 100 $\mu g/l$ bensulfuron and quinclorac, with the Albufera Lake water.

The response of bensulfuron was quite variable depending on storage conditions. Photodecomposition was important for this chemical. The quinclorac behavior is less clear.

TABLE 4. Mean length of the main root in mm ± standard deviation, (Albufera Lake water).

	Storage condition			
	Covered with alum.foil		Without alum.foil	
	Bottle			
	Open	Closed	Open	Closed
Bensulfuron	17.5±1.5	21.6±0.9	21.9±1.3	47.3±4.9
Quinclorac	44.5±5.8	44.1±8.6	41.0±5.6	52.5±5.1

Table 5 shows the response to six sulfonylureas at an initial concentration of 100 $\mu g/l$ stored under two regimes. The root growth reduction was generally greatest in the case of bensulfuron and chlorsulfuron, and least with primisulfuron, cinosulfuron and tribenuron. Between 30 days and 100 days of cold room storage, there was little loss in activity of the six sulfonylureas, but at 25°C there was significant degradation for all except bensulfuron and chlorsulfuron and degradation was particularly marked, in the case of tribenuron.

TABLE 5. Mean length of the main root in mm ± standard deviation, (tap water).

	1 DAS	30 DAS		100 DAS	
	lab.t^c	4°C	25°C	4°C	25°C
bensulfuron	16.8±1.5	16.9±0.6	21.4±0.8	17.8±0.9	21.5± 2.4
cinosulfuron	25.2±3.0	20.3±1.0	21.8±3.2	22.5±0.2	26.8± 1.5
chlorsulfuron	16.0±3.5	15.2±1.1	18.4±4.0	15.6±2.2	17.9± 0.5
primisulfuron	28.6±3.5	26.4±0.4	29.3±1.3	35.2±5.6	39.9± 0.7
tribenuron	22.6±0.9	22.6±2.7	46.3±3.6	26.1±2.2	120.6±10.9
triasulfuron	20.7±1.7	18.8±4.4	22.6±2.9	19.6±3.8	26.4± 4.5

DAS = days after start; lab. t^c = laboratory temperature.

CONCLUSIONS

Sulfonylurea and quinclorac activity in water continue for longer periods than may be desirable. This is particularly so under low temperature conditions and -for some compounds in the absence of photodecomposition.The source of water also influences the rate of chemical dissipation.

Photodegradation is more important for cinosulfuron than bensulfuron.

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REFERENCES

Gómez de Barreda, D.; Lorenzo, E., (1991) Bensulfuron and quinclorac detection in soils and water. *Brighton Crop Protection Conference- Weeds 1991,* 515-520.

Gómez de Barreda, D.; Lorenzo E.; Carbonell, E.A.; Cases, B.; Muñoz, N. (1993) Use of Tomato (Lycopersicon esculentum) Seedlings to Detect Bensulfuron and Quinclorac Residues in Water. *Weed Technology,* **7**,376-381.

Kashibuchi, D.H.; Rosebrock, H.; Beck, J. (1990) Behaviour of quinclorac in soils. Results of bioassay. *Proceedings of the IIth Asian Pacific Weed Science Society Conference,* 173-178.

Yuyma, T.; Ackerson, R.C.; Takeda, S.; Watanabey, N. (1988) Soil and water relationships on the behaviour of bensulfuron methyl (DPXV 5384) under the paddy field condition. *Weed Research Japan* **32**,282-191.

THE TRANSPORT OF PESTICIDE RESIDUES TO SURFACE WATERS IN SMALL CLAY-BASED CATCHMENTS

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ABSTRACT

The fate of seven commonly applied pesticides was investigated in ten small predominantly agricultural, clay-based catchments ranging in area from a few hectares to 15 km². All sites provided the opportunity to assess the loss to surface waters from relatively impermeable clay soils. Three of the sites were representative of land converted from agricultural use under the MAFF set-aside policy. The inputs from diffuse agricultural loss and point source inputs were targeted separately, where appropriate. The pesticides studied comprised six herbicides which are used widely in the UK and have been found in river systems together with one insecticide. All catchments were instrumented to include a range of hydrological monitoring facilities and automatically triggered water samplers. Whenever possible, detailed records of agrochemical usage and cropping were collected. This paper reviews the pesticide concentrations observed and assesses the importance of pesticide loss from clay soils together with changing weather patterns. The likely source of some of the pesticides studied is also discussed.

INTRODUCTION

In recent years, pesticide residues have been identified in many surface waters (Lees & McVeigh, 1988) with detections above the EC Drinking Water Directive Maximum Admissible Concentration (MAC) of 0.1 µg/l for any single pesticide in potable water (Anon, 1980). In rural areas, there is a potential for pesticide losses from agricultural and non-agricultural areas to interact. Increasing catchment diversity, and a trend towards catchment management planning for water usage and quality, has made it essential that pesticide losses are defined and that the transport mechanisms are more fully understood.

A range of catchments was established in the main UK arable areas in order to examine pesticide residues in raw river water and to identify sources of leaching. This paper describes the experimental study undertaken and reviews the influence of weather and land use on the loss of pesticides to surface waters. The frequency of detection, and the likely sources, of the pesticide residues are discussed.

EXPERIMENTAL METHODOLOGY

Sites

Ten clayland catchments with different land uses were established (Table 1). All sites except Horsham had permanent pipe drainage systems together with mole drainage or subsoiling, although the extent of drainage was variable. The Swavesey site had the most extensive drainage (Harris et al., 1991) whereas at Horsham, in the absence of artificial drainage, excess water from the site was removed over the soil surface. At all sites except Trent-PK, records of land use and, whenever possible, pesticide usage were determined from management records supplied by farmers. In the arable areas, winter wheat was often the dominant crop. Conington CN1 and Horsham were both totally arable prior to conversion to permanent set-aside in the autumns of 1988 and 1991 respectively (Harris et al., 1992a). At Conington-CN2, 40% of the area remained as arable until converted to set-aside in autumn 1989. Trent-LS and Swavesey-CFD included small village developments, whereas Trent-PK and North Weald-NWD included substantial runoff from urban areas.

TABLE 1 Catchment details, mean rainfall given for 1941 - 1970 period. (G=grass, A=arable, W=woodland, S=set-aside, U=urban). Soil types as found in whole catchment.

Main site	Sub site	Area (ha)	Rain (mm)	Land use	Catchment soil groups
(1) North Weald (Essex)	NWA	160	650	G,A,W	Stagnogley
	NWD	310		G,A,W,U	
(2) Trent (Leics)	LS	250	697	G,A,U	Brown earth/stagnogley
	CL	110		G,A	
	PK	1500		G,A,U	
(3) Swavesey (Cambs)	CFD	500	574	G,A,U	Stagnogley/
	HFD	280		G,A,U	alluvial gley
(4) Conington (Cambs)	CN1	20	574	A,S	Stagnogley/
	CN2	30		A,S	calcareous pelosol
(5) Horsham (Sussex)	HM	4	778	A,S	Stagnogley

Hydrology

Rainfall and runoff were continuously monitored on all sites; the runoff was measured by sharp-crested weirs or flumes designed to BS 3680 (BSI, 1981). The effect of sub-surface drainage was monitored at the sites in Cambs. and Sussex by automatic water level recorders or dipwells. However, in the Trent and North Weald catchments, the drainage effect was assessed from crop performance and field observations.

Water sampling

The method of water sample collection described by Harris et al. (1991) for the Swavesey catchment was, in so far as practical, uniform across all sites. Although some samples were collected manually, programmable samplers, triggered automatically and linked to data loggers, enabled sampling to be accurately targeted. Sampling was generally concentrated at catchment outlets, near to the area of pesticide application, but was supplemented by samples from other key points.

The active ingredients selected for analysis were initially the same for all catchments. These were the aryloxyalkanoic acid herbicide mecoprop, the urea herbicides isoproturon, chlorotoluron and linuron, the triazine herbicides atrazine and simazine, and the organophosphorus insecticide dimethoate. In later years, efforts were concentrated on the two triazines and the ureas, isoproturon and chlorotoluron.

Pesticide residue analysis

Samples were analysed as non-filtered and detection limits at the EC MAC (0.1 µg/l) were obtained for all chemicals except mecoprop. Detection limits for mecoprop were more variable in the range 0.2-0.5 µg/l. The analyses were performed using high performance liquid chromatography, gas chromatography and mass spectrometry techniques as appropriate; the extraction, analysis and confirmation procedures adopted are described by Harris et al. (1991). These procedures were undertaken together with analytical quality assurance measures which included storage stability experiments. As two laboratories were involved in the analysis of samples from N. Weald, additional separate quality control procedures were involved including inter-laboratory checks.

RESULTS

Pesticide usage

Pesticide applications were almost exclusively to arable crops. As expected, applications tended to be crop specific, so that areas receiving a particular pesticide were dependent on the crop rotation in the area. Increases in the area of peas, beans and oilseed rape were observed in some catchments during the study period; as a result simazine applications to bean crops increased. The detailed monitoring undertaken at Swavesey showed that some spot and whole field applications of mecoprop were made to problem grassland. Pesticides, applied regularly in autumn and spring, included a wide range of active ingredients. The majority of the pesticides targeted for analysis were applied in at least one year, with mecoprop and isoproturon used widely. Application data, where available, are given for mecoprop and isoproturon (Table 2) and for simazine and chlorotoluron (Table 3).

Hydrology

Total runoff between sites and years varied considerably; the prolonged dry weather from autumn 1990 to 1992 reduced runoff so that, in East Anglian sites in particular, opportunities for water sampling were restricted. In this period, only the Trent catchments received sufficient rainfall to result in substantial runoff events. At Swavesey, where weather patterns were similar to those experienced at Conington, North Weald and Horsham, underdrainage increased the depth to the watertable by an average 250mm. However, due to the exceptionally low rainfall, a watertable was not recorded until late winter in several years. Despite the dry weather, a reduced depth to the watertable and enhanced peak runoff were identified after several years of set-aside at Conington (Harris et al., 1992a).

TABLE 2 Catchment (%) receiving mecoprop (CMPP) and isoproturon (IPU)

Harvest Year	1988		1989		1990		1991		1992	
	CMPP	IPU	CMPP	IPU	CMPP	IPU	CMPP	IPU	CMPP	IPU
Swavesey CFD	30	34	17	23	21	20	17	25	23	28
N.Weald NWA	-	-	-	-	-	-	0	22	6	40
Conington CN1	100	0	Set-aside (No applications)---------------->							
Conington CN2	57	57	Set-aside (No applications)---------------->							
Horsham HM	0	0	100	0	0	0	0	100	0	0

TABLE 3 Catchment (%) receiving simazine (SIM) and chlorotoluron (CHL)

Harvest Year	1988		1989		1990		1991		1992	
	SIM	CHL	SIM	CHL	SIM	CHL	SIM	CHL	SIM	CHL
Swavesey CFD	3	0	2	9	7	10	9	11	0	11
N.Weald NWA	-	-	-	-	-	-	0	17	5	17
Conington CN1	0	0	Set-aside (No applications)---------------->							
Conington CN2	0	0	Set-aside (No applications)---------------->							
Horsham HM	100	0	0	100	0	0	0	0	0	0

Pesticide leaching

Residues of the urea herbicides isoproturon and chlorotoluron were detected in only a few samples in the set-aside catchments at Conington. Most detections were made in the first spring of set-aside or in the first runoff of the following season, the loss representing a flush effect from the soil. The highest concentration detected was 0.2 µg/l for both isoproturon and dimethoate. By spring 1991, no further detections were made with the exception of chlorotoluron on one occasion; this may have arisen from spray drift from adjacent farmland. At Horsham, isoproturon was detected in autumn 1991 in the first year of set-aside, (maximum 0.6 µg/l). By contrast, in the Swavesey HFD and CFD catchments, diffuse losses from agricultural land resulted in detections above the EC MAC for potable water in all years for several of the applied pesticides. This was the case particularly for isoproturon (maximum 8 µg/l, January 1990) and simazine (8 µg/l, April 1990); both were found in nearly 50% of samples taken in the twelve months from April 1989. The highest concentrations detected at Swavesey were in runoff from hard surfaces following heavy spring rainfall and summer thunderstorms; these were identified as point sources arising from farmyard spillages (Harris _et al_., 1991). In these events, mecoprop, simazine and isoproturon were detected at concentrations between 35 µg/l and 240 µg/l in ditches adjacent to farmsteads.

As the Trent catchments were largely unaffected by the dry weather experienced elsewhere, sampling was varied to target the different seasons.

For example, at Trent-LS in 1989/90, the highest detections were made for atrazine (maximum 1.3 µg/l) and chlorotoluron (1.5 µg/l) in winter compared to dimethoate (0.7 µg/l) in summer. In nearby Trent-CL, simazine was detected most frequently (maximum 0.8 µg/l, summer) with occasional peak summer detections for atrazine, dimethoate and mecoprop (0.3 µg/l) and chlorotoluron (0.2 µg/l, winter). In autumn 1990 detections at Trent-LS were confined to atrazine (25% of samples, maximum 3.2 µg/l) and simazine (one detection at 0.2 µg/l). In winter events, detections of autumn applied chlorotoluron and isoproturon were made regularly with isoproturon detected in 80% of samples (2.6 µg/l) and chlorotoluron in 33% of samples (1.1 µg/l). In contrast, all the target pesticides were detected in 1989/90 at the mixed urban/agricultural catchment Trent-PK, with simazine (maximum 0.4 µg/l, summer) and atrazine (3.1 µg/l, summer) seen most frequently. In winter 1990/91 events detections were only made for isoproturon (66% of samples, maximum 0.8 µg/l) and linuron (one sample at 0.3 µg/l).

In winter 1991/92, many of the pesticides were detected regularly at just above the EC MAC for potable water of 0.1 µg/l, the maximum for isoproturon at Trent-LS was 9 µg/l. Pesticides were infrequently detected in the wet autumn 1992.

Results from North Weald were affected by the limited sampling due to the dry weather. As early results showed occasional detections for simazine, atrazine, chlorotoluron and isoproturon only, analyses were subsequently confined to these four herbicides. Detections were fairly frequent in the wetter spring 1992 at both the urban site NWD and agricultural site NWA. For the triazines, the maximum concentrations were found for simazine at 2.3 µg/l (NWD) 0.6 µg/l (NWA). The highest concentration observed in spring 1992 was for chlorotoluron (4.5 µg/l at NWD compared to 3.3 µg/l at NWA).

DISCUSSION AND CONCLUSIONS

Although most of the detections of pesticides were considered to result from diffuse losses following recent applications to agricultural crops, several other sources were identified. For the agricultural areas, a flush of pesticides was detected in the first runoff event following autumn applications. The urea herbicides, isoproturon and chlorotoluron were found frequently along with the triazine simazine. All these active ingredients were applied to autumn and spring crops; an increasing area sown to winter or spring beans receiving simazine was evident in some areas. In contrast, the insecticide dimethoate was detected during summer 1990 at Trent but not during autumn sampling. These results support other findings from primarily agricultural areas; for example, Clarke et al. (1991) reported frequent detections for isoproturon, chlorotoluron, simazine and mecoprop above the MAC for potable water in the Granta catchment in East Anglia. Concentrations in the small catchments reported here (i.e. less than 1500ha) are relevant to agricultural land, close to the area of usage; all catchments were some distance from potable water treatment works. Concentrations were often less than 1 µg/l but peaks of up to 8 µg/l were detected for several pesticides following diffuse loss. In the study, the period of very dry weather reduced the occurrence of surface runoff in some seasons, except in those areas under set-aside or urban development. The low runoff resulted in little loss of pesticides, but equally reduced the opportunity for dilution in larger river systems.

The losses of pesticides recorded under set-aside were relatively small compared to those in managed farmland. However, the presence in particular of the urea herbicide isoproturon at concentrations above the EC MAC for potable water of 0.1 µg/l for a single pesticide gives evidence that losses to surface waters can occur for at least one year after the last application (Harris et al., 1992a).

Point source inputs were evident in both agricultural and urban areas. The losses to surface waters from farmyard spillages, reported by Harris et al. (1991), showed that this could be an important source of chemicals. However, inputs from urban areas, particularly for atrazine, were equally important. Atrazine was detected in many agricultural catchments, its usage almost certainly limited to non-agricultural situations, with the exception of North Weald where a small area of maize in catchment NWA may have received atrazine in 1989. Atrazine contamination of rural watercourses was reported by Harris et al. (1992b) at Swavesey from roadside ditches and from disused railway ballast used as hard-core on field tracks. Approvals for use of atrazine and simazine on non-cropped land were revoked in May 1992.

The results of this study have been brought to the attention of the MAFF Pesticide Safety Directorate in support of the appropriate regulatory action. Future work is concentrating on modelling the transport mechanisms involved to predict the fate of pesticides in surface waters systems.

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REFERENCES

Anon. (1980) EC Council Directive Relating to the Quality of Water intended for human consumption (80/778/EEC). Official Journal of the European Community, No. L229/11-29.

BSI (1981) Methods of measurement of liquid flow in open channels, BS 3680; Part 4A: Weirs and flumes: Thin plate weirs. British Standards Institute, London.

Clarke, L; Gomme, J.; Hennings, S. (1991) Study of pesticides in waters from a chalk catchment in Cambridgeshire. Pesticide Science, 32, 15-33.

Lees, A; McVeigh, K. (1988) An Investigation of Pesticide Pollution in Drinking Water in England and Wales. Friends of the Earth Report, London. pp. 151.

Harris, G.L.; Bailey, S.W.; Mason, D.J. (1991) The determination of pesticide losses to water courses in an agricultural clay catchment with variable drainage and land management. British Crop Protection Conference - Weeds, 1991, 3: 2, BCPC Publications, Farnham, 1271-1278.

Harris, G.L.; Rose, S.C.; Muscutt, A.D.; Mason, D.J. (1992a) Changes in hydrology, pesticides and soil-nitrogen under set-aside. British Crop Protection Council Monograph, No. 50, Set-aside. (Ed.) J. Clarke, BCPC Publications, Farnham, 35-40.

Harris, G.L.; Turnbull, A.B.; Gilbert, A.J.; Christian, D.G.; Mason, D.J. (1992b) Pesticide application and deposition - their importance to pesticide leaching to surface water. British Crop Protection Conference - Pests and Diseases, 2, BCPC Publications, Farnham, 477-486.

BEHAVIOUR AND FATE OF HERBICIDES AND OTHER PESTICIDES APPLIED TO CONTAINER GROWN HARDY ORNAMENTAL NURSERY STOCK (HONS) SYSTEMS WITH OVERHEAD IRRIGATION

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ABSTRACT

Hardy ornamental nursery stock (HONS) is often container grown in systems employing frequent irrigation and considerable applications of nutrients and pesticides. These container systems are often isolated from the underlying soil by an impermeable membrane resulting in near-surface drainage from the beds. An experiment was established to examine the loss of two herbicides and two other pesticides from a peat-based growing medium for HONS. The volume of water passing through the system was measured and samples were taken to determine the concentrations of pesticides present. Peak concentrations were typically in the range 50 to 250 µg/l, but sometimes higher; this is considerably in excess of the limit imposed for pesticides in the EC Drinking Water Directive and could pose a threat to the aquatic environment. Opportunities for remedial measures, including the use of sub-surface irrigation sand beds and re-circulatory irrigation were examined. The implications of alternatives to peat growing media are also discussed.

INTRODUCTION

Although many production methods are used in the container-grown nursery stock industry, most rely on overhead irrigation with a non-water retentive, freely draining, 100mm deep, gravel base forming the standing area of the bed. Some systems provide a break from the underlying soil by use of either a polyethylene or woven polypropylene membrane. This reduces the risk of soil-borne diseases and prevents the invasion of the beds by perennial weeds. However, the membrane also increases the likelihood of drainage water, containing contaminants, rapidly leaving the gravel beds through a central drainage pipe at the base of the bed. Where a more permeable membrane is used some seepage through to the underlying soil profile will occur and may provide some attenuation of the contaminant loss.

To achieve quality HONS, a range of pesticides, including herbicides, are applied during the growing season. There is a potential for rapid loss of these pesticides because the system uses highly porous growing media, gravel beds and considerable overhead irrigation. Some measures, already used by UK growers, might reduce the potential loss of pesticides. These include the use of capillary sandbeds and more carefully-controlled water use and management; these currently represent approximately 20% of HONS beds.

For the majority of growers a comprehensive monitoring of pesticide losses from HONS systems is not practical because pesticide analytical costs are high. To understand the magnitude of the problem it is also essential to know the quantities of drainage water passing through the beds. This can be difficult to ascertain, particularly so where there is no drainage collection system and water movement, together with agrochemical loss, occurs through permeable soils below the bed. However, the current EC Drinking Water Directive (Anon., 1980) means that the quality of our potable water must be protected, with new controls possible by the end of the 1990's.

In spring 1990, a MAFF funded collaborative experiment was established between ADAS, HRI and CSL, MAFF. The objective of the work was to quantify the magnitude of pesticide loss from peat-based growing media in HONS systems and to form recommendations on ways which might reduce this loss. The experimental programme included different methods of irrigation and a pilot re-circulation system. This paper describes the experimental design and data collection and examines the losses of two herbicides and two other pesticides. The significance of the concentrations is discussed together with the long-term implications for the UK horticulture industry.

EXPERIMENTAL DETAILS

The site facility

The unique experimental facility was established in spring 1990 at HRI Efford, Hampshire. Twelve isolated 9m^2 gravel beds were laid out in three blocks and separated from each other by paved access routes. Containers of sphagnum peat-based growing media were irrigated by a central overhead spray line; the irrigation could be applied independently to different beds. Drainage water, following rainfall or irrigation, was monitored as it discharged directly from the bed drainage pipe to a storage tank. The system therefore represented the highest risk HONS situation likely to be experienced with regard to pesticide loss. This was because there was no opportunity for attenuating the pesticide load carried in the drainage water by the intervening soil below the beds or before discharge to surface waters.

Site management

During the first year (1990) all beds were irrigated from overhead to bring the containers close to field capacity (standard irrigation) or at 1.5 times this rate (high irrigation). A split application of fertiliser treatments (including controlled release fertiliser and liquid feed) were also tested alongside the pesticide trial. Mains irrigation was applied direct or after acidification (pH 4.0) with nitric acid to reduce liming deposits on the plants. In the second year, three of the gravel beds were replaced by sand beds to the same depth; sand moisture content was controlled from the base of the bed by a central feeder seep-hose. Other treatments remained the same except that mains irrigation water was applied without acidification. In both years the experimental period extended from June to December; the species used was Chamaecyperis lawsoniana 'Columnaris glauca'.

In the final phase (1992), three further beds were converted to sand and a pilot re-circulatory system added. This involved collecting the discharge from the beds in a darkened polypropylene holding tank, prior to re-application of this water by the seep-hose, as part of the irrigation process. In this phase the species used was Cupressocyparis leylandii.

Hydrological monitoring and water sampling

The hydrological monitoring and water sampling were based on measurements of rainfall and runoff (bed drainflow) dependent on the treatments. On six beds runoff was initially monitored by 0.8 litre volume tipping bucket flowmeters linked to a datalogger. The water was then collected in 120 litre bulk water tanks. The remaining beds had these collector bulk tanks only. A detailed flow-proportional sampling programme was used on two of the beds receiving high irrigation and which were equipped with flow recorders. The two programmable water samplers, previously described by Harris *et al*. (1991), were linked to the datalogger and tipping bucket flowmeter to provide automatic sampling during runoff events. For the remainder, bulk water samples were taken at approximately twice-weekly intervals from the collecting tanks. Manual samples were taken by immersing new 2.5 litre darkened glass bottles into the collection tanks, after the water had been agitated by stirring. Samples were sealed and either transferred to the laboratory within 24 hours of collection, or stored at 4°C prior to transfer to the laboratory for analysis. All tanks were emptied regularly and thoroughly rinsed with mains water between sampling periods.

PESTICIDE ANALYSIS

Active ingredients

Four active ingredients from different generic groups, widely used for HONS production, were either incorporated into the compost or applied after potting. The herbicides chosen were oxadiazon (Ronstar 2G granules - applied at 0.4 g ai/m^2 after potting) followed by an overall spray of simazine (0.11 g ai/m^2) later in the season. In addition, the fungicide furalaxyl (Fongarid - equivalent to 4.27 g ai/m^2) and the organophosphorus insecticide fonofos (Cudgel - equivalent to 3.7 g ai/m^2) were incorporated into the growing media for protection against *Phytophthora* and *Pythium* diseases and vine weevil (*Otiorhynchus sulcatus*) larvae respectively.

Analytical methods

The samples were extracted within 14 days of receipt, using dichloromethane and the extract concentrated and stored in a freezer prior to analysis. All pesticides were determined by gc using a nitrogen-phosphorus detector with identity confirmed by re-analysis of selected extracts using gc-ms. Methods of analysis and quality assurance procedures are described by Harris *et al*. (1991). The reporting limit for the pesticides was 0.1 µg/l in 1990 and 1991; on the basis that most detections exceeded this value, the limit was increased to 1.0 µg/l for 1992 samples to simplify detection methods.

RESULTS

Rainfall - runoff

Rainfall in the study period varied considerably and influenced the need for additional irrigation water. In particular, the first two years were particularly dry with 66% and 64% respectively of the long-term average rainfall (1916-1950) between July and November for the site. In contrast, heavy summer downpours resulted in 185% of the long-term average rainfall for the same period in the third year.

Runoff data for 1990 showed that drainage could be rapid after both natural rainfall and overhead irrigation. Considerable variability was observed between beds, with the highest runoff consistently from beds in the north-east part of the site. Wind funnelling between large greenhouses around the trial was considered to influence input to the beds; (some wind protection was added to the trial at the end of the first year). Typically 15-35% of input (rainfall and irrigation) was recovered as drainage water. In 1991, during irrigation of the three sand beds, the outflow central pipe was blocked off for approximately 24 hours. This saturated the beds. However, although on release of the bung there was no immediate flow, in subsequent rainfall, discharge was rapid. In this year, the highest runoff was from the sand beds (representing 25.5% of input). The high irrigation treatments on gravel beds gave runoff in the range 14-22% compared to 13% of input (rainfall and irrigation) from the standard irrigation treatment. Similar results were seen in 1992; the highest runoff was seen on the sand beds (37% of input) compared to 13-27% for the high and standard irrigation treatments on the gravel beds.

Pesticide losses

Prior to the start of each year's trial, the beds were thoroughly flushed in an attempt to remove any residual pesticides. Oxadiazon and furalaxyl were detected draining from the beds before the trials began; in 1991 low background levels of furalaxyl (maximum 3 µg/l) persisted at the start of the trial. In 1992, however, concentrations of oxadiazon up to 60 µg/l remained after flushing and could have influenced background concentrations detected for this chemical. None of the pesticides under test was found in the mains or acidified water before application. Once the trials were initiated pesticides were detected in most samples above the detection limit. Some of the pesticide concentrations were exceptionally high. To reduce analysis costs, dilutions and repeat analyses were not undertaken for these values; results given provide a good guide to losses.

Pesticides were detected in water samples soon after drainage started. In 1990, oxadiazon was detected in many samples. The highest concentration was 121 µg/l in the first runoff event (21 June, 1990); concentrations in samples from later events were generally in the range 15-50 µg/l. The lowest detection was 15 µg/l in late October. Fonofos was detected at concentrations above 0.1 µg/l in every sample. The peak concentration was 54 µg/l in the first runoff event. Concentrations were typically in the range 15-30 µg/l from July onwards from all beds. Furalaxyl concentrations were even higher (peak 750 µg/l) in the first event and although the concentrations fell over the season they remained higher than for other compounds. The lowest concentration in any sample was 24 µg/l in 1990. Simazine was not applied to the beds until 18 September 1990 and was detected in all samples taken on 21 September in the range 12-19 µg/l, peaking at 40 µg/l in October before falling to less than 5 µg/l by early November 1990.

In 1991, oxadiazon was consistently found, with concentrations generally in the range 10-50 µg/l; the highest concentration detected was 93 µg/l. Simazine was first detected on 10 October 1991 in the first sampling following the application on 1 October. Concentrations frequently exceeded 100 µg/l; the highest concentration detected was 317 µg/I. Furalaxyl was always detected at high concentrations, up to 1000 µg/l at times and only falling below 100 µg/l occasionally. The highest fonofos concentration was 72 µg/l but generally <20 µg/l and often <10 µg/l. Figure 1 shows pesticide loss in late October 1991 after all four pesticides had been applied.

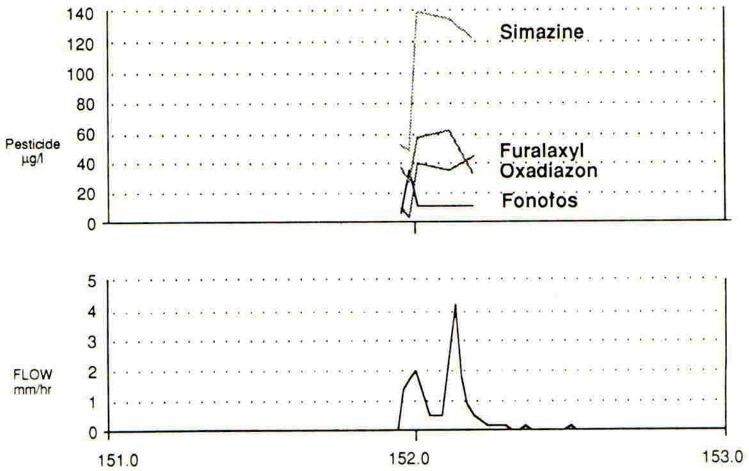

Figure 1. Pesticide losses, 29-30 October 1991. Note: Concentrations for furalaxyl have been divided by ten.

In 1991 the peak concentrations detected for fonofos and oxadiazon were broadly comparable with 1990 data. For furalaxyl, general concentrations were similar but the early peaks were substantially higher. Simazine concentrations were much higher in 1991 than those detected in 1990.

In 1992 high concentrations of pesticides were again observed. Losses were similar for furalaxyl and oxadiazon (maximum 1500 µg/l); this was broadly comparable with furalaxyl in 1991 but much higher for oxadiazon. For fonofos, although general concentrations were similar to those observed in 1991, the peaks were substantially lower. Simazine was not applied in 1992.

The highest annual loads (total loss) observed were in 1991 for furalaxyl and simazine at 117.4 mg (0.3% of applied) and 13.9 mg (1.4% of applied) respectively. The highest annual loads for oxadiazon and fonofos were observed in 1992 at 67.7 mg (1.8% of applied) and 3.5 mg (0.01% of applied) respectively. Total loads of pesticides were often not dependent on the amount of water applied. However, the concentration was highly dependent; increasing the throughput of water (drainage) reduced the peak concentration observed. Loads from the sand beds, including those with re-circulatory systems, were not appreciably different to the gravel beds. Under the trial conditions it was possible to re-apply all the drainage water from these sand beds, reducing effective runoff to zero; there was no apparent build up in concentrations in drainage from the beds.

DISCUSSION

Total pesticide load from the HONS beds was broadly similar to results from studies in agricultural soils where a loss between 0.5 and 1.0% has been found (Harris et al., 1993). The load, as a percentage of that applied, was higher for the more mobile herbicide simazine than strongly adsorbed fonofos, as expected. However, oxadiazon with a Koc of 3200 and half-life of 60 days

(Wauchope et al., 1992) is immobile in soil, yet was detected at high concentrations from the peat-based medium. The importance of localised discharges of water containing high pesticide concentrations will depend on many factors including the quantity of water being discharged and the concentration and volume of water moving in the receiving water. Opportunities for dilution of drainage from HONS systems will be least when river discharges are low (summer) and particularly where the point of entry of the contamination is close to a potable water supply abstraction point.

In the USA and Holland, re-circulation systems have been under development to recycle drainage water to the crop. For UK HONS systems this has not been addressed in detail, although some potential disease problems have been investigated. When developed, total re-circulation systems could theoretically be effective in preventing pesticide losses to surface waters. All these measures are likely to be expensive and where re-application to the HONS beds is a practical option, the full implication of potential disease spread should be considered. At the same time usage of alternatives to peat-based growing media has implications to pesticide loss. Organic matter content is important for adsorption of pesticides in soil. Although oxadiazon behaved differently in the peat-based growing media to that expected, in general if peat is replaced by alternatives such as bark, the binding of pesticides may change and consequently the risk of loss of pesticides. Limited work on alternatives to peat also has shown that the type of compost can affect infestations and insecticide efficacy, with more frequent infestation of vine weevil with a bark medium (Buxton et al., 1992). Alternative potting medium may therefore require greater use of some pesticides with consequent risk of increasing losses to drainage water.

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REFERENCES

Anon. (1980). EC Council Directive relating to the quality of water intended for human consumption (80/778/EEC). Off. Journal European Community, No. L229/11-29.

Buxton, J.H.; Cross, J.V.; Emmett, B.J.; Saynor, M. (1992) Control of vine weevil with controlled release chlorpyrifos granules in containerised nursery stock. Brighton Crop Protection Conference - Pests and Diseases and Diseases 1992, 3, 1229-1233.

Harris, G.L.; Bailey, S.W.; Mason, D.J. (1991) The determination of pesticide losses to water courses in an agricultural clay catchment with variable drainage and land management. Brighton Crop Protection Conference - Weeds 1991, 3, 1271-1278.

Harris, G.L.; Hodgkinson, R.A.; Brown, C.; Rose, D.A.; Mason, D.J.; Catt, J.A. (1993) The influence of rainfall patterns and soils on losses of isoproturon to surface waters. Proceedings Crop Protection Conference in Northern Britain, Dundee, 1993, 274-252.

Wauchope, R.D.; Buttler, T.M.; Hornsby, A.G.; Augustijn-Beckers, P.W.M.; Burt, J.P. (1992) SCS/ARS/CES Pesticide Properties Database. Reviews of Environmental Contamination and Toxicology, 123, 1-164.

FATE OF HERBICIDES IN SOILS UNDER DIFFERENT TYPES OF LAND USE

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ABSTRACT

Contamination of ground water by pesticides is not only caused by their application to agricultural land but also by their use on non-cultivated areas. The objective of this study was to monitor the mobility of three herbicides (simazine, diuron, methabenzthiazuron) in soils under different types of land use (cultivated field, grassland, farm road). For the experimental assessment the herbicides were applied to undisturbed soil cores (diameter 20 cm, depth 40 cm) taken from the selected sites. The lysimeters were maintained under outdoor conditions and disassembled after certain time periods. Leachate and soil layers were analyzed for the active ingredients. Different movement and degradation rates were observed due to the properties of the test substances and soils. The results were compared with data obtained by simulating the movement and degradation of the herbicides using model calculations.

INTRODUCTION

Studies for registration of pesticides are performed in general with soils from agricultural sites and used to predict degradation and leaching behaviour in cultivated and non-cultivated soil types. Since organic carbon and microbial activity are mainly influenced by the management and cultivation of the soil (Jenkinson & Powlson, 1976; Domsch *et al.*, 1979; Santruckova & Straskraba, 1991), mobility and degradation of active ingredients depends on the type of land use of the soil. Data obtained with soils cultivated according to agricultural practice may be not valid to predict the fate of pesticides in non-cultivated soils.

Lysimeter experiments under outdoor conditions as well as computer simulations are useful tools to monitor the fate of pesticides in the environment (Klein, 1991; Hance & Führ, 1992) and are also suitable to vary environmental parameters. This report presents data on the fate of three herbicides in soils from a cultivated field, grassland and farm road and compares lysimeter experiments with model calculations.

MATERIALS AND METHODS

Lysimeter experiments

Undisturbed lysimeters (diameter 20 cm, depth 40 cm; frame of stainless steel, closed at the bottom with a sieve plate) were taken from selected natural sites at Ebbinghof, Schmallenberg, North-Rhine-Westfalia, Germany and maintained under outdoor conditions. Grassland soil cores were sown with grass; the other lysimeters were kept fallow. Characteristic soil data are given in Tables 1 and 2.

Simazine (2.6 kg/ha), diuron (8.4 kg/ha) and methabenzthiazuron (3.7 kg/ha) were applied as formulated products ('Gesatop 500 liquid', Ciba-Geigy; 'Vorox W', Ciba-Geigy; 'Tribunil', Bayer) and spread evenly onto the surface of the lysimeters. Two lysimeters were used for each soil and sampling date. The lysimeters were disassembled directly after treatment (day 0) and after 20, 50, 100 and 150 days. The total amount of

TABLE 1. Particle size distribution of the sieved soil fractions.

	CULTIVATED			GRASSLAND			FARM ROAD		
	depth (cm)			depth (cm)			depth (cm)		
	0-10	10-20	20-40	0-10	10-20	20-40	0-10	10-20	20-40
< 2 mm (%)	96.3	88.9	84.6	88.3	92.1	71.4	45.4	38.5	57.0
2-20 mm (%)	3.7	11.1	15.4	11.7	7.9	28.6	36.1	42.0	21.0
> 20 mm (%)	0.0	0.0	0.0	0.0	0.0	0.0	18.5	19.5	22.0

TABLE 2. Characterization of the 2 mm soil fraction.

	CULTIVATED			GRASSLAND			FARM ROAD		
	depth (cm)			depth (cm)			depth (cm)		
	0-10	10-20	20-40	0-10	10-20	20-40	0-10	10-20	20-40
sand (%)	24.2	25.0	28.9	20.8	22.6	31.7	72.3	57.2	49.7
silt (%)	62.0	61.3	57.3	68.9	67.4	54.7	20.5	31.4	37.8
clay (%)	13.8	13.7	13.8	10.3	10.0	13.6	7.2	11.4	12.5
pH	6.9	6.9	6.9	6.3	6.6	6.3	7.7	7.5	7.4
org.C (%)	2.85	2.70	2.30	3.20	4.25	2.00	1.05	1.40	1.45
biomass*									
0 d	53.6	50.4	22.8	152.4	46.2	30.9	27.6	15.2	26.3
150 d	43.4	42.7	27.0	37.3	20.4	13.4	15.0	13.4	20.4

*(mg C/100 g dry soil)

rainfall and additional irrigation amounted to approximately 370 mm after 150 days (corresponding to about 900 mm/year), Figure 1. Dichloromethane extracts of all soil layers (0-10 cm, 10-20 cm and 20-40 cm) and leachate samples were analyzed in duplicate for active ingredients by reversed phase HPLC (Hassink *et al.*, 1993). Results were derived from mean values.

Model calculations

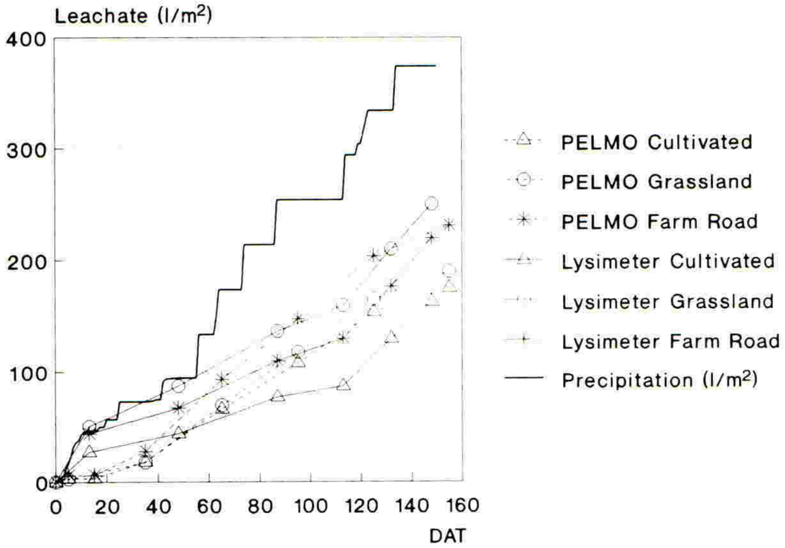
Model calculations were made using the 'Pesticide Leaching Model' (PELMO; source: Fraunhofer-Institut, Schmallenberg, Germany), a modified version of PRZM (Carsel *et al.*, 1984). To simulate the fate of pesticides in soil PELMO considers evapotranspiration, soil sorption and biodegradation using the Haude, Freundlich and Arrhenius equations respectively. Depth dependent temperatures in soil were calculated by using daily air temperatures. The climate simulation was based on actual weather data recorded during the lysimeter study. Soil parameters used in the calculations are summarized in Table 2. The initial amount of applied active ingredients for modelling corresponded to the application rates described above.

Further input parameters were mean values of previously published degradation rates of the active ingredients, determined in field trials (simazine: $DT_{50}=40$ days (Paeschke *et al.*, 1978; EWRS, 1983; Rahman & Holland, 1985; Bunte, 1991); diuron: $DT_{50}=108$ days (Baier *et al.*, 1985; Domsch, 1992); methabenzthiazuron: $DT_{50}=133$ days (Führ & Mittelstaedt, 1976; Pestemer & Malcomes, 1981; Kubiak, 1986; Bunte, 1991)) and K_{oc} values of the active ingredients (simazine: K_{oc} = 105 (on the basis of n = 240 published data); diuron: K_{oc} = 300 (n = 156); methabenzthiazuron: K_{oc} = 630 (n = 14); unpublished compilation from data bank Z. Gerstl, Agricultural Research Organization, Bet Dagan, Israel).

RESULTS AND DISCUSSION

The cumulative waterflow in the lysimeters from the cultivated and farm road soils were almost identical to the amount of leachate calculated by PELMO (Figure 1). The high volume of leachate in the soil cores taken from the grassland site was probably due to a higher soil moisture content at the beginning of the study.

FIGURE 1. Cumulative precipitation and leachate. Comparison of experimental and calculated values.



The disappearance rates of the herbicides simazine, diuron and methabenzthiazuron in soil cores from the cultivated field, grassland and farm road are shown in Figures 2-10. Results obtained by PELMO were compared to the experimental data.

The simulated leaching behaviour of the herbicides was in good agreement with their K_{oc} values. Simazine occurred in the deeper soil layers of all soil types 150 days after application and significant leaching was calculated for the farm road soil (Figure 4). Diuron was predicted to be less mobile and transfer into deeper soil layers was only simulated for the farm road soil (Figure 7). Methabenzthiazuron showed the lowest simulated mobility. The calculated degradation rates of the herbicides were close to the measured values. Differences were observed for the degradation of simazine in the grassland soil and for simazine and diuron in the farm road soil. The latter indicated that DT_{50} values determined with cultivated soils may be not valid to simulate the degradation of herbicides in soils from other types of land use.

Transfer of the herbicides into deeper soil layers during the first 50 days after treatment was not predicted by PELMO. However, significant leaching of the active ingredients was observed at the beginning of the experimental study, after the first rain events.

FIGURE 2. Disappearance of simazine in the cultivated field soil.

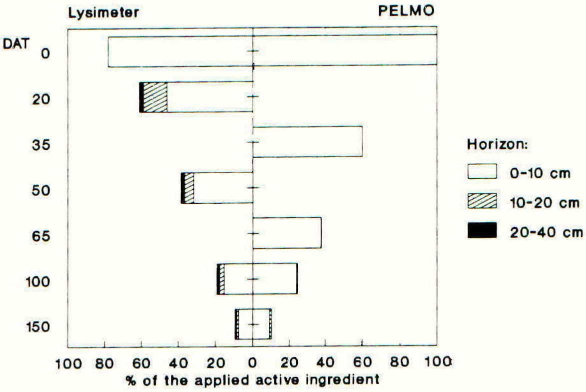


FIGURE 3. Disappearance of simazine in the grassland soil.

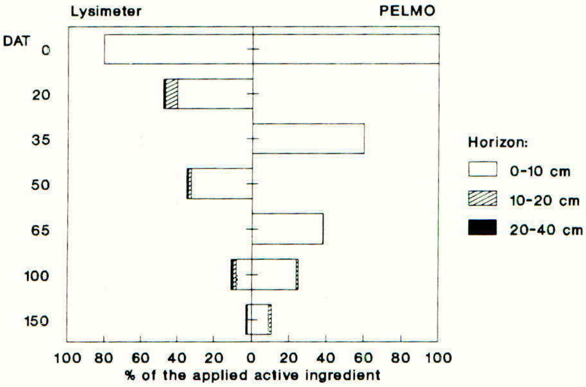


FIGURE 4. Disappearance of simazine in the farm road soil.

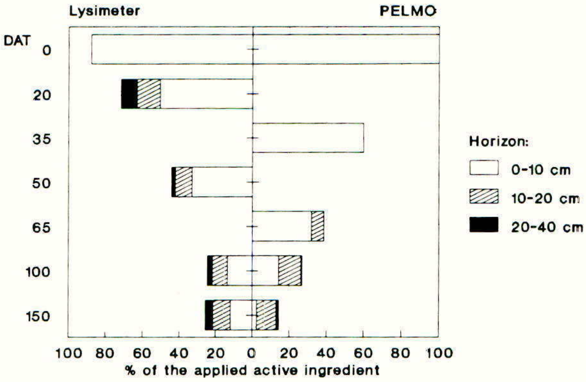


FIGURE 5. Disappearance of diuron in the cultivated field soil.

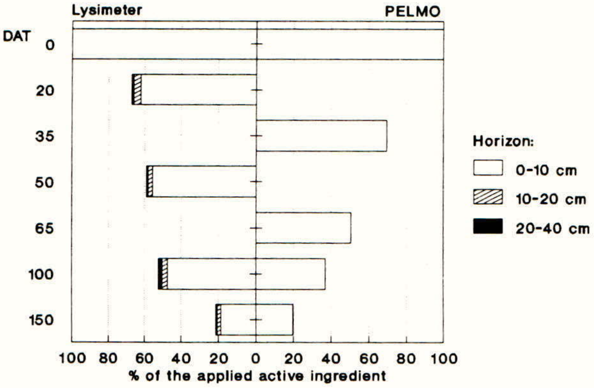


FIGURE 6. Disappearance of diuron in the grassland soil.

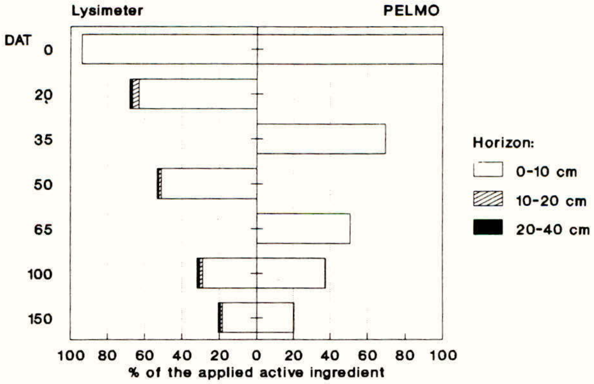


FIGURE 7. Disappearance of diuron in the farm road soil.

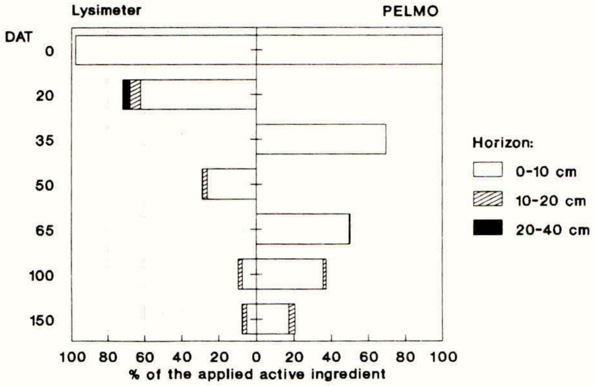


FIGURE 8. Disappearance of methabenzthiazuron in the cultivated field soil.

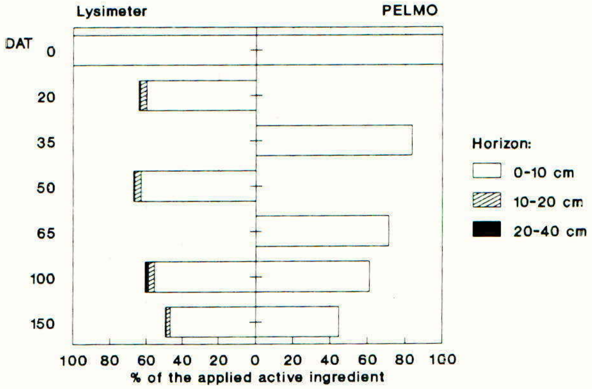


FIGURE 9. Disappearance of methabenzthiazuron in the grassland soil.

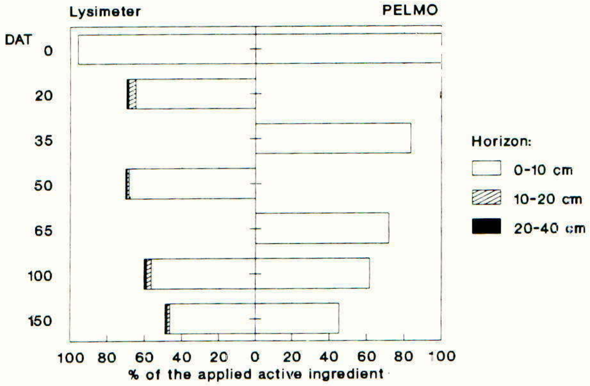
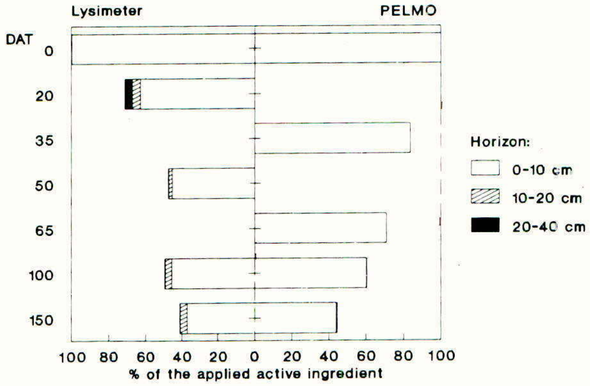


FIGURE 10. Disappearance of methabenzthiazuron in the farm road soil.



20 days after treatment simazine was present at up to 20 % of applied active ingredient in the 10-20 cm plus 20-40 cm soil layers of the lysimeters taken from the farm road (Figure 4). In the course of the study the degradation of simazine in this soil type was delayed by a lower biomass in the upper soil layers and a slower chemical hydrolysis due to a more basic pH (Table 2) (Hurle, 1982; Domsch, 1992).

Diuron and methabenzthiazuron were observed to be less mobile than simazine over the whole testing period and the results for the cultivated field and grassland soils corresponded to their K_{oc} values. About 9 % of the initially applied active ingredients occurred in the 10-20 cm plus 20-40 cm layers of the farm road soil 20 days after treatment (Figures 7 and 10). Degradation of these substances in this soil was faster than in soils taken from the cultivated and grassland sites (Figures 5-10). Due to the lower content of organic carbon in this soil (Table 2) the substances seemed to be more available for metabolic reactions by soil microorganisms.

Generally, the fate of the herbicides simazine, diuron and methabenzthiazuron in soils from different land use types, revealed by outdoor lysimeter experiments, were in good agreement with the model calculations performed with PELMO. However, the leaching behaviour of the active ingredients in the lysimeter soils was probably a more realistic estimate of their mobility in soils from different land use types. The occurrence of the active ingredients in the leachate was not predicted by the pure chromatographic flow simulated by PELMO, but 1-6 % of the initially applied herbicides was detected in the leachates of the lysimeters.

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REFERENCES

Baier, C.; Hurle, K.; Kirchhoff, J. (1985) Datensammlung zur Abschätzung des Gefährdungspotentials von Pflanzenschutzmittel-Wirkstoffen für Gewässer. *DVWK-Schriften*, Heft 74, Paul Parey Verlag, Berlin.

Bunte, D. (1991) Abbau- und Sorptionsverhalten unterschiedlich persistenter Herbizide in Abhängigkeit von Flächenvariabilität und Alter der Rückstände. PhD Thesis, Universität Hannover.

Carsel, R.F.; Smith, C.N.; Mulkey, L.A.; Dean, J.D.; Jowise, P. (1984) User's manual for the pesticide root zone model (PRZM). *Release 1 EPA-600/3-84-109*, U.S. Environmental Protection Agency.

Domsch, K.H. (1992) *Pestizide im Boden*, Verlag Chemie, Weinheim, pp. 155-156 & pp. 252-256.

Domsch, K.H.; Beck, T.; Anderson, J.P.E.; Söderström, B.; Parkinson, D.; Trolldenier, G. (1979) A comparison of methods for soil microbial population and biomass studies. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **142**, 520-533.

EWRS (European Weeds Research Society) Herbicide-Soil Working Group (1983) Collaborative experiment on simazine persistence in soil. *Weed Research*, **23**, 373-383.

Führ, F.; Mittelstaedt, W. (1976) Das Verhalten von Methabenzthiazuron in Boden und Pflanze nach Applikation von Methabenzthiazuron[benzolkern-U-^{14}C] an Sommerweizen unter Freilandbedingungen im Anwendungsjahr und Nachbau. *Landwirtschaftliche Forschung*, Sonderheft 32, 286-294.

Hance, R.J.; Führ, F. (1992) Methods to study fate and behaviour of pesticides in the soil. In: *Lysimeter studies of the fate of pesticides in the soil*, F. Führ, R.J. Hance (Eds.), *BCPC Monograph No. 53*, Lavenham Press Limited, Lavenham, Suffolk, pp. 9-18.

Hassink, J.; Klein, A.; Kördel, W.; Klein, W. (1993) Behaviour of herbicides in non-cultivated soils. *Chemosphere*, in press.

Hurle, K. (1982) *Untersuchungen zum Abbau von Herbiziden in Böden*, Verlag Paul Parey, Berlin, pp. 30-34.

Jenkinson, D.S.; Powlson, D.S. (1976) The effects of biocidal treatments on metabolism in soil. V. A Method for Measuring Soil Biomass. *Soil Biology and Biochemistry*, **8**, 209-213.

Klein, M. (1991) Application and validation of pesticide leaching models. *Pesticide Science*, **31**, 389-398.

Kubiak, R. (1986) Vergleichende Untersuchungen zur Übertragbarkeit von Ergebnissen aus standardisierten Laborversuchen und Agrarökosystemausschnitten auf die reale Feldsituation am Beispiel des Abbau- und Verlagerungsverhaltens der Herbizidwirkstoffe Metamitron und Methabenzthiazuron in einer Parabraunerde. *Bericht Forschungszentrum Jülich*, Jül 2055.

Paeschke, R.R.; Ebing, W.; Heitefuss, R. (1978) Abbau von Herbiziden und deren Einfluß auf die biologische Aktivität im Boden nach erstmaliger oder mehrjähriger Anwendung. *Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz*, **85**, 280-297.

Pestemer, W.; Malcomes, H.P. (1981) Einfluß von Pflanzenschutzmitteln in Wintergetreide auf biologische Aktivitäten im Boden. Teil II: Abbau von Chlortoluron und Methabenzthiazuron. *Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz*, Sonderheft 9, 313-320.

Rahman, A.; Holland, P.T. (1985) Simazine - soil persistence and mobility. *New Zealand Journal of Experimental Agriculture*, **13**, 59-65.

Santruckova, H.; Straskraba, M. (1991) On the Relationship between Specific Respiration Activity and Microbial Biomass in Soils. *Soil Biology and Biochemistry*, **6**, 525-532.

CONTAMINATION OF AQUATIC ECOSYSTEMS BY RUNOFF EVENTS - COMPARISON OF SMALL AND LARGE PLOT EXPERIMENTS

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ABSTRACT

The transport of the herbicides Dichlorprop-p, Isoproturon, and Bifenox via surface runoff was investigated on small and large field plots with simulated rainfall. Dichlorpop-p and Isoproturon were transported mainly in the runoff water phase. Total Dichlorprop-p and Isoproturon losses in runoff mainly depend on the time of runoff initiation. Concentrations in early runoff samples at a precipitation of about 5 mm may lead to herbicide concentrations above 1 mg/l. The concentration of Dichlorprop-p and Isoproturon in the runoff of the large plot were below 200 µg/l with a total loss of 0.02 % of the applied herbicides during a 30 mm rainfall event.

INTRODUCTION

Runoff events are one of the important exposure routes for aquatic ecosystems by pesticides. A lot of data have been published on pesticide losses in surface runoff (Wauchope, 1978; Ahuja, 1986). Due to the great variety of parameters concerning the performance of experiments many runoff studies reported in literature were conducted during natural rainfall events, without knowledge about pesticide application rates and defined conditions of soils, locations, and rainfall (Spalding and Snow, 1989; Michenfelder and Schramm, 1992; Wauchope et al., 1990; Iwakuma et al., 1993).

Generally the data for total losses via runoff given in the literature vary strongly due to the great variety of parameters influencing the total pesticide loss. Data varied between 10-15 % following heavy rainfall soon after application (Baker et al., 1978) to generally less than 5 % (Olness et al, 1975) or less than 0.5 % unless rainfall occurred within 1-2 weeks after application (Wauchope, 1975).

It was the objective of our studies to perform systematic and well defined experiments on small and large plots to achieve an improvement of the estimation of the transfer of pesticides by runoff separated into water and sediment mediated transport mechanisms.

EXPERIMENTAL

The large plot rainfall simulation studies were carried out on two field plots of 20 m by 60 m in a field cultivated with winter wheat (fig. 1). The soil texture is a silt loam with a slope of appr. 8 %. Isoproturon, Dichlorprop-p, and Bifenox were applied as a mixture of commercial formulations with concentrations of 1.16, 1.20 an 0.58 kg/ha, respectively. Spraying was performed in spring 1993. For irrigation, agricultural sprinklers were used with an irrigation intensity of 14 mm/h, and a duration of 2.5 hours.

Runoff samples were collected in sampling vessels at 10, 30 and 50 m from the lower end of the plot within the tractor lane. The runoff of one plot was collected in a duct, total water flux and pesticide concentrations were measured. Soil samples were taken immediately before and after the simulated rainfall. Irrigation was started 24 h after application. The herbicide analyses in runoff (separate water and sediment phase) were performed by HPLC according to the method of Klöppel et al. 1992.

RESULTS AND DISCUSSION

Runoff started in the lanes formed by the tractor during application of the pesticides. Due to the pressure of the wheels, the soil was partly compressed resulting in a surface with partly clogged soil pores. Within these lanes the first runoff samples could already be collected after an artificial irrigation of 5-7 mm (cumulative) whereas runoff from the total plot started after an irrigation of about 12 mm. Consequently, maximum Isoproturon and Dichlorprop-p concentrations were found in the first samples within these lanes.

During the course of irrigation initial pesticide concentrations decreased from the upper values of about 900 µg/l for Isoproturon and Dichlorprop-p at a cumulative irrigation of 7 mm down to values of about 200 µg/l for Isoproturon and Dichlorprop-p at a cumulative irrigation of 30 mm (fig. 2).

As figure 2 shows, no significant differences for the measured concentrations within the three sampling distances occurs. Consequently, during a runoff event no pronounced concentration profile of dissolved pesticides in the runoff water across the field is established. Neither an enrichment of pesticides during the water flow across the field nor dilution by additional precipitation was observed.

Additionally, at the lower end of the plot the total runoff was collected in a duct to obtain mean concentration values for the whole plot. The sampling included runoff from distinct areas where the event started earlier than in other areas due to the natural inhomogeneities within a large plot. Therefore, the concentrations in the total runoff did not exceed concentrations of 200 µg/l for both herbicides. In addition the decrease in concentrations of the pesticides in the runoff was not as pronounced as in the other samplings.

Figure 3 elucidates that total surface runoff starts at 8 mm of irrigation with a low intensity. However the water flux did not increase significantly until the cumulative precipitation had exceeded 20 mm. Nevertheless at the end of the irrigation experiment (30 mm precipitation) there were comparable concentrations of the pesticides in the total surface runoff and at the distinct sampling points within the plot.

There is no significant difference between the two soluble pesticides Dichlorprop-p and Isoproturon whereas Bifenox could never be detected in runoff water. At the end of the experiment about 30 mg herbicide each had left the plot corresponding to 0.02 % of the applied amount.

Tab. 1 elucidates the consequences of differences in the mobility of Dichlorprop-p and Isoproturon: Dichlorprop-p with a high water solubility of 700 mg/l and a low sorption constant of K_{OC} = 23 is more mobile in soil than Isoproturon (water solubility = 65 mg/l; K_{OC} = 129). Consequently, at the beginning of the irrigation Dichlorprop-p is transported into deeper soil layers leading to a significant decrease of its concentration at the soil surface and a reduction of the portion being available for lateral transport. The decrease of the Isoproturon concentration at the soil surface as a result of vertical transport is less pronounced due to its higher K_{OC} value.
With respect to potential concentrations in runoff water both pesticide properties - water solubility and sorption - are contradictory: High water solubility should lead to high concentrations in runoff water but also reduces the runoff available portion during a storm event. On the other side, higher sorbing pesticides are less soluble in the runoff water but also the runoff available portion during a storm event in general is higher. For the presented study the contradictory properties resulted in comparable concentrations for Isoproturon and Dichlorprop-p in the runoff water with generally slightly higher concentrations for Isoproturon.

In these runoff experiments a non-erosive rainfall was simulated by the precipitation of 14 mm/h. Therefore, only minor amounts of sediment were exported from the field and could be subjected to analyses. Respective results are given in table 2.

The pesticide concentrations in sediment can be given by the following ranking: Dichlorprop-p < Isoproturon << Bifenox. Bifenox is exclusively transported in the sediment phase. Although for Isoproturon the concentrations in the sediment phase are slightly higher than in the water phase most of the pesticide is transported in the dissolved form due to the high water volumes transported compared to transported sediment.

Comparison of results from large and small plot experiments

Small plots (4.6 m by 1.5 m) at three different locations in Germany were either planted with barley (3-5 leaves) or left bare. Isoproturon, Dichlorprop-p and Bifenox were applied as a mixture of purchasable formulations with concentrations of 1.16, 1.20, and 0.58 kg/ha, respectively. The same concentrations were also used for the large plot experiments. Rainfall events with intensities of about 70 mm/h were simulated using a Veejet 80100 rainfall simulator. A 1 h rainstorm was followed by a 0.25 h break and another 0.5 h rainstorm. In total, about 105 mm of precipitation were applied during 1.5 hours. The simulation of these heavy rainstorms lead to a higher amount of sediment in the runoff as compared to the large plot experiments described above. Therefore, the total loss of Bifenox was higher than for Dichlorprop-p and Isoproturon. (The results of the small plot experiments are submitted for publication in Chemosphere.)

The comparison of the experiments give the following results for dissolved pesticide concentrations in the water phase.

- In both, small and large plot experiments the concentrations of Isoproturon are slightly higher than those of Dichlorprop-p.
- In both experiments concentration profiles of the pesticides in the water phase depending on the cumulative rainfall are comparable.
- Initial concentrations for the small plot experiments were sometimes higher due to the simulated heavy rainfall and also the runoff event started earlier.
- Pesticides with a similar or higher mobility as Isoproturon are mainly transported dissolved in the water phase and can reach aquatic ecosystems during "normal" rainfalls after application.
- Poorly soluble pesticides like Bifenox can only leave the field by heavy, erosive rainfalls on fields with a certain slope (e.g. > 10 %).
- Both experiments show that most effective conditions for runoff events are those which lead to an early start of the runoff after the beginning of rainfall.

REFERENCES

Ahuja, L.R. (1986). Characterization and Modeling of Chemical Transfer to Runoff. *Adv. Soil Sci.* **4**: 149-188.

Baker, J.L.; Laflen, J.M.; Johnson, H.P. (1978). Effect of tillage systems on runoff losses of pesticides. A rain simulation study. *Trans. ASAE* **21**: 886-892.

Iwakuma, T. (1993). Runoff properties and change in concentrations of agricultural pesticides in a river system during a rice cultivation period. *Chemosphere* **27** (4): 677-691.

Klöppel, H.; Haider, J.; Hoffmann, C.; Lüttecke, B. (1992). Simultaneous determination of the herbicides isoproturon, dichlorprop-p, and bifenox in soils using RP-HPLC. *Fresenius J Anal Chem* **344**: 42-46.

Michenfelder, A.; Schramm, M. (1992). Beregnungsversuche zu: Bestimmung des Austrages von Pflanzenschutzmitteln auf landwirtschaftlichen genutzten Flächen. *Wasserwirtschaft-Wassertechnik* **5**: 206-211.

Olness, A.; Smith, S.J.; Rhoades, E.D.; Menzel, R.G. (1975). Nutrient and sediment discharge from agricultural watersheds in Oklahoma. *J. Environ. Qual.* **4**: 331-336.

Spalding, R.F.; Snow, D.D. (1989). Stream Levels of Agrichemicals during a Spring Discharge Event. *Chemosphere* **19**: 1129-1140.

Wauchope, R.D. (1978). The Pesticide Content of Surface Water Draining from Agricultural Fields - A Review. *J. Environ. Qual.* **7**: 459-472.

Wauchope, R.D; Williams, R.G.; Marti, L.R. (1990). Runoff of Sulfometuron-Methyl and Cyanazine from Small Plots: Effects of Formulation and Grass Cover. J.Environ. Qual. **19**: 119-125.

ACKNOWLEDGEMENT

The study was supported by the Umweltbundesamt, Berlin, under contract No. 1260587.

Tab. 1: Concentrations of the pesticides in the soil before and after the runoff experiment

pesticide	before irrigation	after irrigation		
	0 - 5 cm layer [mg/kg]	0 - 5 cm layer [mg/kg]	5 - 10 cm layer [mg/kg]	10 - 15 cm layer [mg/kg]
Dichlorprop-p	2.18	0.69	0.28	0.21
Isoproturon	1.47	0.34	0.10	0.08
Bifenox	0.78	0.77	0.01	0.01

Tab. 2: Concentrations of the pesticides in sediment and water phase

sampling point	irrigation	concentrations of				
		Dichlorprop-p in		Isoproturon in		Bifenox in
	[mm]	sediment [mg/kg]	water phase [mg/kg]	sediment [mg/kg]	water phase [mg/kg]	sediment [mg/kg]
KFS 1	20.2	0.17	0.31	0.89	0.24	2.83
	27.0	0.23	0.28	0.85	0.22	2.24
	29.6	0.26	0.30	0.92	0.14	2.80
KFS 2	33.6	0.11	0.27	0.75	0.23	2.20
KFS 3	33.6	0.34	0.30	1.11	0.30	3.66

Fig. 1 SIZE AND SAMPLING POINTS OF THE TWO LARGE FIELD PLOTS

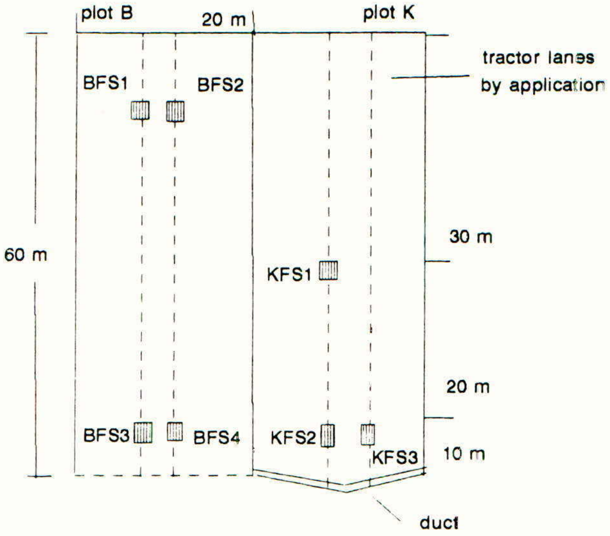


Fig. 3 CUMULATIVE RUN-OFF DEPTH AND CUMULATIVE HERBICIDE LOSSES

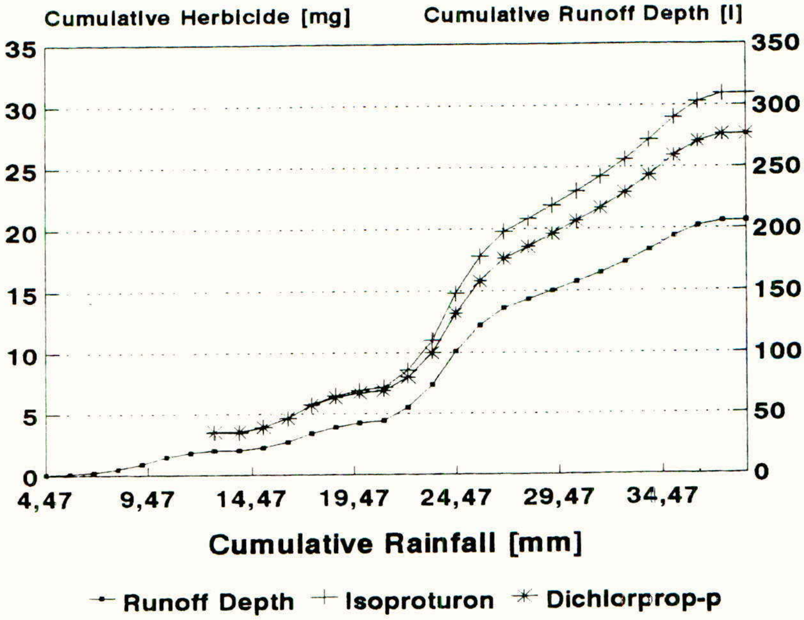


Fig. 2 ISOPROTURON AND DICHLORPROP CONCENTRATIONS IN RUN-OFF

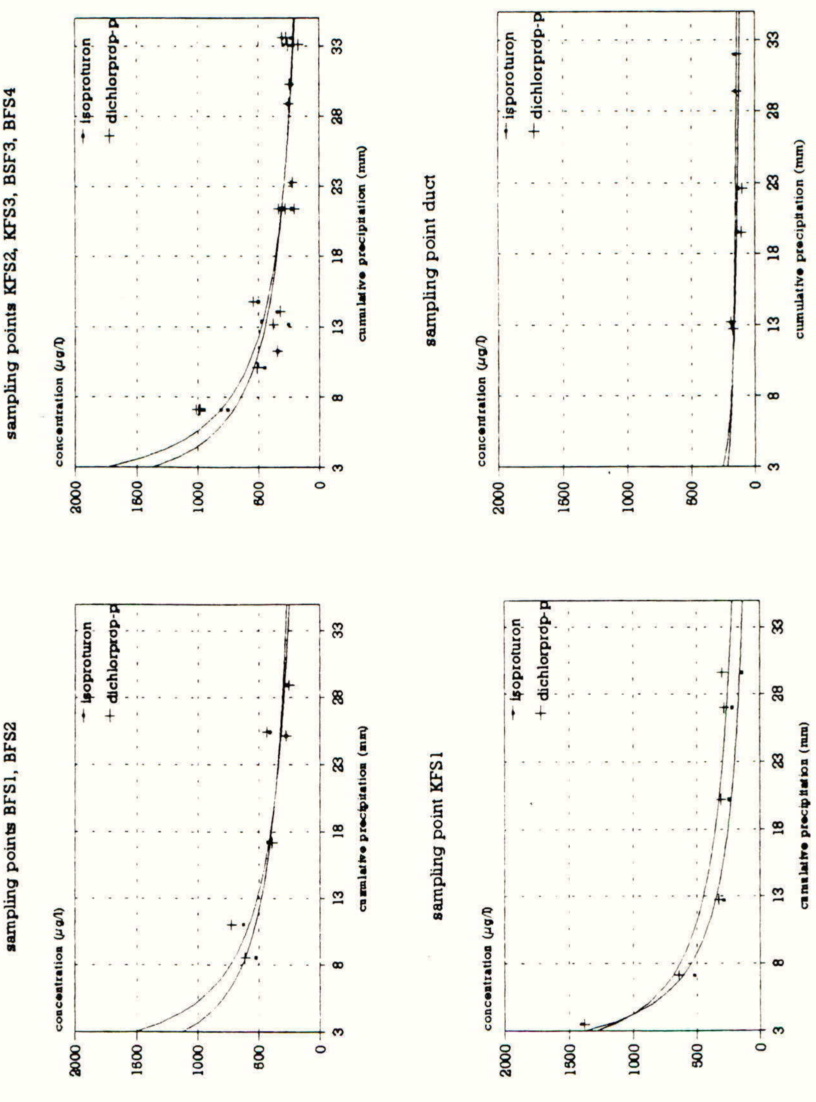
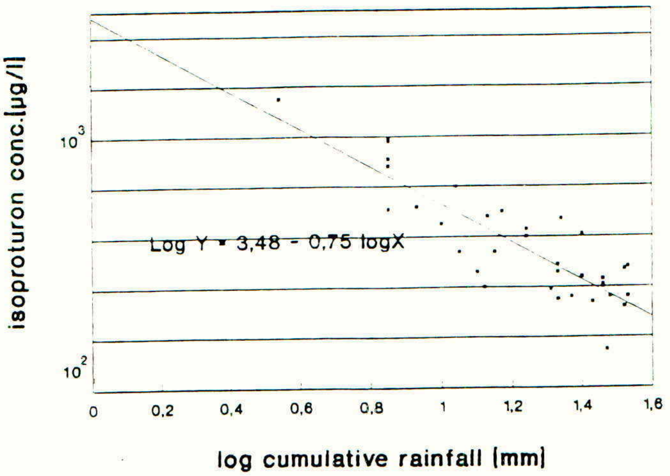
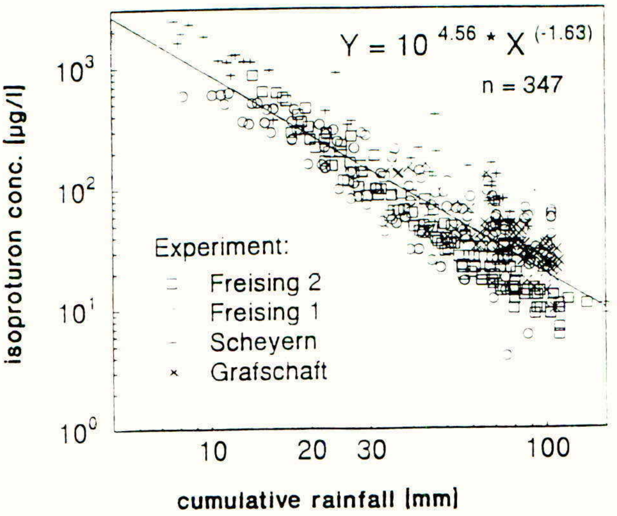


Fig. 4 RELATIONSHIP BETWEEN THE LOGARITHM OF ISOPROTURON CONCENTRATION IN RUNOFF WATER AND THE LOGARITHM OF THE CUMULATIVE RAINFALL

Large Plots



Small Plots



RESIDUE PROFILE OF METOSULAM - A NEW BROAD-LEAF HERBICIDE

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ABSTRACT

DE-511 (ISO common name metosulam) is a broad-leaf herbicide belonging to a new class of chemistry, the triazolopyrimidines, and has been extensively field tested across Europe as a spring applied product.

In a range of field trials conducted between 1990-1992 in wheat, barley, rye and oats at up to 40g ai/ha (4N rate) and maize at 30g ai/ha (1N rate) residues in grain were always less than the lowest validated level (0.10 mg/kg 1990, 0.01 mg/kg 1991-1992). Residues in straw were typically $\leq$0.10 mg/kg.

In six soil dissipation trials covering a range of soil types and climatic zones conducted over three years, half lives of 6-47 days were measured. These field studies indicated there was no significant movement of DE-511 below the 0-10cm horizon.

INTRODUCTION

DE-511 (ISO common name metosulam) is a new, foliar acting, selective herbicide for post-emergence use in cereals and maize for the control of broad leaf weeds by the inhibition of the enzyme acetolactate synthase. It is based on new DowElanco chemistry and is a member of the triazolopyrimidine family of herbicidal compounds (Snel 1993).

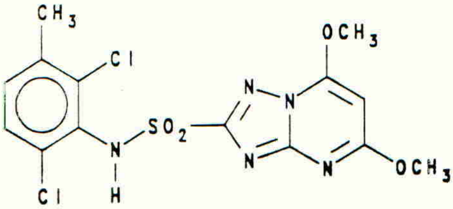
During the pre-development phase of the compound a series of field residue studies were conducted over three years in Northern and Southern Europe, to help define any potential consumer risk and to help understand the environmental fate and behaviour of this herbicide. The trials were carried out with a 100g ai/l suspension concentrate (SC) formulation at low application rates (10-40g ai/ha) to small grain cereals, maize and soil.

This comprehensive trial programme was carried out to the standards of Good Field Practice.

CHEMICAL AND PHYSICAL PROPERTIES

<u>Chemical Name</u> : N-(2,6-dichloro-3-methylphenyl)-5,7-dimethoxy-[1,2,4] triazolo[1,5a] pyrimidine-2-sulphonamide

Chemical Structure :



Empirical Formula : $C_{14}H_{13}N_5O_4Cl_2S$

Molecular Weight : 418.26 amu

Melting Point : 210 - 211.5°C

Appearance : Cream crystalline solid, slight garlic odour

Density : 1.49g cm^3 at 20°C

Vapour Pressure : 4×10^{-13} Pa at 20°C

Water Solubility : 200 mg/l at 20°C

Solubility : Soluble (>5.0g/l) in acetone, acetonitrile, dichloromethane.
Soluble ($\leq$0.2g/l) in n-octanol and toluene

Octanol/Water Partition Coefficient (logP) : 0.9778

Dissociation Constant : 4.8

ADDITIONAL PROPERTIES

Hydrolysis : $t_{1/2}$ >30 days at pH 5-9 and 25°-50°C

Aqueous Photolysis : $t_{1/2}$ 140 days (xenon arc)

RESIDUES IN PLANTS

A field wheat metabolism study (1990) where ^{14}C- labelled DE-511 was applied in spring (GS 32) at 100g ai/ha (10N), showed that DE-511 was poorly absorbed (<5% of applied) from a foliar application and that surface residues were easily removed by rainfall. Therefore, residue accumulation within the plant is low with a 3-hydroxymethylphenyl metabolite and its glycoside as the only other major products present. No significant differences were observed between triazole and aniline ring labelled material demonstrating a lack of cleavage of the sulphonamide bridge. Levels of residual material (in DE-511 ppm equivalents) after fourteen days post application were 0.12ppm (parent) and 0.028ppm (metabolites) with <0.005ppm (0.01% applied radioactivity) present in the grain at harvest. Straw contained 0.01ppm (parent) and 0.005ppm (metabolites) in the extractable fraction. The remaining material was strongly bound associated mostly with the lignin and to a lesser degree cellulose fractions.

Residue field trials were conducted in the UK, France, Germany and Italy (1990-1992). DE-511 was applied in spring to either wheat, barley, rye or oats at either GS30-32 or GS39. Application rates were either at 20 or 40g ai/ha (equivalent to 2N or 4N rate). For maize, DE-511 was applied in late spring/early summer (4-6 leaf GS) at a rate of 30g ai/ha (1N) in Germany and France. In all cases trials were located at sites that gave maximum distribution of soil type and climatic differences within the countries.

Harvest grain and straw from cereal trials were prepared in a knife mill with dry ice. Maize cobs and stover were prepared in a bowl cutter with dry ice. All samples were deep frozen prior to analysis.

PLANT AND SOIL RESIDUE METHODOLOGY

DE-511 was extracted from cereals and maize with acetone/water. After acidification the extract was partitioned with diethyl ether.The ether was partitioned with bicarbonate which was then acidified and DE-511 was partitioned back into ether. This ether phase was evaporated and the residuum purified by extractive methylation, which utilised the formation of an ion pair with tetrabutyl ammonium hydroxide followed by methylation with methyl iodide and extraction into toluene. The toluene phase was then further purified using a silica cartridge with acetone/toluene to elute DE-511 methyl. The eluate is evaporated to dryness and the residuum reconstituted in mobile phase. Quantification was by LC/UV at 254nm.

For soil, DE-511 was extracted with acetonitrile and 0.2M hydrochloric acid. After evaporating to a small volume DE-511 was partitioned into methyl-tertiary-butyl ether prior to an aminopropyl cartridge clean-up, using formic acid/dichloromethane for elution. The eluate was evaporated and reconstituted in dichloromethane, prior to a silica cartridge clean-up. The remaining procedure was the same as for cereals apart from the UV detection wavelength which was 240nm.

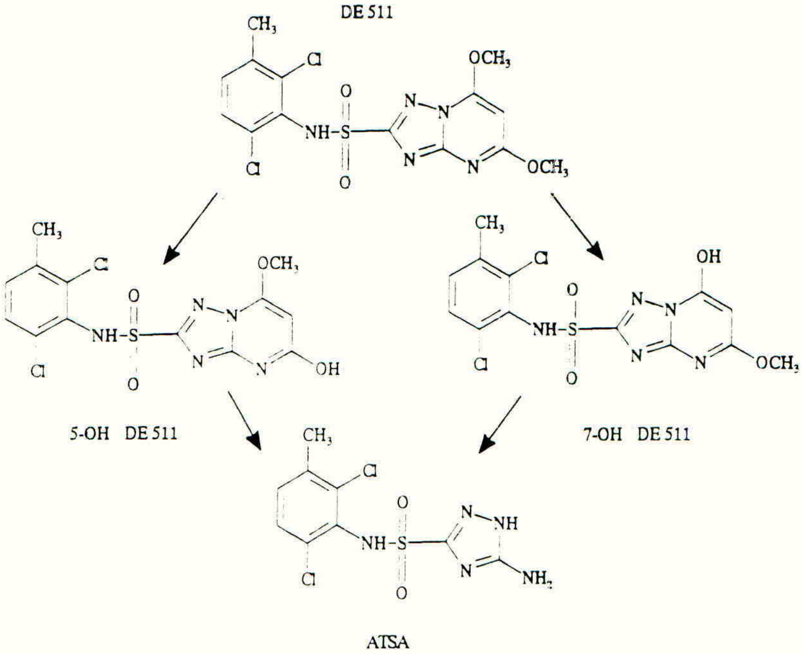
RESIDUES IN SOIL

Soil laboratory studies (Baloch, 1992) have shown that DE-511 degrades via the 5- and 7- hydroxy analogues to form 5-amino-N-(2,6-dichloro-3-methyl phenyl)-1H-1,2,4-triazole-3-sulphonamide (ATSA) (Figure 1), by a process of demethylation and partial opening of the pyrimidine ring. Following BBA guidelines (BBA, 1986) only one of the four soils from these laboratory experiments produced a DT_{90} >100 days (120 days). Therefore, a series of field dissipation studies were carried out at different locations in Germany and the UK. Based on these laboratory data, and the very low application rate, it was decided to analyse for parent only.

In each trial, bare soil plots were treated with a SC formulation containing 100g ai/l DE-511, at either 20 or 40g ai/ha. The 20g ai/ha treatments were applied at timings equivalent to GS 30-32 of cereals in neighbouring fields. At the 40g ai/ha treatment, timings were equivalent to maize 4-6 leaf GS in surrounding fields. All trials were carried out on agriculturally viable soils. Plot size at each site was 3m x 29m divided into four subplots. Five cores were taken from each subplot to give for each sampling time, 20 cores. Soil cores were taken pre-application, then

0, 7, 14, 28 days and 2, 4, and 7 months after application to a minimum depth of 30cm using either a 'Humax' motor driven corer (5cm dia.) or a manual 'Coremaster' (5cm dia.). All cores were deep frozen within eight hours of sampling. Soil cores were cut into 0-10, 10-20, 20-30cm horizons and equivalent horizons bulked prior to air drying and sieving sequentially through 2.1mm and 1.0mm sieves.

Figure 1. Metabolic pathway for DE-511 in soil



RESULTS and DISCUSSION

Plant Residues

Cereal and maize residue methodology was successfully applied to samples from European residue field trials. Excellent selectivity was achieved down to a lowest validated level (LVL) of 0.01 mg/kg (0.10 mg/kg in the first year of trials) for grain and 0.10 mg/kg for straw and stover.

In cereal trials, typical concentrations taken immediately post application of DE-511 in immature plants (GS 30-32) treated at 20g ai/ha (2N) were 0.23 - 0.64 mg/kg (mean 0.50 mg/kg), declining to no detectable (ND) residues after 1 month post application. In grain at both 20 and 40g ai/ha following either GS 30-32 and GS 39 timings, no residues of DE-511 were detected. Residues in straw ranged from ND - 0.30 mg/kg, levels found corresponding to application rate and timing. Overall mean straw residues, even at the later growth stage and higher application rate, were typically <0.10 mg/kg (Table 1).

All these residue values for DE-511 in cereal grain and straw are in excellent agreement with data generated from the plant metabolism study and theoretical calculations based on the low applied dose and crop yields. The generated data show that even at exaggerated application rates coupled with late timings no residues of DE-511 were found in grain.

Residues in maize showed a similar picture. Applications made at 4-6 leaf GS and 30g ai/ha produced residues of 0.9 - 3.0 mg/kg of DE-511 immediately after application, declining to no detectable residues after 14 days in immature plant samples, and in harvest cobs and stover (Table 1).

Table 1. DE-511 Residues (mg/kg) in European cereals and maize at harvest

		GS 30-32		GS 39	
Crop	No of Trials	Grain(Straw) 20g ai/ha	Grain(Straw) 40g ai/ha	Grain(Straw) 20g ai/ha	Grain(Straw) 40g ai/ha
Wheat	11	ND (ND)	ND (<0.10)	ND (<0.10)	ND (<0.10)
Barley	9	ND (ND)	ND (<0.10)	ND (<0.10)	ND (0.30)
Rye	2	ND (ND)	- -	- -	- -
Oats	2	ND (ND)	- -	- -	- -
		Application at GS 4-6 Leaf and 30g ai/ha			
		cobs	stover		
Maize	9	ND	ND		

- not trialed

The stability of DE-511 in wheat grain, straw and immature plant under frozen storage conditions was proven.

SOIL RESIDUES

The developed residue methodology for determining DE-511 in soil selectively removed the 5 and 7 hydroxy and ATSA metabolites plus soil co-extractives enabling a LVL of 1.0 μg/kg (ppb) to be achieved. The LVL was sufficient to enable valid interpretation of the data. Stability of DE-511 in soil under frozen storage conditions was proven.

Half lives (DT_{50}) determined by regression analysis from the 0-10cm horizon of the dissipation trials ranged from 6-47 days with a mean of 25 days (Table 2). First order rate kinetics were demonstrated for soil half life in 5 of the 6 trials. No relationship between soil characteristics and soil half life was identified from these studies. This compares to half-lives of 1-11 days generated in the laboratory. No significant residues of DE-511 were found below the 0-10cm horizon at the six sites.

Table 2. Half life values derived from European dissipation trials

Site	pH	%OM	CEC meq/100g	Sand %	Silt %	Clay %	Half-life/ Days
Ismaning, D	7.3	4.9	23.3	1	90	9	6
Marcham, UK	7.9	2.1	15.0	70	12	18	7
Herford, D	6.8	2.3	13.1	47	36	17	20
Crimplesham, UK	7.5	1.9	6.9	84	7	9	27
Rohr, D	7.1	4.9	21.4	36	42	22	41
Grebin, D	5.6	2.0	7.8	47	36	47	47

Batch adsorption/desorption studies gave Kd values of 1-9 for various soil types. Laboratory non-aged soil leaching studies showed <1.0% of DE-511 leached from sandy loam and loamy sand columns with <20% leaching from a 93% sand column. However, field data generated from high sand content soils at Crimplesham and Marcham gave no residues of DE-511 below the 0-10cm horizon. The values from the adsorption/desorption study are somewhat lower than expected when compared to the laboratory leaching data and field dissipation trials. More representative aged soil desorption studies demonstrated a greater affinity for binding and consequently higher Kd values (2-30).

CONCLUSIONS

Soil residue studies demonstrated a short to moderate half-life for DE-511. The residue level below 10cm was consistently lower than 1.0 µg/kg (ppb). From the consumer perspective, the recommended use of DE-511 in cereals and maize, will not result in exposure to finite residues via edible commodities.

ACKNOWLEDGEMENTS

The authors wish to thank Ed Olberding, John Perkins and Kerry Hale for their early stage work on crop and soil method development.

REFERENCES

Snel M; Watson P; Gray N; Kleschick W A and Carson C M (1993) DE-511, a new low rate triazolopyrimidine sulfonanilide herbicide for control of broad leaved weeds in cereals and maize. 45th Int. Symp. on Crop Protection, Ghent. In Press.

Baloch R. (1992) Degradation and Metabolism XRD-511 in soil under aerobic conditions. Unpublished.

BBA (1986) Persistence of Plant Protection Products in the soil - Degradation, Transformation and Metabolism. BBA Guideline part IV, 4-1, Biologische Bundesanstalt fur Land-und Forstwirtschaft, Germany.

PERSISTENCE AND LEACHING OF ISOPROTURON AND MECOPROP IN THE BRIMSTONE FARM PLOTS

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ABSTRACT

Two widely-used herbicides, isoproturon and mecoprop, were applied to winter cereals in the autumns of 1990 and 1991. The study plot, at Brimstone Farm in Oxfordshire, is on a structured clay soil and is mole drained. Drainage water and soil cores, taken over a period of 4 months after herbicide application, were examined for these herbicides. Drainflow was late starting in both years due to the dry autumn/winters. Only isoproturon was found in drainage, mecoprop being rapidly degraded in soil before drainflow occurred. Computer simulations, using the model CALF with laboratory measurements of sorption and degradation in the soil, described behaviour in the topsoil but could not predict the macropore flow of isoproturon.

INTRODUCTION

Movement of pesticides into groundwater and surface waters has become a cause for public concern. The main class of pesticides found as contaminants in the UK are herbicides, primarily because they comprise the major usage (65-70% by weight) of crop protection chemicals. In general, the herbicides found in water are of low toxicity to mammals, but drinking water still has to meet the blanket maximum value permitted by the EC of 0.1 $\mu g\ l^{-1}$ for a single pesticide. In areas of the UK that are intensively farmed, it can be difficult for the water companies always to meet this stringent limit. Such an example is East Anglia, where extensive growing of cereals has led to two widely used compounds, isoproturon and mecoprop, being sometimes found in drinking water.

Whilst pesticides can be removed from drinking water, for example by large filters of activated carbon, clearly it is desirable to adopt farming practices that minimise the risk of initial contamination. Particular interest has centred on both light sandy soils, in which sorption of pesticides is weakest, and structured soils, in which some water carrying traces of pesticides can move rapidly down macropores. This paper reports on the movement to sub-surface drainage of isoproturon and mecoprop applied over two seasons to a structured clay soil.

MATERIALS AND METHODS

Experimental design

The work was done on part (Plot 6, area 0.19 ha) of the ADAS SWRC/AFRC IACR collaborative facility at Brimstone Farm, Oxfordshire (Cannell *et al.*, 1984; Harris *et al.*, 1993a). The soil type is a heavy structured clay of the Denchworth series (60% clay fraction, organic matter content 4.6%), this being a type occurring widely in Southern England and which, when drained, is well suited to arable agriculture. The study plot was mole-drained (150-mm wide expander, summer 1988) to a depth of 0.55 m and a mole channel spacing of 2 m; each plot was hydrologically isolated by polythene membranes and intercepter drains to a depth of 1.0 m. Winter wheat was grown on the plot in 1990/91 and winter barley in 1991/92. Autumn applications of isoproturon (2.45 kg a.i. ha^{-1} , as Arelon WDG) and mecoprop (2.4 kg a.i. ha^{-1}, as Isocornox) by hydraulic spraying were made on 8th October 1990 and 9th October 1991. Spring applications of isoproturon (1.65 kg a.i. ha^{-1}) and mecoprop (1.17 kg a.i. ha^{-1}, as Musketeer) were applied on 10th April 1991 and 5th April 1992.

Sampling procedure for soil and drainflow

Meteorological data were obtained from an on-site weather station. Drainflow was measured by a V-notch weir with water samples taken by programmable samplers linked to data-loggers; these samples were taken at the inlet to the weir chamber. In winter 1990/91, detailed sampling over several days of the first storm event (January 1991) was undertaken. In 1991/92, samples were taken over several small flow events from November to March.

Soil was sampled from the plot using a steel corer with an aluminium split liner. Soil cores (length 0.9 m, diameter 0.075 m) were taken immediately prior to application, and at intervals up to 4 months thereafter. Cores were divided into eight sections (0-0.025, 0.025-0.05, 0.05-0.10, 0.10-0.20, 0.20-0.30, 0.30-0.45, 0.45-0.60 and 0.60-0.90 m) with corresponding sections from four replicate cores generally being combined.

Laboratory incubations to determine herbicide persistence in soil

Soil from Brimstone Farm (20 g samples, water content as taken from the field) was treated with isoproturon or mecoprop at 5 $\mu g\ g^{-1}$ (100 μg herbicide added in 20 μl acetone), and the soil water content then adjusted to the desired value. The samples, in glass bottles, were incubated in the dark at 5, 10 or 15°C. At intervals, soil samples from duplicate bottles were analysed for the appropriate herbicide.

Herbicide sorption to soil

Sorption coefficients (K_d) were measured in batch tests in glass centrifuge tubes, using initial herbicide concentrations of 1.0 to 10 $\mu g\ ml^{-1}$ in 0.01M $CaCl_2$ (20 ml) shaken with 2-mm sieved soil (2.0 g for isoproturon, 10 g for mecoprop) for 1 to 24 h. After shaking, the tubes were centrifuged, and the aqueous phase analysed by hplc.

Analytical methods

These have been reported in outline previously (Harris *et al.*, 1993a).

For the water samples, it was not considered useful at the low concentrations encountered to correct for recovery; in practice, no mecoprop was found in the water samples, whilst the recovery of isoproturon was in any case good at 73%. Presence of isoproturon in these samples was confirmed by scanning the uv spectrum using diode array detection on the hplc. Detection limits were 0.1 $\mu g\ l^{-1}$ for isoproturon and 0.2 to 0.5 $\mu g\ l^{-1}$ for mecoprop. For the soil samples, the measurements, which were obtained by hplc, were corrected for recovery (97.1% for isoproturon and 87.5% for mecoprop, detection limits 0.05 and 0.1 mg kg^{-1} respectively).

RESULTS

Both winters were very dry; the drainflow from plot 6 in 1990/91 (December to April) was 34 mm and in 1991/92 only 9.6 mm, compared to 215 mm in 1989/90. In the 1990/91 season the first major flow event occurred in January 1991 (Figure 1), this being some six weeks later than in a typical year. No mecoprop was found; concentrations of isoproturon were initially around 30 $\mu g\ l^{-1}$, falling to about 5 $\mu g\ l^{-1}$ after 5 days (Harris *et al.*, 1993b). The amount of isoproturon in drainage over this event was 0.009% of

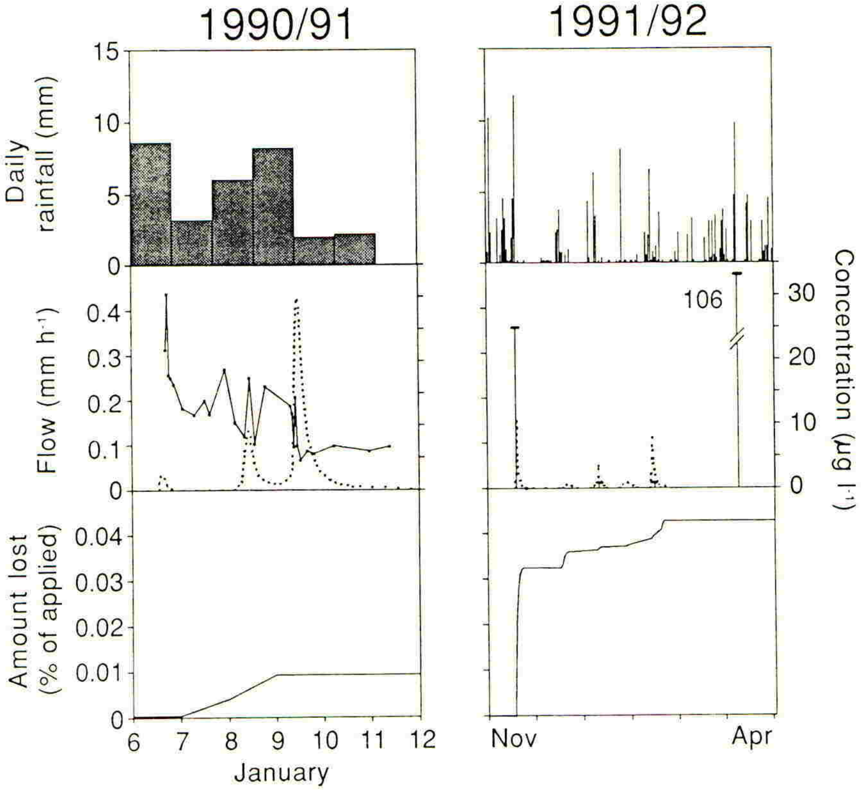

FIGURE 1. Rainfall and drainflow (dotted line), with concentrations and accumulated amounts of isoproturon in drainflow (a) over the first storm event in winter 1990/91 (b) over the winter period 1991/92 (only four water samples available for analysis).

applied. The 1991/92 season was again very dry, and only four samples of water (combined over each flow event) could be obtained for analysis from November 1991 to April 1992. As in 1990/91, no mecoprop was found, and concentrations of isoproturon were 25 $\mu g\ l^{-1}$ in the November flow, followed by a rapid decline save for a high concentration of 106 $\mu g\ l^{-1}$ in the very small April flow following the spring application; the total amount leached from the autumn application was 0.04% of that applied.

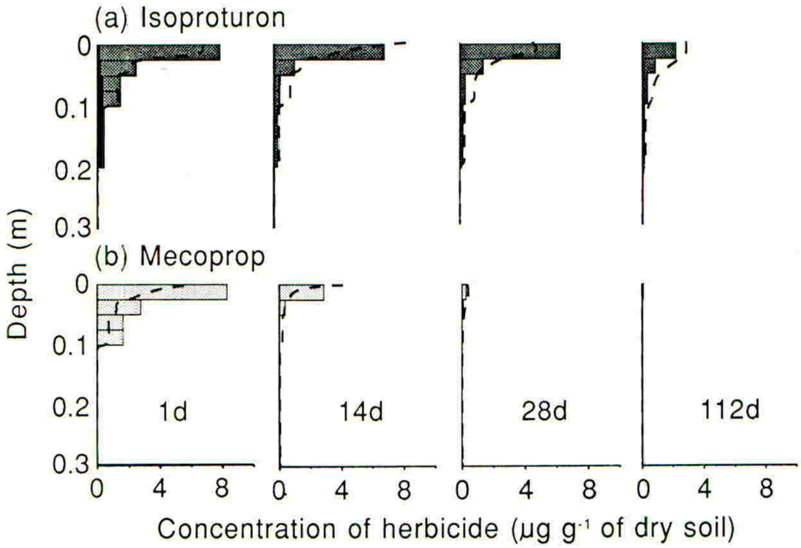

FIGURE 2. Persistence and leaching of isoproturon and mecoprop applied at Brimstone Farm, 9th October 1991. The black area at day 1 indicates carryover of isoproturon from the previous year. The dotted line shows the CALF simulations.

The distribution of the two herbicides in the field following application on 9th October 1991 is shown in Figure 2 (no compound was found below 0.30 m depth; measurements were also made at 7 and 56 d but these are omitted to simplify the presentation). These distributions are similar to those observed in this experiment in 1990/91 (Harris *et al.*, 1993a), no doubt due to both these autumn/winter periods having a similar weather pattern particularly with regard to the below-average rainfall.

The degradation of both compounds in the laboratory incubations in topsoils followed first-order kinetics (Figures 3 and 4), and half-lives were determined using the Maximum Likelihood Programme (Ross, 1987). Mecoprop was rapidly degraded, with a half-life of 3.6 d at 10°C and 80% field capacity; isoproturon was more persistent, with a half-life of 75 d under these conditions. Lower temperatures and drier soils slowed degradation; in particular, the degradation of mecoprop was greatly slowed at 40% field capacity.

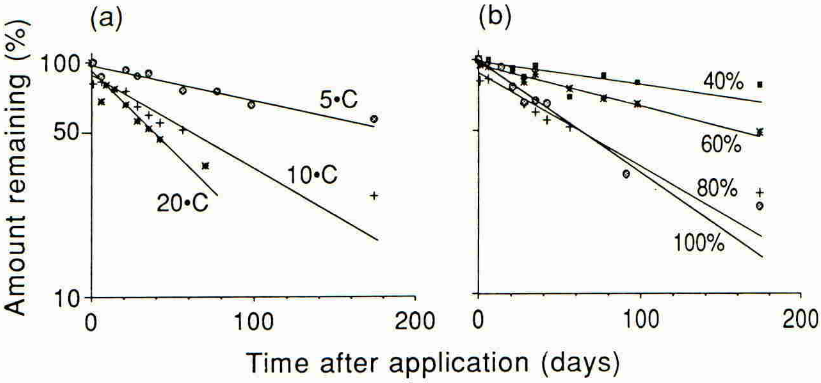

FIGURE 3. Degradation of isoproturon in Brimstone Farm soil (a) effect of temperature at 80% field capacity (b) effect of moisture content (% field capacity) at 10°C.

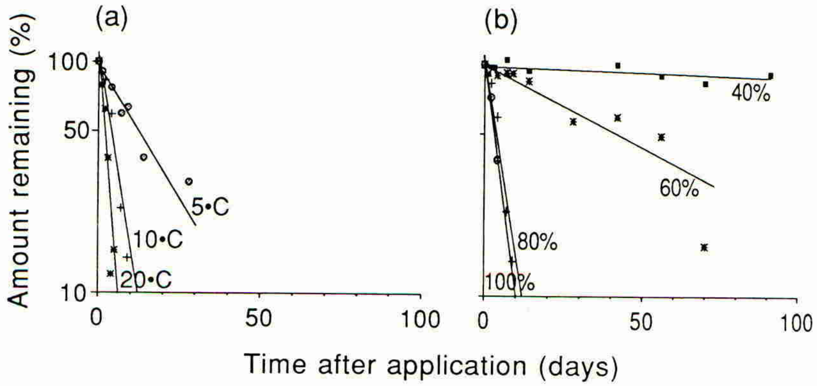

FIGURE 4. Degradation of mecoprop in Brimstone Farm soil (a) effect of temperature at 80% field capacity (b) effect of moisture content (% field capacity) at 10°C.

Sorption followed a linear isotherm and was independent of the equilibration time of up to 24 h in these tests. Isoproturon was moderately sorbed by the topsoil from Brimstone Farm (K_d = 2.9 l kg^{-1}), whilst mecoprop was weakly sorbed (K_d = 0.6 l kg^{-1}) being a weak acid.

Using the independent measurements of herbicide behaviour made in the laboratory, the model CALF (Nicholls, 1982) was able to simulate well the behaviour of isoproturon and mecoprop in the topsoil (Figure 2). However, attempts (not presented) to predict concentrations in drainage water were not successful, because CALF (and the other commonly used models such as PRZM) do not allow rapid flow of pesticides in macropores. Measurements of degradation and K_d are currently being made in the subsoil from this site but, though these are substantially different from values in topsoil, use of preliminary estimates of these parameters in CALF did not improve the description of field behaviour in these two dry years.

DISCUSSION

The short persistence of mecoprop, as observed both in the field and laboratory, explains why mecoprop did not occur in drainflow despite its weak sorption; the rather dry winters in these two years caused a late start to drainflow, giving time for prior degradation. In contrast, isoproturon was still present in the soil in substantial amounts (~40%) some 4 months after application, and so was available for loss to drainflow over a long period.

Neither compound was found below 0.30 m in the soil when the drains were flowing (the method of analysis would have detected concentrations of isoproturon in soil equivalent to 10 $\mu g\ l^{-1}$ in soil water), and furthermore there was not a water table in the surface layers on the plot during the drainflow. Thus the appearance of isoproturon in drainage water from 0.55 m deep was not due to chromatographic flow but was brought about by rapid flow of water to the mole drains with by-passing of the main body of soil. The amounts of isoproturon found in drainage water over each winter was less than 0.5% of that applied, but nonetheless concentrations were up to 30 $\mu g\ l^{-1}$ in the first flows. A wetter season with autumn rainfall may produce more loss in drainflow, especially of mecoprop; ways of modifying the drainage to reduce these losses, for example subsoil cultivation to break the continuity of macropores, are being investigated.

The behaviour in topsoil could be simulated, though not that of macropore flow; the model CALF will be modified to incorporate this feature. However, macropore flow is likely to be variable, depending on the climatic and other site factors such as cropping regimes, and so it is likely that predictions of pesticide concentrations in drainage water will always be uncertain. This should be borne in mind in possible modelling of the role of specific catchments in the contamination of surface waters.

ACKNOWLEDGEMENTS

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REFERENCES

Cannell, R.Q.; Goss, M.J; Harris, G.L.; Jarvis, M.G.; Douglas, J.T.; Howse, K.R.; Le Grice, S. (1984) A study of mole drainage with simplified cultivation for autumn sown crops on a clay soil. 1. Background, experiment and site details, drainage systems, measurement of drain flow and summary of results, 1978-80. *Journal of Agricultural Science, Cambridge*, **102**, 539-559.

Harris, G.L.; Nicholls, P.H.; Bailey, S.W.; Howse, K.R.; Mason, D.J. (1993a). Factors influencing the loss of pesticides in drainage from a cracking clay soil. *Journal of Hydrology* (in press).

Harris, G.L.; Hodgkinson, R.A.; Brown, C.; Rose, D.A.; Mason, D.J.; Catt, J.A. (1993b) The influence of rainfall patterns and soils on losses of isoproturon to surface waters. *Proceedings Crop Protection in Northern Britain*, 247-252.

Nicholls, P.H.; Walker, A.; Baker, R.J. (1982) Measurement and simulation of the movement and degradation of atrazine and metribuzin in a fallow soil. *Pesticide Science*, **12**, 484-494.

Ross, G.J.S. (1987) Maximum Likelihood Program, NAG Limited, Oxford.

A NEW APPROACH TO THE DESIGN OF A LYSIMETER FACILITY

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ABSTRACT

The recently constructed lysimeter facility near Manningtree, U.K. has incorporated several novel features. Leachate is collected by gravity flow through stainless steel tubing leading to a covered leachate collection pit located 4 to 8 m away from the lysimeters. Lysimeters are located inside 2 m square nets, one centred over each lysimeter. Soil cores collected in GRP cylinders are buried directly in the soil. A simple spraying system gives good results for spraying radiolabeled compounds. These features have helped bring about a simple and economic lysimeter facility capable of producing high quality studies.

INTRODUCTION

Lysimeters have become a widely used technique, especially in Europe, for studying the potential movement of agricultural chemicals through the upper metre of soil (Fuhr *et al.*, 1991; Fuhr and Hance, 1992, ECPA, 1993). Since lysimeter cores can be placed outdoors and crops grown on the surface, actual use conditions can be approximated. The ability to use radiolabeled compounds allows the detection of very small amounts of compounds that may be present in the leachate exiting the bottom of the lysimeter.

Most existing lysimeter facilities use one of two approaches to leachate collection. The most common method is to collect leachate in a sump at the bottom of the lysimeter, which is then pumped out at specified time intervals. Another approach used at some facilities is to have an access pit underneath or to the side of the lysimeters. In many facilities, lysimeter cores are collected in fabricated steel or stainless steel tubes which must be discarded after use. Many lysimeter facilities have a large wire mesh structure to protect the area in which lysimeters are located.

During early 1991, a lysimeter facility was established at Aldhams Farm near Manningtree, Essex, U.K. to conduct studies suitable for submission to registration authorities. The facility was designed to comply with the German guidelines on lysimeter studies (BBA, 1990) using lysimeter cores readily available in the U.K. Within these limitations and those imposed by the need for radiation safety, the opportunity was taken to devise a simple and economical facility, using a different approach to leachate collection. This poster describes the features of the lysimeter facility.

DESCRIPTION OF LYSIMETER FACILITY

The lysimeter facility consists of 14 cylindrical soil cores buried flush with the ground surface arranged around a covered leachate collection pit (Figure 1). Each core is 0.5 m^2 in surface area and 1 m in depth, enclosed in a GRP (glass reinforced plastic) cylinder and sealed into a galvanised pan. The cores were provided by the Soil Survey and Land Research Centre, Silsoe using the method described by Yon (1992). Cores of this type are widely used in British lysimeter facilities. Advantages of GRP over stainless steel are that its thermal characteristics are more like those of soil and is cheaper.

For leachate collection, stainless steel tubing connects the bottom of the lysimeter with the collection vessels housed 4 to 8 m away in a 2 m deep concrete lined pit with a covering shed. The tubing gradient is at least 1 in 20. Details of the collection system are provided in Figures 2-4. This simple design for leachate collection requires no pump, sump, or other tank. The design also has the advantage of reducing expensive construction work.

FIGURE 1. General diagram of the lysimeter facility showing the arrangement of lysimeters around the leachate collection pit.

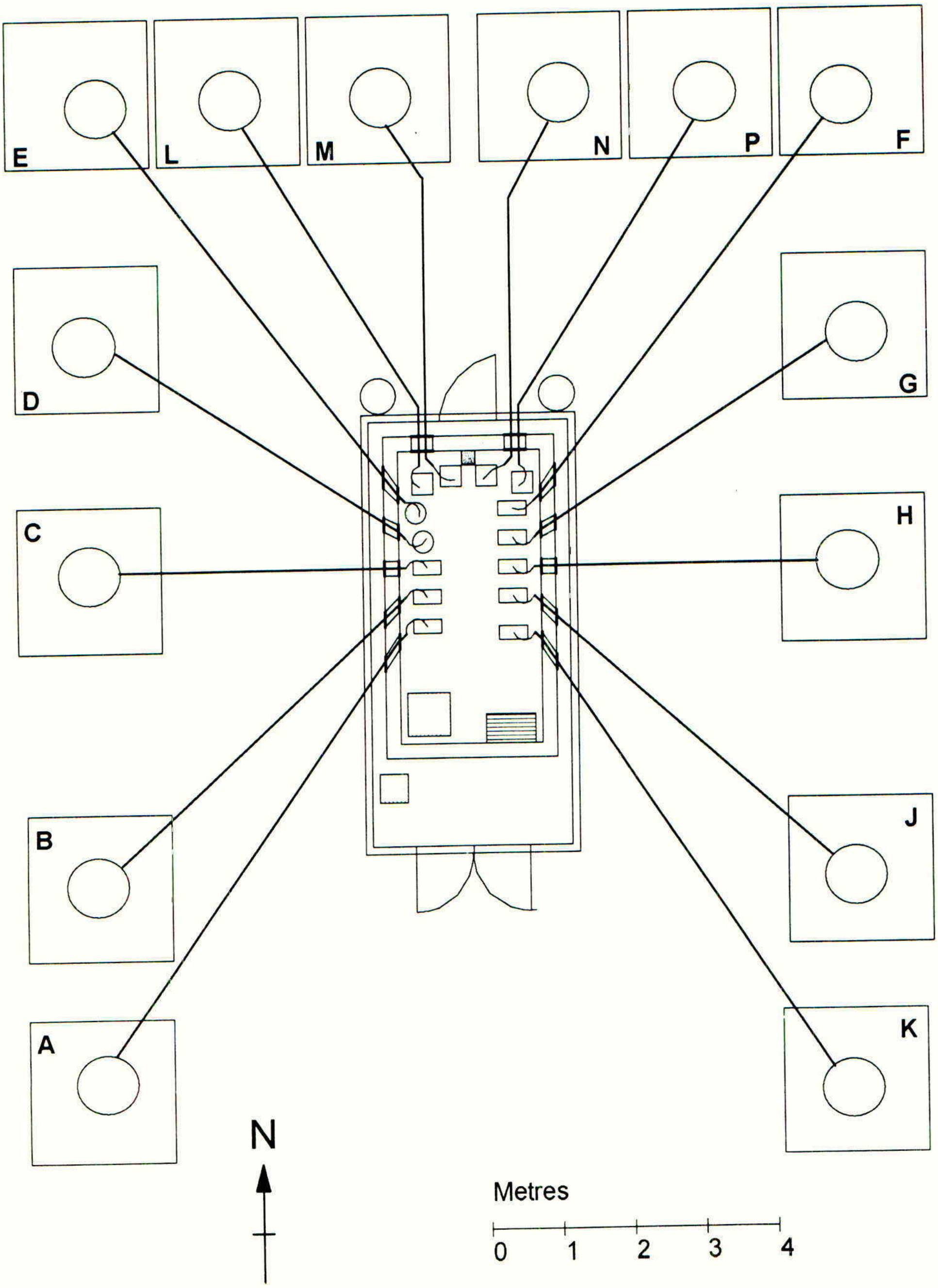
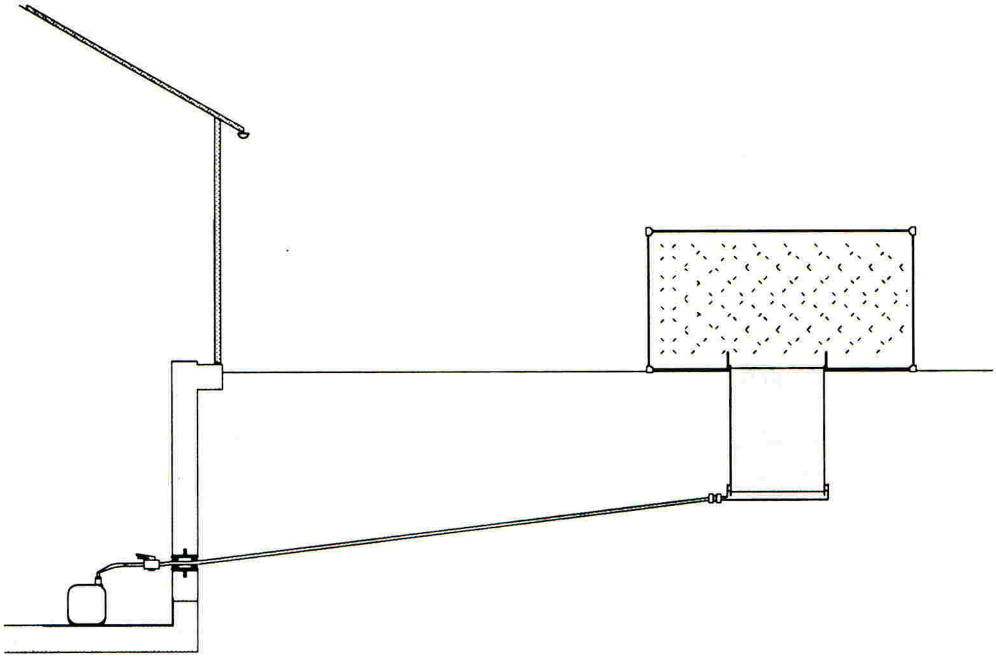


FIGURE 2. Connection of a lysimeter to its leachate collection vessel.



Because the lysimeters are located away from the collection pit, good simulation of normal field conditions is ensured.

Each lysimeter is surrounded by a 2 m square netted area of guard crop. Individual nets, necessary for the exclusion of birds and animals, have the advantage of easy removal and are cheaper than a wire mesh covering the entire facility. Test and guard crops are planted, managed, and harvested to simulate good agricultural practice.

At completion of studies, cores will be removed by hand digging and disconnection of tubing. This procedure is not as elegant as in facilities where the lysimeter is located inside a permanent sleeve. However, it must be cost effective since the small labour cost over the period of a study is more than offset by the elimination of the capital expense associated with the sleeve.

Since the facility is located in an area of low rainfall, irrigation is usually necessary for compliance with the BBA guidelines. A monthly accounting period is adopted and irrigation is added in 4-6 mm lots to reach the Hamburg average.

SPRAYER

In many of the lysimeter studies, applications of radiolabeled material must be sprayed uniformly over the soil surface. Experiments with various solid cone nozzles have shown that a good pattern over an 80 cm diameter circle is provided by a Lurmark Fullspray FN 0.8 brass jet. A simple spraying device of brass fittings, jet holder, and spring-loaded anti-drip strainer is mounted centrally above the lysimeter in a polyethylene lined cage (Figure 6). Compressed carbon dioxide is used as a propellant. After application, losses on sprayer parts and the polyethylene are quantified and have amounted to less than the 10 percent allowed for in dose calculations.

FIGURE 3. Diagram of the covered leachate collection pit.

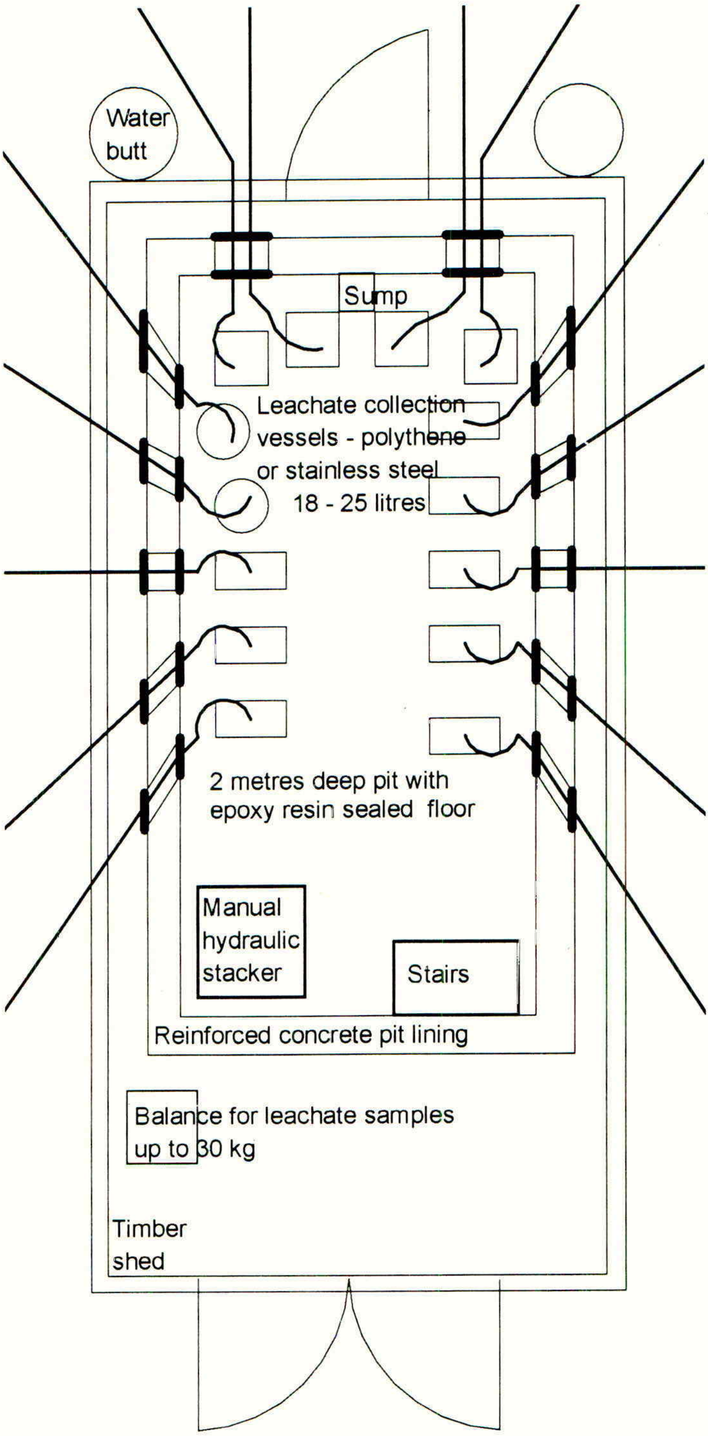


FIGURE 4. Schematic of a single lysimeter.

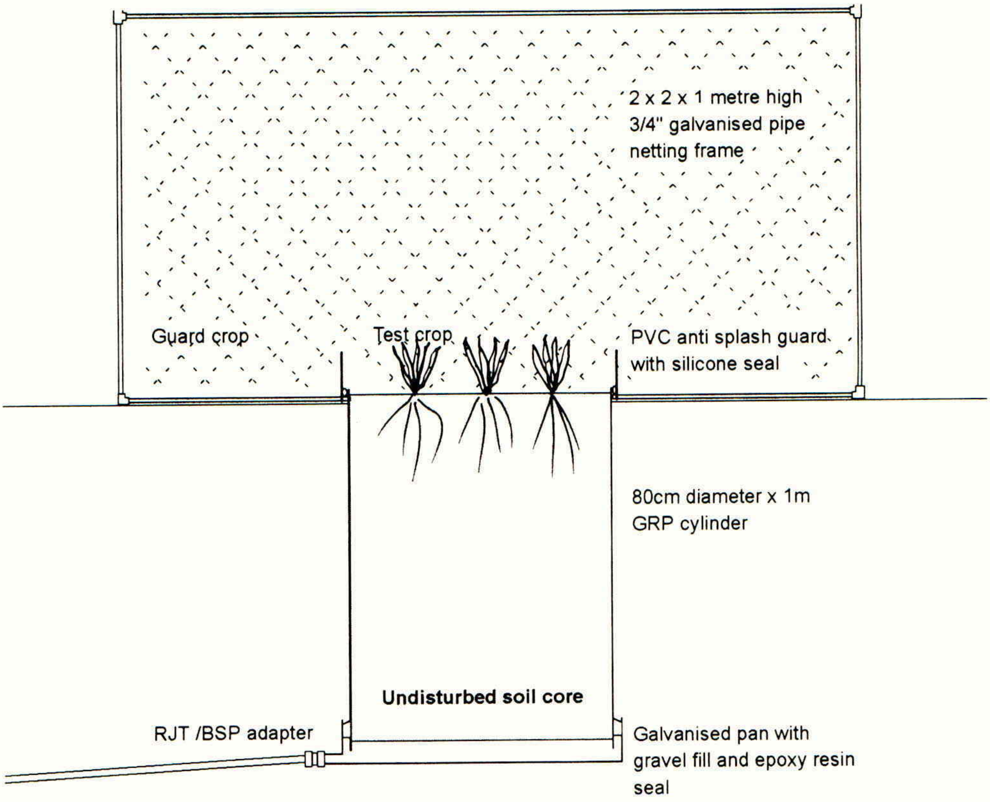


FIGURE 5. Leachate collection apparatus.

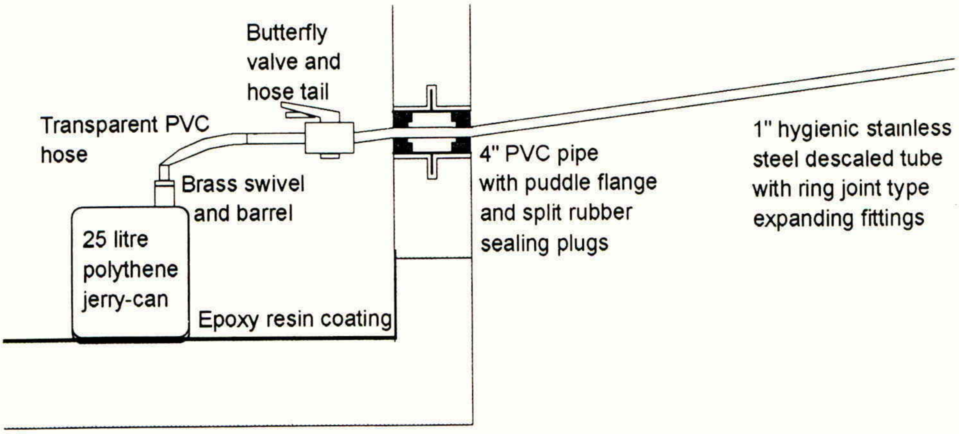
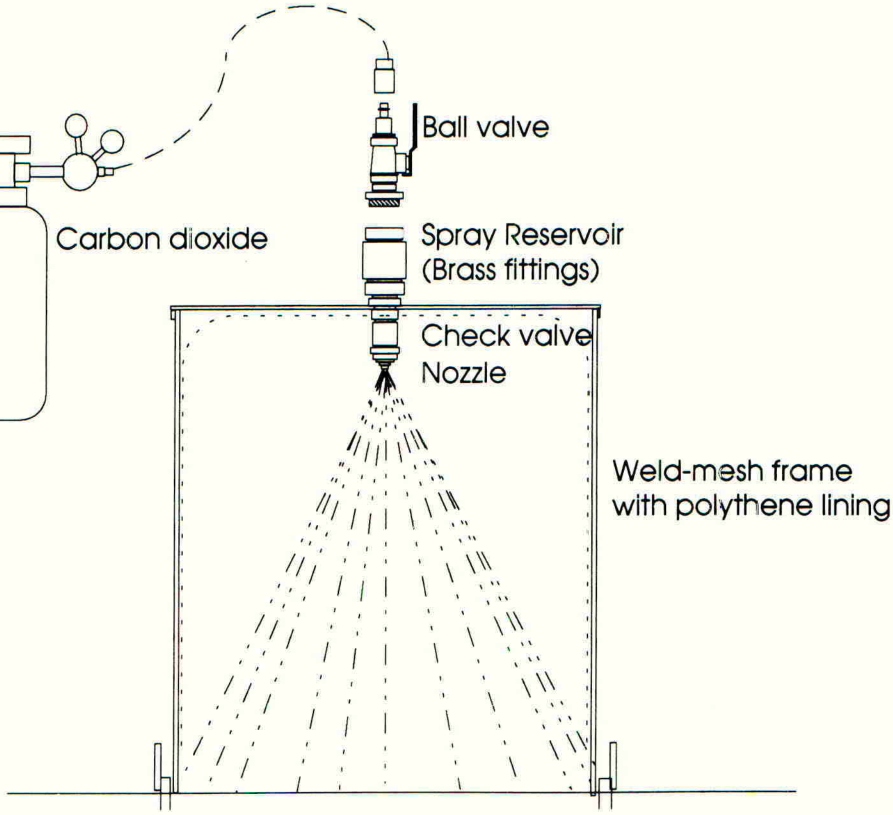


FIGURE 6. Sprayer.



REFERENCES

BBA (1990) Lysimeter Studies for the Displacement of Pesticides into the Subsoil. In: *Guidelines for the Testing of Agricultural Pesticides with the Registration Procedure, Part IV 4-3*, Braunschweig, Germany: Biologische Bundesanstalt.

ECPA (1993) *The Regulatory Use of Lysimeter Studies and Computer Modeling for the Evaluation of Pesticide Mobility in the Soil*, Brussels: European Crop Protection Association, 27 pp.

Fuhr, F.; Steffens, W.; Mittelstaedt, W.; Brumhard, B. (1991). Lysimeter Experiments with ^{14}C-Labelled Pesticides-An Agroecosystem Approach. In: *Pesticide Chemistry Advances in International Research, Development, and Legislation*, H. Frehse (Ed), New York: VCH, pp. 37-48.

Fuhr, F.; Hance, R.J. (1992) *Lysimeter Studies of the Fate of Pesticides in the Soil, BCPC Monograph No. 53*, Bracknell: BCPC Publications, 192 pp.

Yon, D.A. (1992) *The Letcombe Lysimeter Station*. In: *Lysimeter Studies of the Fate of Pesticides in the Soil*, F. Fuhr and R. J. Hance (Eds), *BCPC Monograph No. 53*, Bracknell: BCPC Publications, pp. 65-72.

SURVEY OF ATRAZINE IN SURFACE WATER AND GROUNDWATER IN MAIZE GROWING AREAS OF SOUTH AFRICA

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ABSTRACT

Atrazine was monitored in surface and groundwater in extensive maize production areas of the Transvaal Province of the Republic of South Africa, from September 1991 to February 1992. In about 20 percent of all samples, residues were detected and the identity of the pesticide confirmed using gas chromatograph-mass spectrometry with ion trap detection.

INTRODUCTION

Atrazine residues are common pollutants of surface water and groundwater in various countries world wide. Residues of the compound have also been detected in surface waters in the Orange Free State Province of the Republic of South Africa (RSA) (Hassett *et al*,1987). However, to date no atrazine residues have been reported in groundwater in the RSA. In this study maize producing areas of another province namely the Transvaal, were surveyed for atrazine pollution of surface and groundwater. Two separate farming areas were selected where atrazine is used intensively to control broad-leaved weeds. The surveys were done during the 1991/92 maize production season.

MATERIALS AND METHODS

Reagents

Chemicals used were dichloromethane, toluene and hexane (High Purity UV grade, Burdick and Jackson); anhydrous sodium sulphate (analytical reagent grade - PAL chemicals); and sodium chloride (RPE - Carlo Erba).

Standards

Standard dilutions were made from an atrazine standard, supplied by EPA (USA) with a 99.4% purity.

Apparatus

Rotary evaporators, equipped with water baths and vacuum pumps; Gas chromatograph (GC) (Varian Vista 6000) equipped with a glass column (2030 mm long with 3mm i.d.) packed with 3% carbowax 20m on Chromosorb W-HP 80/100 mesh, and coupled to an alkali flame detector, GC (Varian Model 3400) fitted with a 30 m x 0,32 mm i.d. DB-5 capillary column with film thickness

1µm (J&W Scientific, Calif.) coupled to a Finnigan Mat Model 800 Ion Trap Detector (ITD). Conditions for the first GC mentioned above were as follows: carrier gas (N_2) flow 30ml/min; detector gases, dry air ± 175 ml/min; hydrogen 4.5 ml/min, oven temperature was 200°C isothermal; inlet temperature 220°C. The second GC used an optimum linear flow of carrier gas (helium) of 24 cm/ sec at 230°C with the temperature program for the oven as follows: 60°C for 1 min; ramp to 230°C at 50°c/min; 230°c for 20 min; ramp to 250°c at 50°C/min; 250°C for 10 min; back to 60°C for a new cycle. Version 4 software was used with the ITD and the detector was operated in the full scan mode for m/z 100 - 250 at 1 sec intervals. Samples were injected with a Varian Model 8100 autosampler with programmable injector.

Sampling

Water samples were collected during the period September 1991 to February 1992 on farms near the Eastern Transvaal towns of Bronkhorstspruit, Delmas, Devon, Bethal, Hendrina, Kriel and Van Dyksdrif. Samples were also collected in September 1991 and November 1991 on farms in the vicinity of the Western Transvaal towns of Lichtenburg, Coligny and Koster (Figure 1).

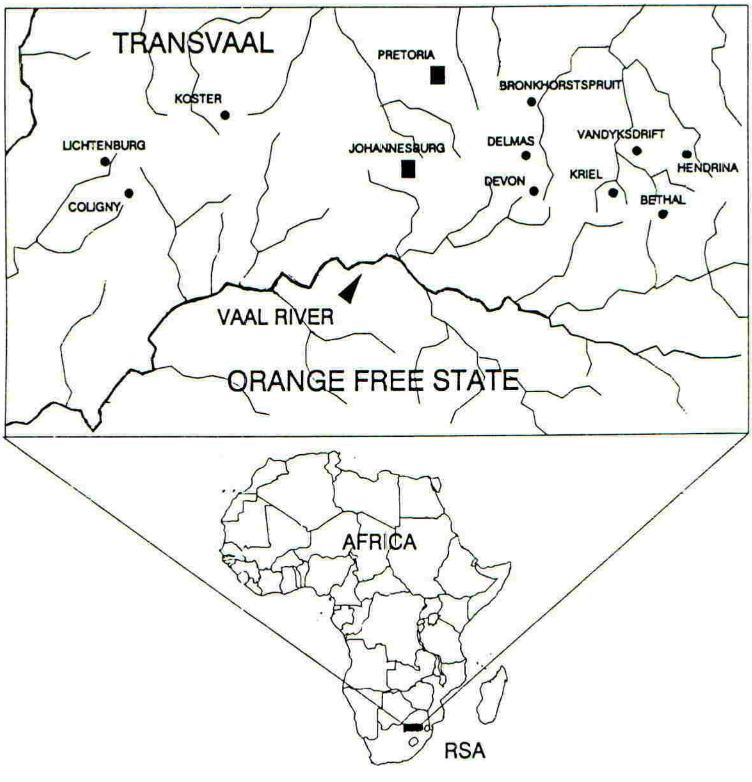

Figure 1 Distribution of towns in sampling areas

The above mentioned areas are situated on plains within a summer rainfall region, receiving rain mostly in the form of thunderstorms. The showers result in surface run-off from maize fields into rivers, farm dams and pans. From these sources water samples were collected as surface water. Groundwater samples were taken from boreholes from which water is pumped to the surface for irrigation as well as for animal and human consumption. Altogether 40 surface and 41 ground (borehole) water samples, collected at 22 and 27 localities respectively were analysed. Samples (in brown bottles) were immediately transported to the laboratory in Pretoria where they were kept at 4°C before extraction commenced.

Sample extraction:

A 1L water sample was shaken three times with dichloromethane (100ml) in a separatory funnel and the solvent layers dried through anhydrous sodium sulphate, collected in a flask and evaporated to about 0.5ml under vacuum using a rotary evaporator; 10ml toluene was added and evaporation (under partial vacuum) was continued until about a drop of solvent remained. The flask was then rinsed with successive small volumes of hexane and the final volume of the sample was made up to 10ml in hexane and stored at 4°C.

The extraction procedure described above was adapted from a residue method by Thompson *et al* (1977). No column cleanup was done. Occasional emulsions formed during the liquid partitioning step, were eliminated by addition of sodium chloride in the separatory funnel. Recoveries of atrazine in blank water samples spiked with standard ranged from 79 to 99 percent with an average of 92.5 percent. With each series of 10 samples, 2 blank reagent samples were subjected to the same procedures to check laboratory contamination.

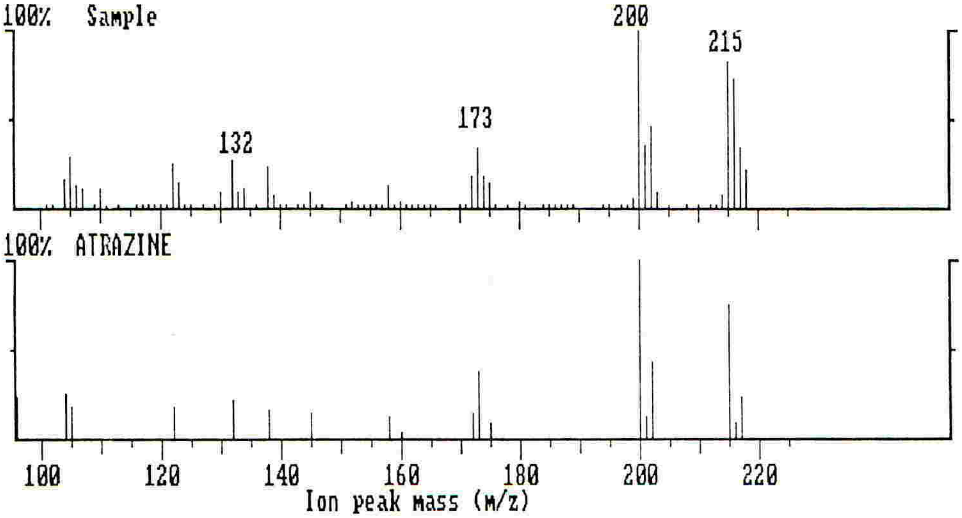

Figure 2 Ion chromatograms generated at the atrazine retention time: water sample chromatogram (above) and library chromatogram of atrazine standard (below)

Screening and confirmation tests

Screening tests (GC-AFD) were carried out and if a peak was detected at the retention time of atrazine, confirmation of identity of the herbicide was performed using the GC-ITD with a similar approach as by De Beer *et al* (1989). To lower the detection limit for the confirmation test, samples were concentrated (under a stream of nitrogen) to 1ml final volume. The ITD was optimised in the Automatic Gain Control mode for maximum sensitivity, and mass spectra were analysed.

Confirmation of identity was done by monitoring for the molecular ion (m/z 215) and three other major ions of atrazine (m/z 132, 173 and 200). The following conditions were regarded as important for positive confirmation: the retention times of the sample and standard peak had to correspond; each of the four major ions in the sample had to have the same retention time as that of the corresponding ion from the standard; and the relative intensities of the four major ions in the mass spectrum of the sample had to match those in the mass spectrum of the corresponding standard. An example of the mass chromatogram of a sample in which atrazine was confirmed, is presented in Figure 2.

Atrazine was quantified by integrating one specific ion (m/z 215) and comparing its integration value with that of the same ion in a known concentration of a standard. The minimum detectable concentration for the ITD was 150 ng atrazine/L water.

RESULTS AND DISCUSSION

Of the 40 surface water and 41 groundwater samples analysed, 8 samples each had atrazine residues detected and confirmed (Table 1). Surface water samples were taken at different dates at localities R7, D2, D3, and D6, but atrazine was detected only once at each of these localities (Table 2). All 3 samples taken at different dates at locality D8 (a farm dam) contained atrazine at exceptionally high concentrations, as indicated in Table 2. Pollution of the dam at D8 was probably caused by the rinsing of spraying pumps close to the dam by farm workers in Oct 1991 (Personal communication, Mr. Grobler, farm owner).

Of the 8 groundwater samples found positive for atrazine, 2 were taken at the same locality (B9) at different dates, however further samples taken in Dec. 1991 and Feb. 1992 contained no detectable residues. Although 4 samplings were done on different dates at locality B10, detectable residues were only found once (Table 2).

From the results of the monitoring of water samples from the Transvaal maize production areas, it is clear that atrazine residues occur in surface and groundwater at different localities and dates during the growing season. About 20 percent of all samples contained detectable residues at the nanogram or subnanogram level per litre.

TABLE 1: Number of samples collected in eastern and western Transvaal and number in which atrazine was detected

	Surface water	Groundwater
Number collected	40	41
Number of localities	22	27
Number found "positive"	8(20%)	8(19,5%)

TABLE 2: Samples of surface- and groundwater in which atrazine residues were detected

Locality	Town	Source and date collected	Atrazine µg/l
R7	Kriel	River 13 Dec. 1991	2.50
D2	Bethal	Dam 13 Dec. 1991	14.97
D3	Hendrina	Dam 13 Dec. 1991	8.78
D4	Hendrina	Dam 25 Sep. 1991	0.88
D6	Kriel	Dam 13 Dec. 1991	0.73
D8	Bethal	Dam 22 Okt. 1991	106.57
D8	Bethal	Dam 13 Dec. 1991	298.20
D8	Bethal	Dam 18 Feb. 1991	156.10
B9	Bethal	Borehole 25 Sep. 1991	3.38
B9	Bethal	Borehole 22 Okt. 1991	0.49
B10	Hendrina	Borehole 25 Sep. 1991	2.17
B27	Hendrina	Borehole 13 Dec. 1991	3.89
B15	Lichtenburg	Borehole 26 Sep. 1991	4.36
B17	Lichtenburg	Borehole 26 Sep. 1991	0.29
B18	Lichtenburg	Borehole 26 Sep. 1991	1.34
B19	Lichtenburg	Borehole 26 Sep. 1991	0.52

The presence of atrazine residues in groundwater is the first reported finding in the RSA. During the 1991/92 maize growing season, the RSA had one of its severest droughts in many years. How such abnormal low rainfall may affect the leaching of atrazine in soil or its wash-off to surface water sources is not known. It can be postulated that the occurence of atrazine in groundwater sources possibly is the result of applications during the previous season.

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REFERENCES

De Beer, P.R.; Sandman, E.R.I.C.; Van Dyk, L.P. (1989) Gas chromatography with ion trap detection to determine six herbicides in atmospheric samples. *Analyst* **144**, 1641-1645.

Hasett, A.J. Viljoen, P.T.: Liebenberg, J.J.E. (1987) An assessment of chlorinated pesticides in the major surface water resources of the Orange Free State during the period September 1985. *Water S.A.*, **13**, 133-136.

Thompson, J.F.; Reid, S.J.; Kantor, E.J. (1977) A multiclass, multiresidue analytical method for pesticides in water. *Archives of Environmental Contamination and Toxicology* **6**, 143-157.

REDUCING THE IMPACT ON THE ENVIRONMENT OF AGRICULTURAL PESTICIDES

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ABSTRACT

An experimental programme is described which aims to evaluate methods of reducing watercourse contamination by agricultural pesticides. Included are studies on pesticide transfer and associated mechanisms, the validation of models and the implementation of management practices. Pesticide transfer is measured by field scale experimentation involving the collection of drainage and runoff samples. In laboratory conditions, pesticide availability in soil solution is studied using glass microfibre filters, at soil moisture levels below field capacity. Potential pesticide mobility in runoff is estimated using rainfall simulation plots, which permit pesticide partition between solid and liquid phases to be followed in dynamic conditions for both active ingredients and formulations. The results of these various experiments are used to validate mathematical models. They are also useful to estimate the environmental impact of preventative methods, in particular improvements in agricultural practices (choice of pesticide, rate, timing, etc) and field management (grass buffer strips).

INTRODUCTION

It is likely that neither restrictions on pesticide use nor the banning of some active ingredients will be sufficient to guarantee drinking water quality in accordance with European Community standards. In order to reconcile the demands of water quality and chemical protection of crops, the latter being essential to obtain produce of good quality, it is necessary to understand the mechanisms of pesticide transfer to surface water.

Within this context ITCF, INRA and CEMAGREF have started a research programme aimed at reducing the impact of pesticides on water quality. This study involves four main lines of research :

- the evaluation of the amounts of agricultural pesticides which may contaminate surface water by runoff or through the drainage system of cultivated land;

- understanding the physical, chemical and biological mechanisms of pesticide transfer, by studying the behaviour of a number of active ingredients in soil, soil solution and runoff;

- the validation and the adaptation of existing mathematical models describing pesticide behaviour in soil and transport towards watercourses, using the results of the experimental programme and which may also generate a data base;

- the adaptation of agricultural practices and testing of the effectiveness of grass buffer strips, to limit the transfer of pesticides in the environment.

All these concerns are brought together at the Water Quality Station of the "La Jaillière" experimental farm (Loire Atlantique/Maine et Loire), where plots provide outdoor experimental facilities at the field scale.

EVALUATION OF PESTICIDE TRANSFER TO SURFACE WATER

Experimental equipment

The experimental station is located in the domain of the ITCF called "La Jaillière", situated between the cities of Angers (Maine et Loire) and Nantes (Loire Atlantique). The climate (temperate oceanic), the soils (hydromorphic sandy loams over schist) and the agricultural practices are representative of a large part of the north west quarter of France. The station includes 8 plots of 0.5-1 ha. Six are individually equipped with drainage systems and hydrologically isolated (Figure 1). Five plots are fitted with runoff collection facilities (Penel & Lesaffre, 1989). This kind of experiment, with simultaneous runoff and drainage measurement, is unique in France. The runoff collection system has been especially designed to analyse runoff flows and the amount of pesticides transferred. It consists in plastic gutters layed downslope of the plots. Drainage and runoff from each plot are carried through buried pipes to a recording station equipped with automatic samplers. The plots are also equipped with tensiometers and piezometers. Two crop rotations are being studied : 1) winter wheat/catch-crop Italian ryegrass/forage maize, 2) peas/winter wheat.

Measurements

For the plots, agronomic, bioclimatic and hydraulic parameters are recorded. The pesticides contained in runoff and drainage samples are analysed.

- Agronomic records : crop husbandry, soil sections, the yields of crops and the amount of pesticides applied.
- Bioclimatic records : hourly rainfall and soil temperature.
- Hydraulic records : hourly soil water potential, watertable level, drainage and runoff flows (Dutertre, 1993).
- Water quality records : pesticide amounts in soil, drainage and runoff, either on a time basis (every eight hours), or on weekly cumulative samples.

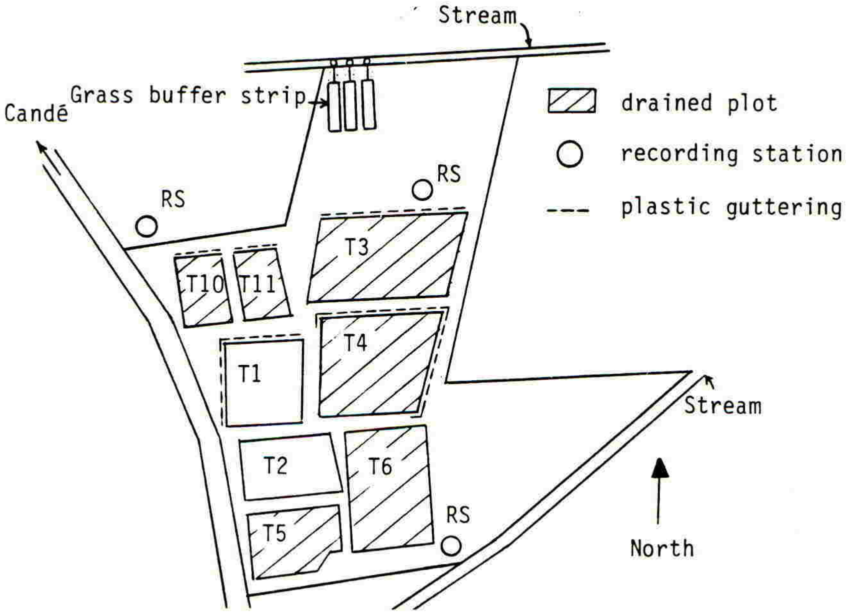

Figure 1. General plan of the Water Quality Station.

STUDYING MECHANISMS

Availability of pesticides in soil solution

Availability of pesticides in soil solution may be evaluated in laboratory conditions (Gaillardon *et al.*, 1991). Dry soil is treated with an aqueous solution of a ^{14}C-labelled compound. At intervals, soil solution is sampled by means of glass microfibre filters, which retain soil water by capillarity when placed in contact with the soil. Water volume and pesticide amount in filters are determined by weighing and radioactivity counting, and concentration and percentage of pesticide in soil solution are calculated. To ensure that no degradation occurres, the soil is extracted with an appropriate solvent at the end of the experiment. The extract is concentrated and then analysed for AI and breakdown products by tlc. Measurements may also be conducted at low temperature to prevent degradation.

Measuring the amount of pesticide in soil solution allows adsorption and desorption studies of pesticides by unsaturated soils. For example, one day after treatment of a clay loam with 10µg of isoproturon or diuron per g of soil, at 29% soil moisture content, the soil solution contained 28% or 10% respectively of the applied herbicide and these percentages decreased to 23% or 5% respectively two weeks after treatment. Herbicides were rapidly adsorbed by soil initially but adsorption continued for a long time. Small amounts were adsorbed during the slow phase of adsorption, inducing a decrease in herbicide concentration in soil solution, especially for the most adsorbed herbicide (Figure 2). Current studies with diuron show that adsorption increases when herbicide dose is reduced and might be influenced by soil moisture content. Qualitative data on the soil solution may also be gained and thus changes in pesticide (or metabolite) partition between liquid and solid phases of soil may be observed during degradation (Gaillardon & Sabar, 1993).

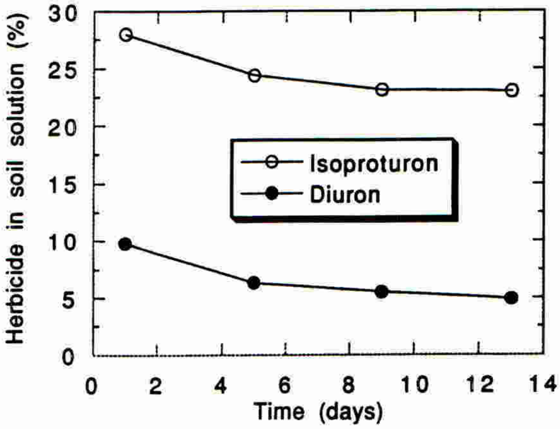

Figure 2. Changes in percentage of diuron and isoproturon in the soil solution of a clay loam treated with 10µg/g. Soil moisture content 29%. SD of mean = 1 (3 replicates).

Pesticide transfer in runoff

The partition of pesticide between water and suspended particles carried in runoff has been studied by means of a rainfall simulator (Gouy, 1993). An oscillating-nozzle rainfall simulator (Asseline et Valentin, 1978), applied intense rainfall (70 mm/h for one hour) to the surface of a 1 m^2 plot filled with 10 cm depth of soil packed into a metal tray and inclined at an angle of 16%. The tray was constructed with troughs to collect runoff and direct it into a glass bottle. Four formulated pesticides were applied together : atrazine (wettable powder), simazine (wettable powder), lindane (soluble concentrate) and methidathion (soluble concentrate), at an application rate for each AI of 70 mg/m^2. Pesticides were surface applied on bare soil, 15 hours before rainfall simulation. Three different soils were used : 1) a loamy sand (Ardières, organic matter = 0.2%); 2) a sandy loam (Jaillière, organic matter = 2%) and 3) a calcareous silt loam (Charente, organic matter = 2%). In order to evaluate variation in adsorption coefficient on suspended particles during a storm, runoff was sampled at 5 minute intervals during the first 30 minutes of runoff and at 10 minute intervals thereafter.

A measure of total eroded particle load was made for each sample. Runoff samples were filtered through a 1.2 micron porosity fibre-glass filter. Pesticide content of suspended particles and filtered water were analysed by gas chromatography. Adsorption coefficients, Kd, were calculated for each time period. Kd = Cs/Cw, where Cs is the pesticide concentration in the soil or solid phase (µg/g) and Cw is the pesticide concentration in solution (µg/ml) at equilibrium.

Pesticide transfer into runoff was found to be highly dependant on the soil type. Using the Ardières soil, only 0.2 to 0.5% of total amount applied was carried off in runoff compared to 3 to 8% with the Jaillière soil and 8 to 30% with the soil of Charente. In all three cases, more than 70% of each pesticide was distributed in the water phase. Pesticide concentrations in solution in runoff decreased over time, as did the amount adsorbed per g of suspended particles and the adsorption coefficients Kd varied by several orders of magnitude during a storm. These values of Kd were much greater than values corresponding to standardised methods with pure AI's on soils. This can be seen with the Ardières soil, where mean suspended particle load was lower. When relating Kd and suspended particle load for each time period, Kd decreased with particle load increase and this relationship could be described using a power function, (Figure 3).

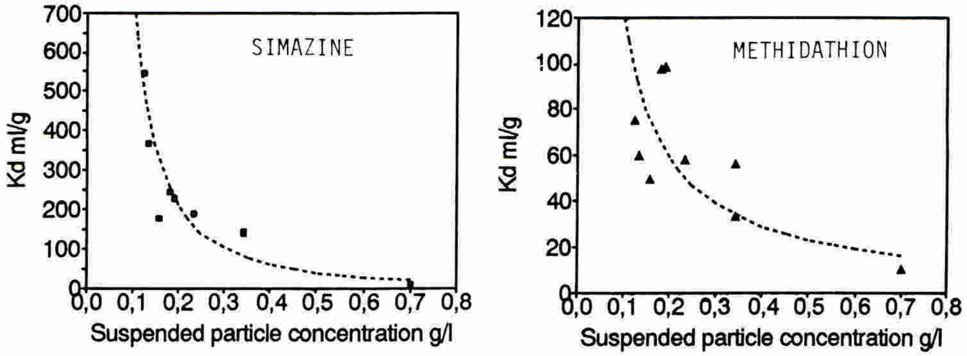

Figure 3. Relationship between Kd of suspended particles in runoff and the corresponding suspended particle concentrations (Ardières soil). Power function adjustment.

THE VALIDATION OF MODELS

Models are required to predict the risk of pesticide transfer to surface water. Most current models require validation and modification to simulate pesticide transfer. The models being studied consider pesticide interaction with soil and pesticide transfer through infiltration (INRA) (PRZM, Carsel *et al*, 1984), drainage (CEMAGREF, Antony) (SIDRA, Lesaffre & Zimmer, 1988) and runoff (CEMAGREF, Lyon) (CREAMS, Knisel, 1980). The results of experiments at various scales (laboratory, rainfall simulation plot, lysimeter, field) are used to test and improve the modelling. One of the objectives of this study is to predict the influence of various agricultural pratices on pesticide transfer.

AGRICULTURAL MANAGEMENT TO REDUCE PESTICIDE TRANSFER

At the begining of 1992, a study started examining the methodology necessary to evaluate the effectiveness of grass buffer strips to reduce pesticide transfer in runoff. The experimental system consists on three plots of wheat (5×25 m), located up-slope from a grass buffer strip 12 metres long. Each plot is hydrologically isolated. According to the position of the collection system, the effectiveness of 0, 6 or 12 metre grass buffer strips can be compared. During rain, total runoff on each plot is collected and analysed, measuring the total volume of runoff, the suspended particle load and the pesticide content of both liquid and solid phases.

FUTURE WORK

A campaign of measurement is planned for autumn 1993. It will consist of testing the performance of the gutter system to collect runoff, testing the sampling timing for runoff, validating the methods of pesticide analysis and analysing the residues of atrazine, terbuthylazine, isoproturon, diflufenican, carbofuran, lindane, flusilazole and fluvalinate in runoff and drainage samples. With regard to the grass buffer strips study, a unique event occurred in spring 1993 and isoproturon and diflufenican transport was monitored. However, more information is necessary before conclusions can be drawn.

REFERENCES

Asseline, T.; Valentin, C. (1978) Construction et mise au point d'un filtromètre à aspersion. *Cahier de l'ORSTOM. Ser. Hydrol.*, **15**, (4), 321-348.

Carsel, R.F.; Smith, C.N; Mulkey, L.A.; Dean, J.D.; Jowise, P. (1984) Users Manual for the Pesticide Root Zone Model (PRZM). Release 1, ERL, US EPA, PB85 158913.

Dutertre, A. (1993) L'expérimentation "drainage - qualité des eaux" de la Jaillière. *Acte des journées d'étude AFEID, AFGR, SNED "Hydraulique Agricole et Environnement"*, La Rochelle, Juin 1990, 59-64.

Gaillardon, P.; Fauconnet, F.; Jamet, P.; Soulas, G.; Calvet, R. (1991) Study of diuron in soil solution by means of a novel simple technique using glass microfibre filters. *Weed Research*, **31**, 357-366.

Gaillardon, P.; Sabar, M. (1993) Changes in the concentrations of isoproturon and its degradation products in soil and soil solution during incubation at two temperatures. *Weed Research*, in press.

Gouy, V. (1993) Contribution de la modelisation a la simulation du transfert des produits phytosanitaires de la parcelle agricole vers les eaux de surface. *Thesis*. ULP de Strasbourg, CEMAGREF de Lyon, 350 pp.

Knisel, W.G (1980) CREAMS, a field scale model for chemicals, runoff and erosion from agricultural management systems. Knisel (Ed) USDA. *Conservation Research Report*, **26**, 643 pp.

Lesaffre, B.; Zimmer, D. (1988) Subsurface drainage peak flows in shallow soils. *Journal of Irrigation and Drainage Engineering, ASCE,* **114**, (3), 387-406.

Penel, M.; Lesaffre, B. (1989) Surface runoff on drained and undrained plots. *ASAE-CSAE Summer meeting. Paper 892104*, 11 pp.

BRIGHTON CROP PROTECTION CONFERENCE - Weeds - 1993 6D-15

A NEW APPROACH TO THE DETERMINATION OF THE DEGRADATION KINETICS OF ^{14}C-LABELLED PESTICIDES UNDER FIELD CONDITIONS

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ABSTRACT

A system has been developed whereby soil segments can be removed from undisturbed soil core at different sampling intervals. To achieve this, metal tubes were inserted vertically into a lysimeter soil. The surface of the entire lysimeter was then cultivated according to good agricultural practice. Only the surface of the soil in the tubes was treated with the radioactively labelled active ingredient in order to allow an exact determination of the translocation behaviour of parent compound, known and unknown metabolites and the formation of bound residues. At each sampling date, an entire soil tube was removed from the lysimeter for analysis. The results of this field trial were compared with those of the laboratory test being carried out simultaneously. By the example of ^{14}C-methabenzthiazuron it was demonstrated that all important parameters can be exactly monitored under practice-relevant conditions when using this sampling system.

INTRODUCTION

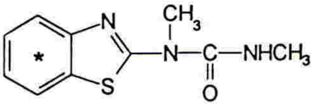
Methabenzthiazuron, N-2-benzothiazolyl-N,N-dimethylurea, is a broad-spectrum herbicide which can be used for pre- and post-emergence application. The active ingredient gives good control of numerous species of broad-leaved and grass weeds. It is absorbed both by the aerial parts of the plants and by the roots.

The degradation behaviour as well as the metabolization of a plant protectant under standard laboratory and field conditions is determined using methabenzthiazuron as an example. The test is carried out with radioactively labelled active ingredient in order to allow an exact detection of the proportion of bound residues and the translocation behaviour.

MATERIAL AND METHODS

Radiochemical

The tests were carried out with [phenyl-UL-^{14}C]methabenzthiazuron. The radiolabelled active ingredient had a specific radioactivity of 1.58 MBq/mg (42.7 µCi/mg) and a radiochemical purity of >99% according to TLC and HPLC.



* labelling position

Tested soil

The two soils specified in the Guidelines (Schinkel *et al.*, 1986; BBA, 1990) were composed as follows:

		Soil texture					
soil	depth cm	sand 2000-50 μm	silt 50-2 μm	clay <2 μm	C org	pH H_2O	pH $CaCl_2$ (0.01M)
lab study BBA Speyer 2.2 loamy sand	0- 30	86%	8%	6%	2.60%	6.3	6.2
field study BBA lysimeter soil Monheim sandy loam	0- 30	72.4%	22.6%	5.0%	1.35%	6.9	6.4
	30- 70	72.0%	22.4%	5.6%	0.63%	7.0	6.4
	70-100	78.3%	12.2%	9.5%	0.18%	7.1	6.5

Soil treatment

The rate of application was at the commercial use rate of 2.8 kg a.i./ha or 4 kg formulated product/ha.

Laboratory test

The active ingredient was added to the soil Speyer 2.2 via a subsample (10 g) in order to avoid differences between the individual samples and influences of the solvents. After evaporation of the solvent, the subsample was thoroughly mixed with the remaining soil and then the soil was distributed among the incubation vessels (Figure 1). The Radioactivity of 577.4 KBq and 365 μg active ingredient were contained in 100 g dry weight of soil. This corresponds to 2.74 kg a.i./ha based on penetration in a 5 cm soil layer and a density of 1.5 g/cm³. The vessels were incubated in the dark at 20°C. During the test, the soil moisture was maintained at 40% of the maximum water capacity. The biomass was determined at the beginning and the end of the test.

Field study

The study was carried out with an undisturbed soil core (lysimeter) which had been installed in the control area of the Pflanzenschutzzentrum Monheim. The lysimeter was established in 1990 by means of a steel frame and had a surface area of 1 m² and a depth of 1.1 m. In February 1992, five stainless steel tubes with a diameter of 25 or 23 cm and a length of 65 cm were pushed into the 1 m² lysimeter from the top for later sampling (Figure 2).

FIGURE 1. Lab study (incubation vessel for aerobic soil metabolism)

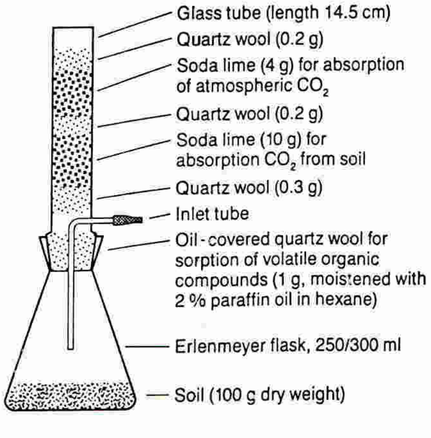
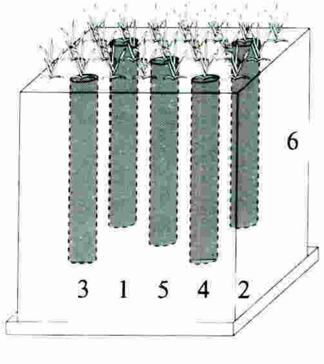


FIGURE 2. Field study (lysimeter)



1 - 5 :tubes with undisturbed soil
6 :1 m² - lysimeter

Summer wheat was sown on the entire lysimeter surface on March 24, 1992 while the active ingredient was applied on March 26, 1992 to the area of the tubes only. The radiolabelled active ingredient was applied in form of the commercial 70 WP-formulation by incorporating the dispersion into the amount of soil (252 g or 211 g, resp.) corresponding to the layer of 0.3 cm in the tubes. The treated soil was uniformly distributed in the tubes. Determination of the losses allowed to exactly indicate the applied amount of radioactivity for each tube:

Parameter		Surface area dm^2	Active ingredient mg	Radioactivity MBq	kg a.i./ha
Control	0 sample	-	13.8	23.00	2.8
Tube (Figure 2)	1	5.0	13.7	22.94	2.7
	2	5.0	11.6	19.45	2.3
	3	5.0	13.7	22.86	2.7
	4	5.0	11.3	18.85	2.3
	5 (center)	4.2	11.3	18.95	2.7

Sample processing

Laboratory study

One entire incubation vessel each was processed on days 0, 1, 3, 7, 14, 30, 60 and 100 by extracting the soil three times with methanol and twice with ethyl acetate. The trap attachment was analyzed for $^{14}CO_2$ and other volatile compounds.

Field study

One tube (round lysimeter) each was pulled out of the 1 m^2 lysimeter 19, 60, 103, 130 and 200 days after application of the active ingredient and the remaining cavity was filled with soil. The plants grown on the removed soil were cut at ground level and extracted with acetone. The radioactivity of the extract and of the residue was determined. The soil was investigated in layers: 0-5 cm, 5-10 cm, 10-20 cm, 20-30 cm, 30-35 cm and 35-40 cm. A total of 50 individual samples of about 3.5 g each were taken from the air-dried, thoroughly mixed soil. The mixed sample was extracted 3 times with methanol and twice with ethyl acetate.

Radioactivity measurements

Liquid samples were measured in a liquid scintillation counter (Rackbeta 1219, LKB Co.) using scintillation gel (®Instant Scint. Gel, Packard Co.). The radioactivity in the soil was determined by combustion of three samples of approximately 1 g each in an oxidizer (OX-300, Harvey Instrument Corporation). The liberated $^{14}CO_2$ was collected in a suitable scintillation cocktail (®Carbosorb and ®Permafluor E+, Packard Co.). For determination of $^{14}CO_2$, the soda lime was dissolved with 18% hydrochloric acid (10 g soda lime with 60 ml hydrochloric acid) and the liberated $^{14}CO_2$ was passed into a ®Carbosorb-Permafluor E+ cocktail. The oil-coated quartz wool of the trap attachment (Figure 1) was extracted with ethyl acetate.

Chromatography

The soil extracts were subjected to HPLC- and TLC-analysis. HPLC analysis was performed on a liquid chromatograph HP 1500 with a radioactivity flow-through detector Ramona 90 using ®Li Chrosorb RP 18 columns (5 µm; 250-4). The mobile phase was 65% of a mixture: water-acetonitrile-phosphoric acid (95+5+0.2) and 35% acetonitrile.

Thin-layer chromatographic separations (TLC) were carried out on precoated TLC-plates, silica gel 60 F254 0.25 mm (Merck Co.) and the following solvent system was used (volume ratios): toluene-methanol (9+1)

Mass spectroscopy

The concentrated soil extract from the field trial, day 130, was shaken with dichloromethane. After TLC-separation the isolated metabolites were subjected to mass spectroscopy HP 5970 with GC HP5880A).

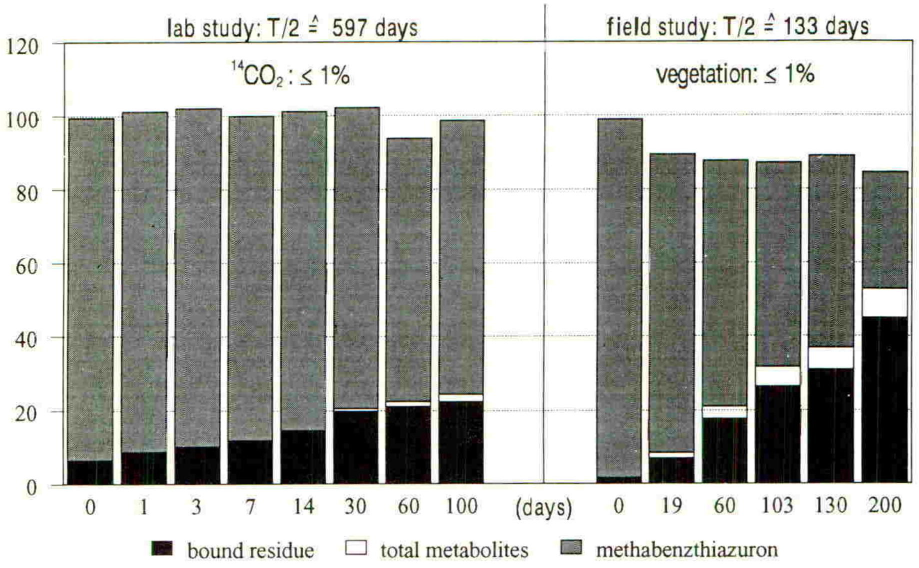
RESULTS AND DISCUSSION

Distribution of radioactivity

Laboratory study

The recovered amount of radioactivity was related to the applied amount of ^{14}C (577.4 KBq ≙ 365 µg a.i./100 g soil) and ranged from 95 to 102%. The bound residue increased continuously with the extracted portion declining correspondingly (Figure 3). The mineralization during the test period was about 1%. The biomass of the soil declined significantly from 444 to 285 mg microbial carbon/kg soil.

FIGURE 3. Material balance and degradation of methabenzthiazuron in soil (% of applied)



Field study

The determined values were related to the amount of radioactivity applied per tube. During the trial period the proportion of extracted radioactivity declined to 40%. The proportion of bound residue increased to 45% (Figure 3). The plants absorbed 1% of the radioactivity. The losses in the balance were predominantly attributed to mineralization. The applied radioactivity was translocated insignificantly only. During the entire trial period, the layers 30 to 35 cm and 35 to 40 cm contained less than 0.1% of the applied radioactivity (Table 1).

TABLE 1. Degradation of methabenzthiazuron (% of applied)

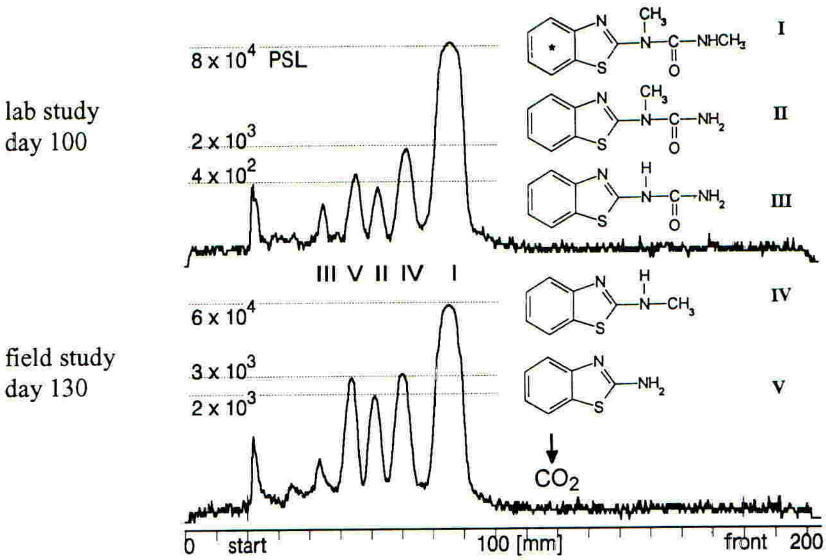
day (tube)	soil layer cm	extracted					bound	total (soil)	vege-tation
		a.i.	metabolites						
		I	II	III	IV	V			
19	0 - 5	80.2	0.7	---	0.3	0.4	6.7	88.4	<0.1
	5 - 10	0.8	---	---	---	---	0.1	1.0	
(1)	10 - 20							0.1	
	20 - 30							<0.1	
	30 - 35							<0.1	
60	0 - 5	65.1	1.5	0.2	0.5	1.0	16.2	84.9	0.2
	5 - 10	1.3	0.1	---	<0.1	<0.1	1.1	2.6	
(5)	10 - 20	0.4	---	---	---	---	0.1	0.5	
	20 - 30							<0.1	
	30 - 35							<0.1	
103	0 - 5	53.0	2.0	0.3	1.3	1.2	22.8	81.1	0.9
	5 - 10	1.7	0.3	---	0.1	0.1	3.2	5.5	
(4)	10 - 20	0.6	---	---	---	---	0.3	0.9	
	20 - 30							0.1	
	30 - 35							<0.1	
130	0 - 5	51.4	1.2	0.2	2.8	1.8	29.1	86.5	0.9
	5 - 10	0.8	---	---	---	---	1.6	2.3	
(2)	10 - 20							0.4	
	20 - 30							0.1	
	30 - 35							<0.1	
	35 - 40							<0.1	
200	0 - 5	28.2	2.0	---	2.7	2.1	36.2	71.5	0.9
	5 - 10	3.0	0.4	---	0.3	0.3	7.5	11.7	
(3)	10 - 20	0.6	---	---	---	---	1.1	1.7	
	20 - 30							0.4	
	30 - 35							<0.1	
	35 - 40							<0.1	

Degradation of methabenzthiazuron and formation of metabolites

In the field trial, methabenzthiazuron was degraded considerably more quickly than in the laboratory test without vegetation. The half-life under field conditions (sandy loam) was 133 days while 597 days were calculated for soil Speyer 2.2 in the laboratory test (Figure 3).

Despite this difference, the metabolites occurring in low amounts only ($\leq 3\%$) were identical in the laboratory test and the field trial (Figure 4). The urea side chain was degraded stepwise to the point of aminobenzothiazole (Mittelstaedt *et al.* 1977; Rouchaud *et al.*, 1988). The compounds I, II, IV and V were confirmed mass-spectroscopically. The metabolite III which occurred in low amounts, was in the range of benzothiazolyl-urea according to TLC.

FIGURE 4. Evaluation of autoradiography (Fujix Bas 2000, Fuji)



CONCLUSIONS

This technique of sampling ^{14}C-treated soil cores has proved to be successful and extended the scope of lysimeters. It was possible to monitor the translocation into the plants, the translocation in the soil, the formation of bound residues, the degradation of the active ingredient as well as the metabolization under practice-relevant conditions over a prolonged period of time and to compare the results with those of the laboratory test. The system is extremely well suited to detect the translocation behaviour even of unknown metabolites at an early stage.

ACKNOWLEDGEMENTS

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REFERENCES

BBA (1990) Biologische Bundesanstalt für Land- und Forstwirtschaft Richtlinien für die Prüfung von Pflanzenschutzmitteln im Zulassungsverfahren Teil IV, 4-3, Lysimeteruntersuchungen zur Verlagerung von Pflanzenschutzmitteln in den Untergrund.

Mittelstaedt, W.; Still, G.G.; Dürbeck, H.; Führ, F. (1977) Extraction and Identification of the Major Metabolite of [carbonyl-^{14}C]Methabenzthiazuron after Degradation in the Soil. *J. Agric. Food Chem.* 1977, 25, 908.

Rouchaud, J.; Roucourt, M.; Benoit F.; Ceustermans, N.; Gillet, J.; Plumier, W.; Vulstike, G. (1988) Metabolism of Methabenzthiazuron on the Soil of Pea Crops. *J. Agric. Food Chem.* 1988, 36, 642-645.

Schinkel, K. Nolting, H.-G.: Lundehn, J.-R. (1986) BBA, Richtlinien für die amtliche Prüfung von Pflanzenschutzmitteln, Teil IV, 4-1 Verbleib von Pflanzenschutzmiteln im Bodenabbau, Umwandling und Metabolismus.

PESTICIDE DRIFT FROM KNAPSACK SPRAYERS TO DITCHES AND DITCH BANKS

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ABSTRACT

Pesticide drift from knapsack sprayers fitted with different types of nozzle was investigated along a field edge. Drift deposition was measured at various wind speeds using water-sensitive paper. Drift deposition depends on nozzle type and wind speed. Flat spray tips cause more drift deposition than cone nozzles, probably owing to the larger spray angle. Deposition increases with wind speed. At a wind speed of 2.5-3.5 m/s, there was max. 9.08% drift deposition halfway down the ditch bank and 0.03% in the ditch (2.0-mm flat spray tip). At 7.5 m/s for flat spray tips these figures are max. 49.17% and 6.21%, respectively. All cone nozzles except the adjustable nozzle cause a max. deposition of 0.93% halfway down the ditch bank and 0.06% in the ditch.

INTRODUCTION

In the Netherlands, field edges, ditch banks and even ditch beds are frequently sprayed with herbicides (De Snoo & Wegener Sleeswijk, 1993). Of 88 farmers interviewed, 95% create a 'sterile strip' about 35 cm wide along the perimeter of their arable fields. In most cases knapsack sprayers are used for this purpose, with the herbicide Glyphosate being most commonly applied, to combat *Elymus repens* (Couch grass). Little is known about herbicide drift from knapsack sprayers used along field edges. In the context of Dutch pesticide policy there is an ongoing debate as to whether it is necessary and possible to prohibit spraying along the outermost 50 cm of arable fields (MANF, 1991). In this study the drift deposition from knapsack sprayers fitted with different types of nozzle was investigated under various weather conditions (wind speed). This research forms part of the Dutch Field Margin Project in the Haarlemmermeerpolder.

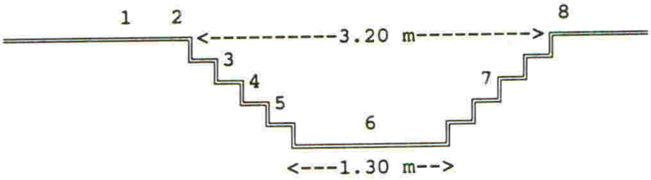
METHOD SUMMARY

The experiment focuses on two variables: nozzle type and wind speed. Other factors that might be important for pesticide drift were kept as constant as possible. Sprayers were filled with water only, with a working pressure of 2 bar. The wind direction was always perpendicular to the ditch. The walking speed was about 4.6 kilometres per hour. The spray height varied between 15 and 30 cm and was dependent on the nozzle type. Seven nozzle types from six farmers were used (Table 1) with a single type of knapsack - sprayer (Birchmeyer, hand pump). Drift deposition (d.d.) resulting from the nozzles was measured at different distances from the sprayed field edge (Fig. 1).

TABLE 1: Investigated spray nozzles (from Birchmeyer, 1991) with measured spray angles and flow rate in ml/min

nozzle type	trademark	spray angle	flow rate
cone nozzle, 1.5-mm	Duro	60 °	530
cone nozzle, 1.3-mm	Duro	45 °	650
adjustable nozzle (1.3-mm hollow cone)	Birchmeyer	70 °	280
cone nozzle, '120'	Birchmeyer	55 °	600
narrow cone nozzle	Birchmeyer	45 °	550
flat spray tip, 1.6-mm	Floodjet	105 °	910
flat spray tip, 2.0-mm	Floodjet	130 °	1350

FIGURE 1: Deposition measurements along field edge



1 = 0.5 m into field; 2 = field edge (spray target); 3 = 0.3 m down ditch bank; 4 = 0.6 m down ditch bank (halfway); 5 = 0.9 m down ditch bank; 6 = ditch; 7 = opposite ditch bank; 8 = opposite field edge

D.d. was measured using water-sensitive papers (WSP, Ciba Geigy). These yellow papers turn blue when sprayed with water, the amount of blue indicating the quantity of water deposited. WSP measuring 12.5 by 2.5 cm was placed on a piece of triplex 10 cm above ground level. The amount of blue was measured directly with a video-area meter. With this set-up there is no need for a copying machine, as used by Sinha et al. (1990), to increase resolution. Each WSP was measured on three 10 cm^2 sample areas (total sample area about 25 cm^2) The detection limit was a covering of 0.01%. D.d. was calculated as a percentage of the deposition on the field edge itself.

The deposition on the field edge might be more than indicated by the amount of blue, owing to overlapping droplets that do not spread out. The dose-area relation was therefore investigated in a separate experiment in which the WSP was sprayed several times with a standardized spray burst from a set distance. The experiment was carried out twice with the 1.5-mm cone nozzle (fine droplets) and twice with the 1.6-mm flat spray tip (large droplets).

The accuracy of the method was also investigated using a calcium tracer. For this purpose a standard spraying run was carried out with a solution of 5 g $CaCl_2 2H_2O$ per litre. The experiment was performed with the 1.5-mm cone nozle and the 2.0-mm flat spray tip. The calcium solution was sprayed on the WSP as well as on adjacent strips of filter paper (12.5 x 2.5 cm). The calcium in the filter paper was subsequently extracted with HCl and titrated with 0.001 M EDTA-Complex (Skoog, 1977).

RESULTS

The relation between the quantity of sprayed water and the amount of blue (dose-area relation) is linear up to 80% coverage of the WSP (Fig. 2). Above this value the curve levels off. The results of the tracer experiment indicate a linear relation between the amount of blue and the quantity of calcium, for both the cone nozzle and the flat spray tip (Fig. 3). These two control experiments show that the use of WSP to measure the deposition from knapsack sprayers is a reliable method.

FIGURE 2: Dose-area relation between amount of blue on WSP (%) and quantity of sprayed water

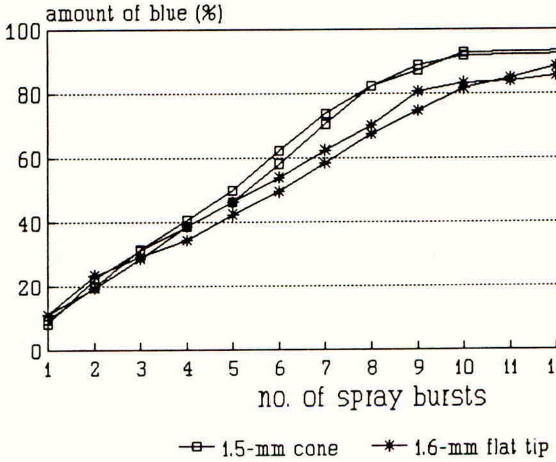


FIGURE 3: Relation between amount of blue on WSP and quantity of calcium tracer

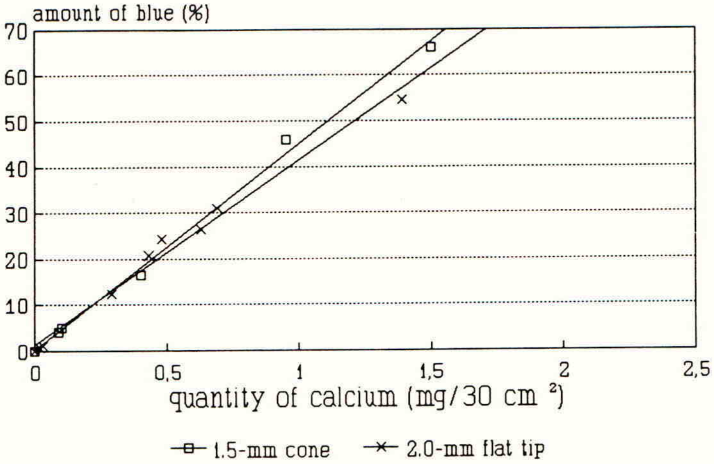
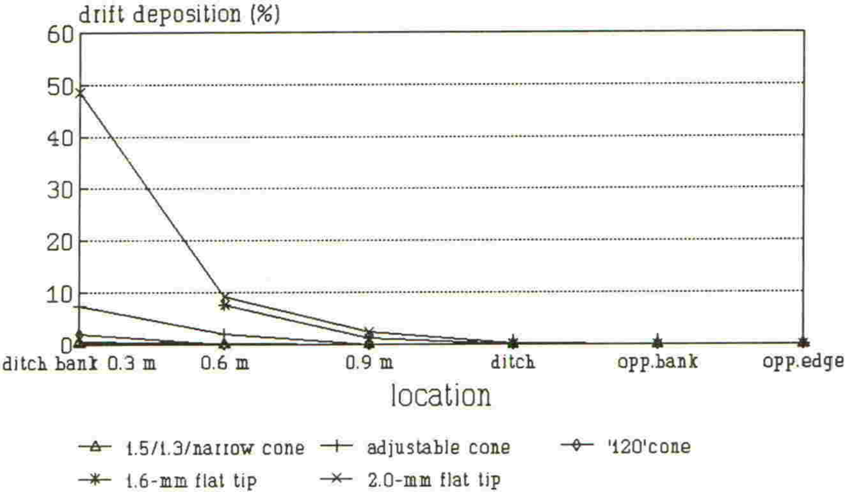


Fig. 4 shows the d.d. from the seven nozzle types at a wind speed of 2.5 - 3.5 m/s (low wind speed). There are major differences among the various nozzle types. The flat spray tips cause more d.d. than the cone nozzles. The 2.0-mm flat spray tip has the highest d.d.: 48.55% at 0.3 m, 9.08% at 0.6 m and 2.25% at 0.9 m down the ditch bank. Among the cone nozzles the adjustable cone nozzle has the highest d.d.: 7.41% at 0.3 m and 1.98% at 0.6 m down the ditch bank. The narrow cone nozzle has the lowest d.d.: only 0.07% at 0.3 m down the ditch bank. None of the nozzles cause d.d. in the ditch, or on the opposite ditch bank or field edge, except the 2.0-mm flat spray tip, which has 0.03% d.d. in the ditch. No d.d. was measured 0.5 m into the field.

FIGURE 4: Drift deposition from knapsack sprayers with seven different spray nozzles at 2.5-3.5 m/s wind speed



The wind speed is of major influence on drift deposition. Fig. 5 shows, for each nozzle type, the relation between wind speed and d.d. 0.6 m down the ditch bank (Fig. 5a) and in the ditch (Fig. 5b). For all nozzle types, d.d. increases with wind speed. At higher wind speeds, too, the flat spray tips also cause more d.d. than the cone nozzles. Halfway down the ditch bank (0.6 m), the 2.0-mm flat spray tip has a d.d. varying from 8.77% at 1 m/s to 49.17% at 7.5 m/s. The 1.6-mm flat tip and the adjustable cone tip also cause high d.d. on the ditch bank: maximum 22.93% and 12.67%, respectively. The other four nozzle types have a maximum d.d. of 0.93% halfway down the ditch bank. The '120' cone nozzle has the lowest d.d.: from 0 at 1 m/s to 0.20% at 9.5 m/s.

Measured in the ditch, the flat-tip nozzles again have the highest d.d.: up to 6.21% at 7.5 m/s wind speed. The cone nozzles cause no more than 0.06% d.d. in the ditch, apart from the adjustable cone nozzle, with 0.18%. The '120' and 1.3-mm cone nozzles cause no d.d. at all in the ditch, even at very high wind speeds. It is noteworthy that the 1.6-mm flat spray tip has a higher in-ditch d.d. than the 2.0-mm flat spray tip (3.22%), although the latter tip causes more d.d. at other distances.

FIGURE 5: Drift deposition from seven nozzle types under different wind speed conditions

FIGURE 5a: Deposition 0.6 m down ditch bank

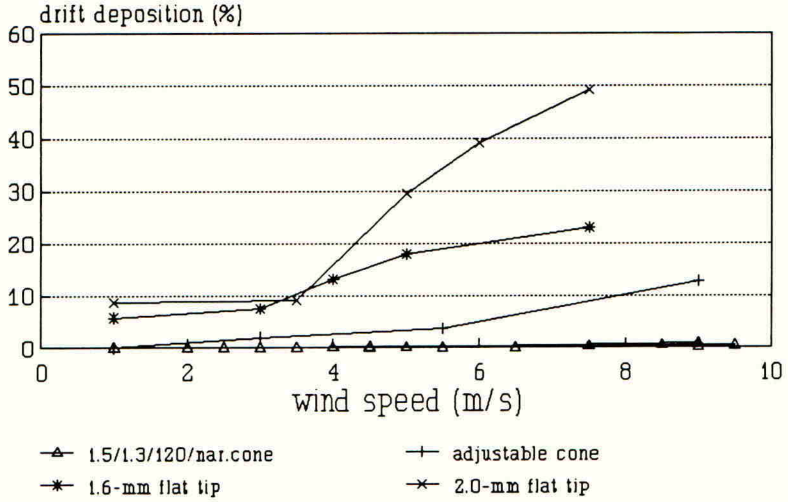
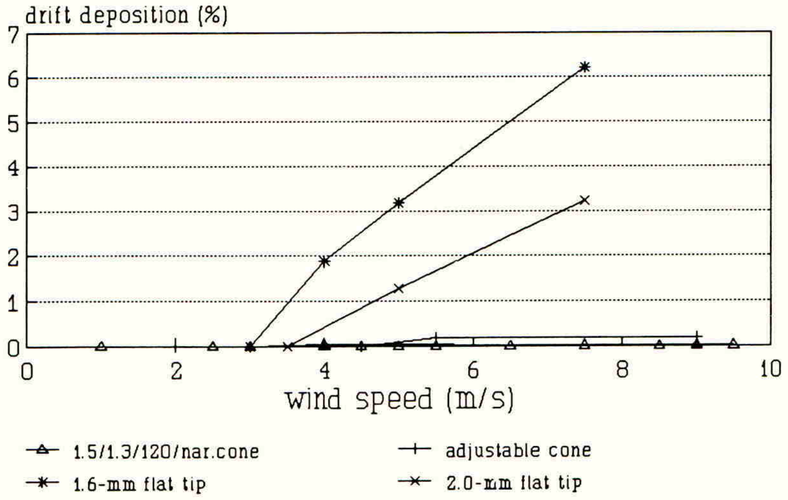
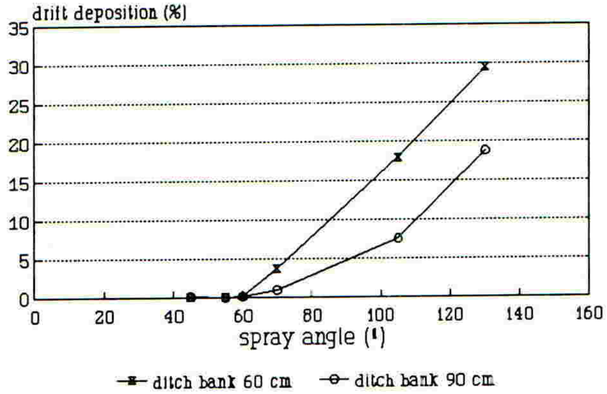


FIGURE 5b: Deposition in ditch



There appears to be a correlation between the spray angle and the percentage drift deposition, d.d. increasing with spray angle (Fig. 6). When the field edge is sprayed with flat spray tips, the ditch bank is also partially sprayed because of the large spray angle (cf. Fig. 5a: at very low wind speed, d.d. is also about 6-9%). The cone nozzles have a small, tight aperture, causing a small emission. The 1.3-mm adjustable cone nozzle has a larger emission because of the wide, hollow cone.

FIGURE 6: Relation between spray angle and drift deposition 0.6 m and 0.9 m down ditch bank at 5 m/s wind speed



DISCUSSION

To prevent crop damage, farmers always spray herbicides when the wind blows off the crop and into the ditch. The results show that drift deposition in the environment depends on nozzle type and wind speed.

At low wind speed (2.5-3.5 m/s) there is hardly any herbicide drift from knapsack sprayers into the ditch. However, there is substantial deposition on the ditch bank when flat spray tips are used. As the wind speed increases, drift deposition also increases, reaching relatively high values with the flat spray tips as well as the adjustable cone nozzle. Because of their wide spray angle, the flat spray tips and the adjustable cone nozzle are less suitable for spraying field edges.

To reduce drift deposition from knapsack sprayers it is recommended not to spray at a wind speed above 3.5 m/s and to prohibit the use of nozzles with spray angles greater than 60 °. Moreover, it has been demonstrated that the use of spray shields can reduce pesticide emissions to the environment (by 63%), at the same time increasing the efficiency of spraying operations (Awadhwal et al., 1991).

REFERENCES

Awadhwal, N.K., E.F. Cabrido and G.R. Quick. 1991. Minimizing drift and exposure from knapsack sprayers. *J. Environ. Sci. Health.* **B26 (5&6)**, 589-600.

Birchmeyer, 1991. *Sprayers for Plant Protection 1992/1993.* Birchmeyer & Cie. AG. Künten.

Ministry of Agriculture, Nature Management and Fisheries; NL. 1991. *Multi-year Crop Protec tion Plan; Government order. Netherlands Second Chamber, session 1990-1991, 21 677, nos. 3-4.* SDU Publishers, The Hague.

Sinha, S.N., K.H. Lakhani and B.N.K. Davis. 1990. Studies on the toxicity of insecticidal drift to the first instar larvae of the Large White Butterfly Pieris brassicae (Lepidoptera: Pieridae). *Ann. Appl. Biol.* **116**, 27-41.

Skoog, D.A. & D.M. West, 1977. *Fundamentals of analytical Chemistry.* 3rd edition. Holt Rinehart & Winston, New York.

Snoo, G.R. de & A. Wegener Sleeswijk, 1993. Use of pesticides along field margins and ditch banks in The Netherlands. *Proc. Int. Symp. on Crop Protection Gent, 4-5-1993.*

MONITORING PESTICIDE MOVEMENT INTO SUBSURFACE DRAINS

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ABSTRACT

Pesticide losses to subsurface drains were monitored in field trials on an agriculturally important loamy silt soil in the "Soester Börde", a typical crop growing area in Germany. Over a one year period, the drainflow was measured and the drain water was analysed for four applied herbicides.

Significant differences were observed comparing spring and autumn applications. The herbicides applied in spring 1992 were only found in concentrations $\leq 0.15\ \mu g/l$ (chloridazon, metamitron) in the drain water; pendimethalin was not detected in the drains during this spring/summer period. Following the autumn application, maximum concentrations of about 62 $\mu g/l$ for isoproturon and 0.7 $\mu g/l$ for pendimethalin were observed. Between 0.09 % and 0.4 % of the applied isoproturon, but less than 0.001 % of pendimethalin leached to the drains from November 1992 to April 1993. The experimental results indicate that both preferential flow and nonequilibrium sorption were occurring on a field-scale.

INTRODUCTION

Subsurface drainage is a common water management practice in agricultural areas with shallow groundwater or seasonally perched water tables. The artificial drainage may enhance the transport of pesticides and other chemicals to surface water. Pesticides in subsurface drains, which discharge into ditches or ponds, may cause an impact on these ecosystems. Furthermore, pesticides in subsurface drain flows may indicate poor quality of the water leaching to the groundwater below.

There are several reports in the literature of pesticides in drain water. In drain water from silty and sandy loam soils atrazine was detected at concentrations up to 10 $\mu g/l$ (Muir and Baker, 1976; Kladivko *et al.*, 1991); carbofuran was detected at concentrations up to 150 $\mu g/l$ (Kladivko *et al.*, 1991). In contrast to these results, Bunte and Pestemer (1988) did not find atrazine residues in drain water over many years of atrazine application.

In field studies random samples of drain water have usually been taken for analysis. Since no continuous measurement of the drainflow has been conducted, only rough estimates of the total pesticide discharge rates have been possible (Hurle and Lang, 1992; Meinert and Häfner, 1987; Muir and Baker, 1976).

The overall objective of this study was to monitor field-scale losses of pesticides to subsurface drains after herbicide applications in spring and autumn on a loamy silt soil under normal agricultural practice. Specific aims were:

a) continuous measurement of the total drainflow,
b) determination of concentrations and discharge rates of pesticides in the drain water and
c) assessment of the relative importance of preferential flow.

MATERIALS AND METHODS

Field Sites

The field monitoring was conducted at two sites in the "Soester Börde", a typical crop growing area in Germany where 25 to 35 % of the cropland is under-drained (personal communication: Landwirtschaftskammer Westfalen-Lippe). A 5.0 ha area is located in Welver-Borgeln (plot 1); plot 2 (1.1 ha) and plot 3 (0.7 ha) are located in Bad Sassendorf-Bettinghausen. The three field plots have surface slopes of less than 1 % and are characterized as loamy silt (2 % sand, 75 % silt, 23 % clay) with an organic carbon content of 1.2 % in the 0-30 cm soil layer. Subsurface drains (6.5 and 10.0 cm diameter; plot 1 - plastic tubing, plot 2 and 3 - clay pipes) were installed at spacings of 5 to 9 m and at an average depth of 80 to 110 cm more than ten years ago.

Total drainage from each plot area was sampled and measured in a central collection pipe. A measuring and sampling unit (ISCO Models 3700 and 3230) was installed on each collection pipe to monitor automatically the flow rates and to conduct event-triggered sampling of the drain water. The drainflow samples were continuously collected on a time-related basis. In order to assess potential fast flow of the pesticides through macropores and potential non-equilibrium sorption/desorption processes, up to 12 separate samples per day were taken during the first four weeks after pesticide application and during the first three days after the beginning of each new drainflow event. At other times, composite daily samples were taken.

Test Procedure

Herbicides with different water solubilities and soil sorption coefficients were chosen as test substances to obtain information on the dominant leaching processes occurring on a field-scale. Whereas pendimethalin is characterized by a high soil sorption coefficient (K_{oc} = 4009), the soil sorption coefficients of the other test substances are relatively low (chloridazon = 33, isoproturon = 130, metamitron = 40) (Kördel *et al.*, 1993).

The herbicides were applied as formulated products according to normal agricultural practice in spring 1992 (plot 1: chloridazon, metamitron, pendimethalin) and in autumn 1992 (plot 1 and 2: isoproturon, pendimethalin). The treatment scheme of the field sites is summarized in Table 1. Plot 3 was not treated but used for additional monitoring of the drain-flow in the autumn/winter period. Over the whole experiment, the drain water was analysed for all applied herbicides according to the method described by Traub-Eberhard *et al.*, 1993.

To study the effect of heavy rain events on pesticide leaching and drain flow, artificial irrigation on plot 2 (22.2 l/m^2 in October 1992) and on plot 3 (30.0 l/m^2 in April 1993) was performed.

RESULTS

Precipitation and Water Removal by the Drains

The weather during the study period (May 1992 to April 1993) was relatively wet. In June, October and November 1992 and January 1993 precipitation was > 150 % above the 30-year mean.

TABLE 1. Treatment scheme of the field sites

herbicide	date of treatment [day/month/year]	application rate [kg AI/ha] and timing	crop	study site
chloridazon (formulated as 'Pyramin WG'^{R})	12/04/92	1.30 (pre-em)	sugar beet	plot 1
isoproturon (formulated as 'Arelon liquid'^{R})	09/11/92	1.00 (pre-em)	winter wheat	plot 1
	25/11/92	1.00 (post-em)	winter barley	plot 2
metamitron (formulated as 'Goltix WG'^{R})	13/05/92	1.05 (post-em)	sugar beet	plot 1
	28/05/92	1.40 (post-em)	sugar beet	plot 1
pendimethalin (formulated as 'Stomp SC'^{R})	03/05/92	1.60 (pre-em)	maize	plot 1
	09/11/92	0.80 (pre-em)	winter wheat	plot 1
	25/11/92	0.80 (post-em)	winter barley	plot 2

TABLE 2. Drainflow

month	plot 1		plot 2		plot 3	
	(l/m^2)	(% of rainfall)	(l/m^2)	(% of rainfall)	(l/m^2)	(% of rainfall)
May 92	0.06	0.20	-	-	-	-
Jun. 92	0	0	-	-	-	-
Jul. 92	<0.01	<0.01	-	-	-	-
Aug. 92	0.01	0.01	-	-	-	-
Sept. 92	0.04	0.07	0 *	0 *	0 *	0 *
Oct. 92	0.28	0.34	0	0	0	0
Nov. 92	4.59	4.43	5.37	5.46	7.85	7.98
Dec. 92	13.03	25.40	8.33	14.41	9.73	16.83
Jan. 93	47.95	36.83	37.55	28.84	48.50	37.25
Feb. 93	11.37	35.31	5.55	22.46	7.62	30.85
Mar. 93	0.28	2.62	<0.01	<0.01	0.04	0.29
Apr. 93	0.15	0.22	0	0	1.27	1.30

\- = not recorded
* from 19/09/92

<u>additional artificial irrigation</u>
plot 2: 22.2 l/m^2 in Oct. 92
plot 3: 30.0 l/m^2 in Apr. 93

FIGURE 1. Drainflow (a) and precipitation (b) from November 1992 to April 1993 (plot 1)

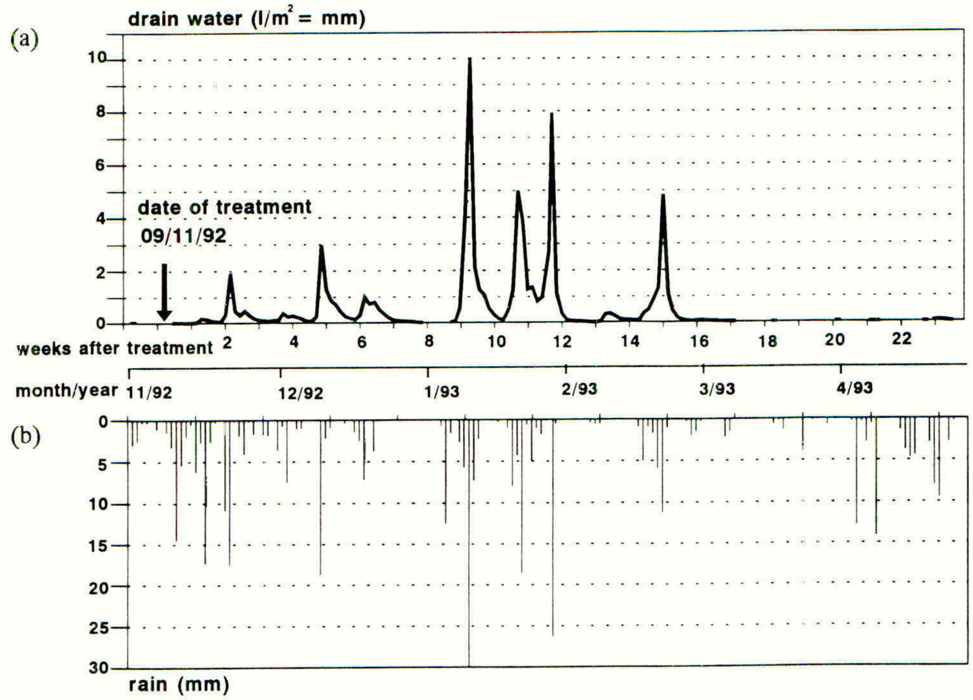


FIGURE 2. Isoproturon in the drain water of plot 1 (autumn treatment)

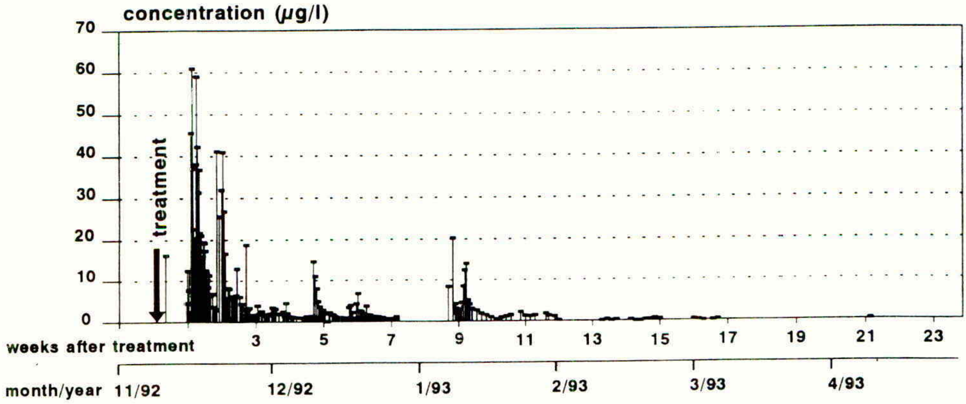


FIGURE 3. Drainflow (a) and precipitation (b) from November 1992 to April 1993 (plot 2)

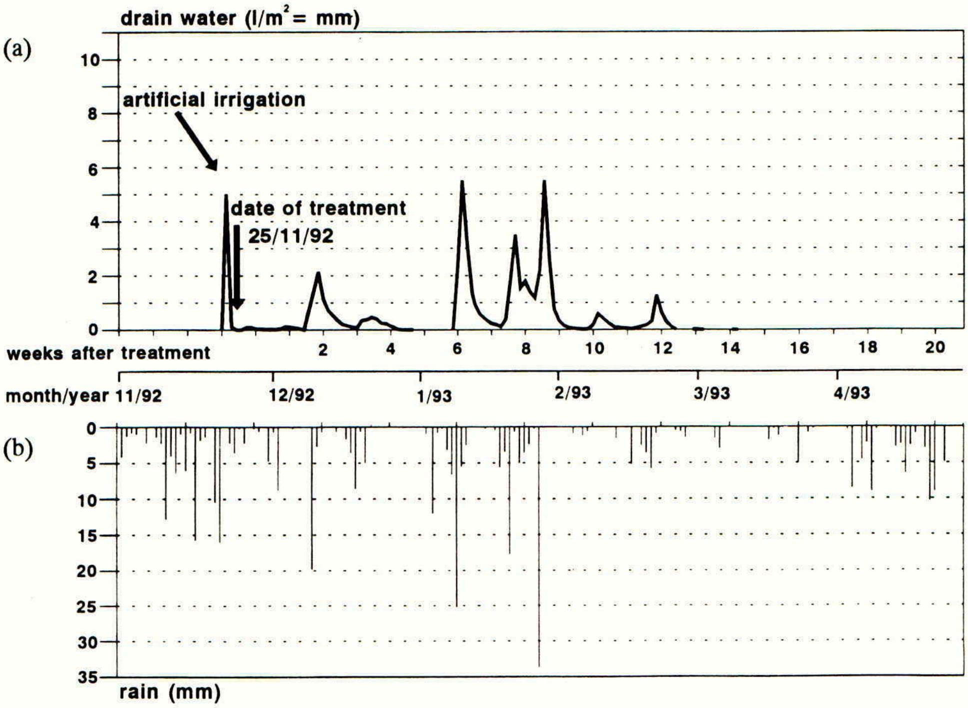


FIGURE 4. Isoproturon in the drain water of plot 2 (autumn treatment)

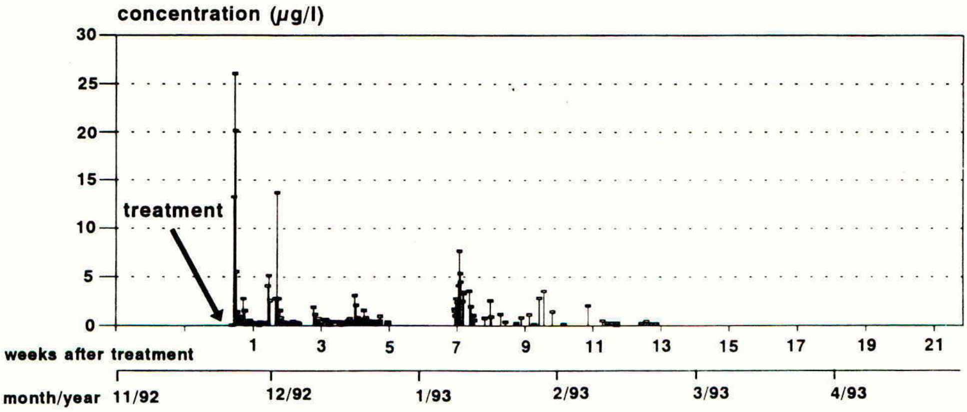


FIGURE 5. Pendimethalin in the drain water of plot 1 (autumn treatment)

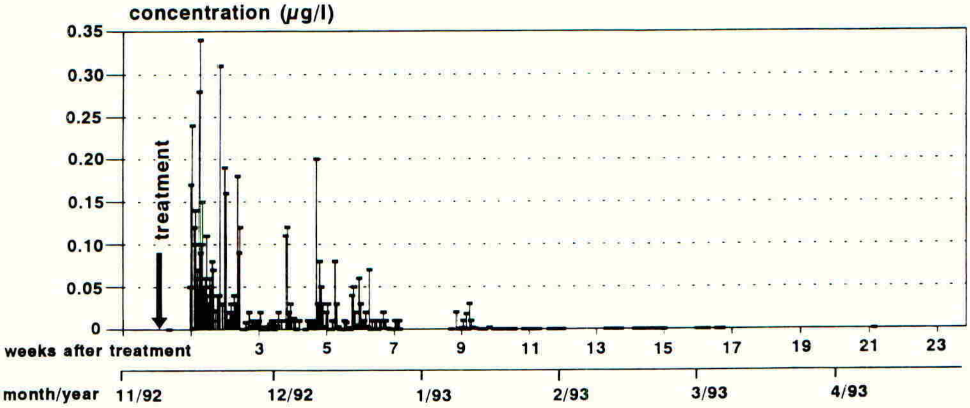
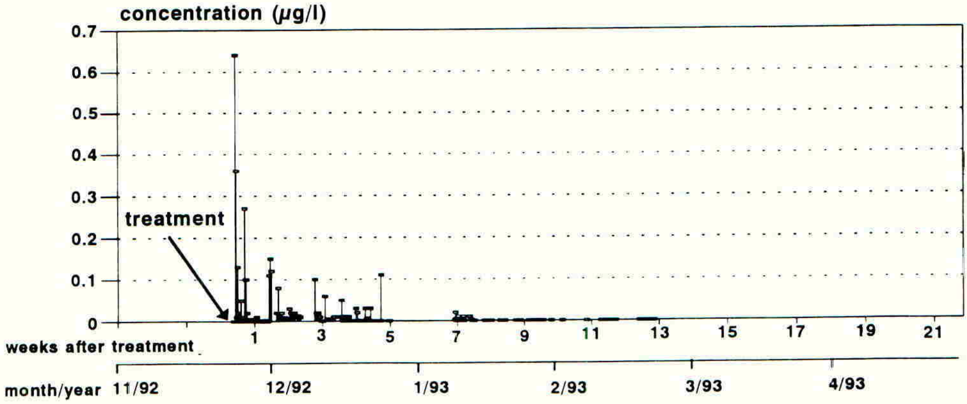


FIGURE 6. Pendimethalin in the drain water of plot 2 (autumn treatment)



Total drainflow was equivalent to 0 to 37 % of the total monthly precipitation depending on field site and season (Table 2). Whereas high drainflow occurred in the winter months, from May to October only isolated drainage events with a total amount of less than 1 % of the precipitation occurred. In the middle of November continuous drainflow started, the drainflow ceasing at the end of December during a frosty period for about one week and then continuing again till the end of February (Figures 1 and 3). Over the whole experimental period the three plots showed similar flow. The relatively major drainflow event (5 l/m^2) of plot 2 on November 23, 1992 is due to the additional artificial irrigation of 22 l/m^2, which was applied in late October. Similarly the irrigation of plot 3 in April resulted in higher amounts of drainflow.

Pesticide Losses to the Drains

Comparing spring and autumn application, significant differences with respect to concentrations and discharge rates of pesticides in the drain water were observed. The herbicides applied in spring 1992 were only found in trace levels. Typical concentration ranges during the spring/summer flow period in 1992 were 0.03 to 0.15 μg/l for chloridazon and 0.01 to 0.02 μg/l for metamitron. Pendimethalin was not detected in the drain water during this period (detection limit: 0.01 μg/l).

Following the autumn application, maximum concentrations of about 62 μg/l for isoproturon (plot 1) and 0.7 μg/l for pendimethalin (plot 2) were observed. In spite of different soil sorption coefficients, both isoproturon and pendimethalin arrived at the drains at the same time and were found in the first drainflow which occurred after the autumn application. However, concentrations in the drainflow did reflect differences in sorption coefficients. In the period from November 1992 to April 1993 the average concentration for isoproturon was 4.4 μg/l (plot 1) and 1.5 μg/l (plot 2) but only 0.002 μg/l (plot 1) and 0.003 μg/l (plot 2) for pendimethalin. The highest pesticide concentrations in water were observed in the first week after the autumn applications (see Fig. 2, 4, 5 and 6). Concentrations declined as the flow continued. The isoproturon concentrations increased again to maximum concentrations of about 20 μg/l (plot 1) in January after a frosty period. The isoproturon concentrations then decreased to values of about 0.4 μg/l (plot 1) and 0.2 μg/l (plot 2) until March 1993 (about 3 to 4 months after application). Pendimethalin was only detectable up to early January 1993.

From November 1992 to April 1993 the total isoproturon losses in the drainflow were 0.8 and 3.5 g/ha corresponding to 0.09 and 0.40 % of the amount applied to the soils of plots 2 and 1, respectively. Losses of pendimethalin were less than 0.001 % of the applied dose. The highest pesticide losses to the drains occurred in January 1993 during a time of considerable drainflow (Traub-Eberhard *et al.*, 1993).

DISCUSSION

According to the results of the field trials, artificial drainage by subsurface drains can enhance the transport of pesticides to surface water. For crop production areas like the "Soester Börde", in which subsurface drainage is practiced quite extensively, the loss of pesticides might have water quality implications.

Autumn application of isoproturon on a loamy silt soil led to high concentrations and discharge rates in the drain water. In contrast to the autumn/winter season and as a result of higher evapotranspiration during the growing season, only isolated drainage events occurred in spring and summer. Although chloridazon and metamitron are characterized by lower soil sorption coefficients than isoproturon, these compounds were only detected in minor concentrations in the drain water after application in spring. These findings are probably due to increased degradation rates during spring and summer.

The experimental results indicate that both preferential flow and non-equilibrium sorption are occurring on a field-scale. The herbicides appeared in the drains faster than predicted from their properties by the "Pesticide Leaching Model" (PELMO; source: Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, 57392 Schmallenberg, FRG), which assumes chromatographic transport. According to PELMO, a chemical with a low soil sorption coefficient (K_{oc} = 20) and a soil half-life of 18 days, applied in November to the surface of a loamy silt soil at a rate of 1.5 kg AI/ha, would not be expected to reach one meter depth within 20 days of application. The early arrival of both isoproturon and pendimethalin in the drains (depth 80-110 cm) two days after treatment is consistent with preferential flow concepts and suggests that the initial part of the flow event is dominated by fast flow through macropores (Hallberg *et al.*, 1986). This seems to happen especially after the autumn treatment on dry, loamy silt soil (plot 1).

On both field plots the highest pesticide concentrations were observed at the beginning of drainflow after the autumn treatment. Concentrations decreased as the flow continued; the average concentrations of isoproturon and pendimethalin then clearly reflected differences in sorption coefficients. These results may be explained by a highly saturated soil solution at the beginning of a rain event, followed by fast flow transport of this solution. If the drainflow continues, the desorption of the herbicides in the top soil layer is not fast enough and this results in lower concentrations in the drain. Such non-equilibrium sorption/desorption processes might be responsible for relatively high isoproturon concentrations of up to 20 μg/l, which were measured in January 1993 after the soil thawed. In this case the slowly achieved equilibrium was re-established.

ACKNOWLEDGEMENTS

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REFERENCES

Bunte, D.; Pestemer, W. (1988) Herbiziddynamik im Boden. *Forschungsbericht 1986-1988 Sonderforschungsbericht 179*, Braunschweig 1988; Wasser- u. Stoffdynamik in Agrar-Ökosystemen, 179-199.

Hallberg, G. R.; Baker, J. L.; Randall, G. W. (1986) Utility of tileline effluent studies to evaluate the impact of agricultural practice to ground water. *Proceedings of Conference on Agricultural Impacts on Ground Water*, Ohmaha, NE. 11-13 August. National Water Well Assoc., Dublin, OH., 298-326.

Hurle, H.; Lang, S. (1992) Pflanzenschutzmittel im Drainagewasser. *Wasser und Boden, DVWK-Nachrichten* **1**, 4-5.

Kladivko, E. J.; van Scoyoc, G. E.; Monke, E. J.; Oates, K. M.; Pask, W. (1991) Pesticide and Nutrient Movement into Subsurface Tile Drains on a Silt Loam Soil in Indiana. *J. Environ. Qual.* **20**, 264-270.

Kördel, W.; Stutte, J.; Kotthoff, G. (1993) HPLC-screening method for the determination of the adsorption coefficient in soil - comparison of different stationary phases. *Chemosphere*, in press.

Meinert, G; Häfner, M. (1987) Möglichkeiten und Probleme bei der Anwendung von Pflanzenbehandlungsmitteln in Wasserschutzgebieten. *Schr.-Reihe Verein WaBoLu* **68**, Gustav Fischer Verlag, Stuttgart.

Muir, D. C. G.; Baker, B. E. (1976) Detection of Triazine Herbicides. Their Degradation Products in Tile-Drain Water from Fields under intensive Corn (Maize) Production. *J. Agric. Food. Chem.* **24** (1), 122-125.

Traub-Eberhard, U.; Kördel, W.; Klein, W. (1993) Pesticide Movement into Subsurface Drains on a Loamy Silt Soil. *Chemosphere*, in press.

DETERMINATION OF THE POTENTIAL FOR POLLUTION OF GROUND AND SURFACE WATERS BY ALACHLOR IN OILSEED RAPE AND FODDER MAIZE: SUMMARY AND REGULATORY INTERPRETATION

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ABSTRACT

A three year environmental fate study was established to investigate the possible contamination of water sources by the herbicide alachlor. Suitable field catchments were identified where fodder maize and oilseed rape were grown and where soils were present that have a high potential for surface water and shallow groundwater pollution. Presence of alachlor in surface waters, soil water leachate, drainage water and surface run-off samples was monitored. Detailed investigation of soil chemical and hydrological properties was carried out to enable extrapolation of the data to areas of different soils and climate for European regulatory submission. A summary of these results are presented along with interpretation and conclusions for the possibility of water contamination by the herbicide.

INTRODUCTION

Alachlor is used extensively in Europe and the USA to control a range of annual grasses and broad-leaved weeds in spring fodder maize and autumn oilseed rape. The potential for this product to contaminate both surface waters by run-off or drainflow and shallow groundwaters by leaching has been assessed in a three year environmental fate study. The product is classified as moderately mobile with a K_{oc} of 170 ml g^{-1} and is slightly persistent with a field half life of around 15 days. Experimental sites were established and monitored, following the application of the herbicide, in spring sown fodder maize and autumn sown oilseed rape from autumn 1990 to spring 1993. Williamson and Carter (1991) describe the rationale for site selection, experimental design, instrumentation and site monitoring procedures. Field experiments of this kind or lysimeter studies are often requested by regulatory authorities to determine whether a pesticide or its metabolites do have the potential to contaminate water and with what magnitude or frequency the events occur following application. The data generated is however specific to the soil and agro-climatic conditions monitored and interpretation with regard to a regulatory decision can be difficult. Unless continuous monitoring equipment is used sampling strategies are difficult to determine and the resulting data easily misinterpreted unless full details of the hydrological response of the experimental system are taken into account. Soil and agro-climatic conditions across the UK vary considerably both spatially and temporally (Hollis and Carter 1990) whilst extrapolation to other European countries is difficult to perform due to the disperse nature of relevant European databases. This study has collected data from experimental sites which are typical of both UK and European conditions.

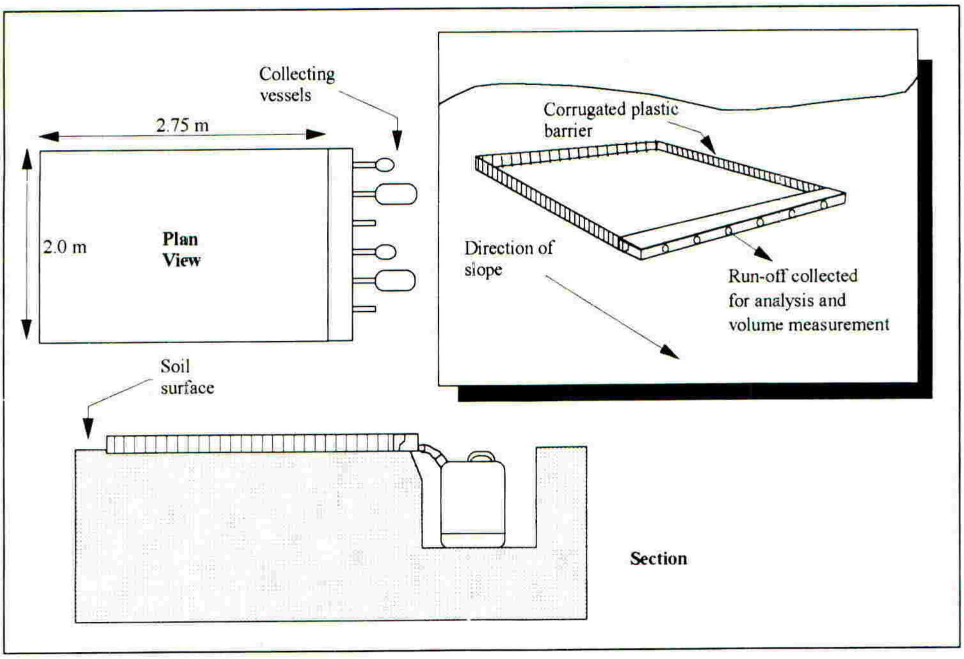
EXPERIMENTAL SITE SELECTION

Experimental sites were located on farms in close proximity to Temple Balsall, East of Birmingham, UK. The experimental soils were chosen for their hydrological properties using the Hydrology Of Soil Types (HOST) system (Boorman and Hollis, 1990) to represent either high potential for surface or groundwater pollution. The individual soil series varied at the different sites but the hydrological classification remained the same. Individual site location was made after consultation with the 1:25000 soils map for the area (Beard, 1984) and a local soil survey. Detailed soil profile description, physical and chemical analyses were carried out at the site to fully characterise the soil and to confirm its suitability. Information on the artificial drainage system of the each field was obtained and sampling points located at field drain outlets. Hydrological surveys were carried out and strategic sampling points located on surface waters (ditches, streams and ponds) in the catchment area. A 15 × 15m plot was designated for intensive instrumentation and process monitoring and three replicate sets of sampling equipment were installed within this area.

SAMPLING AND MONITORING PROCEDURES

Sampling and monitoring equipment is described in detail by Williamson and Carter (1991). Additional to the previous studies replicate 2.0 × 2.75 m run-off traps were installed at selected points within the study field to collect run-off water and transported sediment samples. The traps were constructed (after the Spring 1991 study) to allow collection of run-off generated from a specific area of soil surface (figure 1).

FIGURE 1. Design of run-off traps to intercept surface/overland flow.



The herbicide concentrations in run-off during the Spring 1991 were significant and therefore the use of 'enclosed area' of the run-off trap allowed calculation of run-off 'loadings'. Surface water and drain water samples were collected manually at the sampling points. The study sites were sampled both on a routine eg. fortnightly or monthly and on a 'trigger event' basis eg. after rainfall of >10 mm in 24 hours using Birmingham Airport weather station data as a reference. Weather parameters were recorded on an hourly basis on site with an automatic weather station.

FIELD STUDY ANALYTICAL RESULTS

Alachlor was applied as either at pre-emergence or at 3-4 leaf stage using a rate of 1.92 kg ha^{-1} on all study sites. A synopsis of the analytical results for the autumn and spring seasons of 1990 to 1993 is presented in Table 1. It should be emphasised that the sampling regime was targeted to obtain water samples after significant rainfall events and at sampling points that were likely to detect alachlor movement. The figures in brackets are the number of samples taken during each monitoring season from that source type and are usually made up of a number of separate sampling points. All sampling points were observed on each site visit but field hydrological conditions at the time of sampling dictated which points yielded sufficient water for analysis.

In autumn 1990 very little alachlor was detected in samples from either site and it was not detected in leachate from below 25 cm and 50 cm depth in the clay or sand sites respectively (Williamson and Carter, 1991). No measurable run-off was produced. Alachlor was detected in one drain sample at 0.08 μg l^{-1}. Alachlor was applied on 22/10/90 and 30 mm of rain fell within three days of application. Six further trigger rainfall events occurred up to the end of monitoring at the end of March 1991.

The Spring 1991 study, located in two separate fields exhibited a distinct contrast between the two soil types. Alachlor was applied pre-emergence at the end of May. No alachlor was detected at the sandy site, either in the soil profile at the 25 cm sampling depth, in shallow groundwater at 150 cm or in drainage water. No run-off was produced at this site during the study period. Detections of approximately 1.0 μg l^{-1} were made at the clay site in soil water on occasions to the greatest sampling depth of 80 cm. Alachlor was found in drainage waters on three occasions at 1.42, 3.32 and 0.44 μg l^{-1} but zero concentrations in samples taken from approximately 15m downstream of the drain suggested that observed drain concentrations had no detectable effect on surface water quality due to dilution. Alachlor was detected in surface run-off produced at the clay site with a maximum concentration of 12.9 mg l^{-1} in the first run-off sample 21/06/93 after the first trigger event. No area related volumes were collected from the initial monitoring of run-off but the potential importance of this process is evident given the concentration detected. However alachlor was not detected in the only two ditch water samples available on 08/07/91 suggesting run-off water had not entered the field ditch directly.

The Autumn 1991 study consisted of two experimental sites located on different soils within the same field. Alachlor was applied 18/09/91. High concentrations of alachlor were detected to a depth of 150 cm within 15 days of application and after 55 mm of rainfall which fell in a three day period at the sandy site. This was thought to be due to (and was confirmed by analysis) a significant difference in the bulk density and coarse porosity of re-packed un-structured sandy soil around the installed monitoring equipment. All subsequent studies used bentonite clay to seal monitoring equipment. At the clay site sporadic detections were made to a depth of 80 cm with a maximum concentration of 0.41 μg l^{-1}. Run-off was produced on both soil types with around 0.68 % and <0.08 % of applied alachlor transported in the run-off traps of the sandy and clay sites respectively. Concentrations of alachlor were found after the first rainfall events in the stream water at the outlet of the catchment area initially at 2.28 μg l^{-1} with further detections decreasing but always after rainfall events. Neither drain nor ditch concentrations were high enough to account for these levels considering the additional dilution. Further investigation revealed that the tank filling operation was carried out on an upstream bridge and it is most likely that even a small spillage on the bank side was responsible for the continuing contamination and was not due to contributions from the study field. Six trigger events occurred during the monitoring period.

The spring 1992 study sites were located in separate fields in close proximity to each other and alachlor was applied pre-emergence mid May. Alachlor residues were detected at the sandy site to a depth of 150 cm with a maximum concentration of 0.73 μg l^{-1}. No rain had fell between application and sampling so the concentration detected was either a contamination or a groundwater concentration from the Spring 1991 application, though no alachlor was detected at all during this period. Concentrations were also found at a new clay site to a depth of 100 cm at a maximum concentration of 0.16 μg l^{-1} and appeared to be related in some cases to possible by-pass flow following significant rainfall events. Detections were made in drainage water at the clay site with a maximum concentration of 1.81 μg l^{-1} at the beginning of June following 82 mm of rainfall in a five day period. Run-off was again produced at both sites with losses of 0.10 % and 0.07-0.25 % of applied alachlor transported within the run-off trap area at the sandy and clay sites respectively. No downstream sampling point was available to assess the affect of drainage and run-off losses on stream water quality however a maximum of 0.59 μg l^{-1} was detected in ditch water within two weeks of herbicide application and after 51 mm rainfall in a two day period.

The Autumn 1992 study was carried out in two adjacent fields and alachlor was applied pre-emergence on 21/09/92. The tank filling operations and disposal of excess material to set aside land away from the monitoring area were observed and samples taken from the 'fill up' bridge during the tank filling operation and from ditch water adjacent to the field immediately after application. Whilst no direct contamination of water sources was observed the samples from fill up bridge contained 0.18 μg l^{-1} and the ditch 0.3 μg l^{-1}. Rain fell immediately after application at this site and given that the antecedent soil water conditions were particularly wet the alachlor appeared to be transported into the topsoil and to deeper layer in the clay site very rapidly again-suggesting by-pass flow. Four further trigger events during October occurred and whilst drain and ditch concentrations adjacent to the treated clay field gave a maximum concentration of 0.49 μg l^{-1} the stream water concentration was 0.1 μg l^{-1} on one occasion. Alachlor was detected in the shallow groundwater on the sand at 1.73 μg l^{-1} after four trigger events at the end of October. Run-off volumes for both sites were greater than in previous studies but the percentage of applied alachlor lost was much lower.

The final study in the spring of 1993 was carried out at separate sites in close proximity to one another. Three herbicides, alachlor, atrazine and pendimethalin were applied pre-emergence at their individual recommended maximum rate on 4/05/93 at the clay site and 17/05/93 at the sandy site. The study is still in progress but initial alachlor data are reported here. Alachlor residues were found at the sandy site to a depth of 150 cm with a maximum concentration of 0.37 μg l^{-1} 11 days after application and immediately after 41 mm of rain which fell during a three day period. Concentrations were also found at the clay site at a depth of 80 cm at a maximum concentration of 0.34 μg l^{-1} occurring 17 days after application and immediately after a trigger event. Run-off was produced at both the sites with very small losses of 0.003 % and

0.004-0.006 % of applied alachlor transported on the sandy and clay sites respectively. Detections were made in drainage water at the clay site with a maximum concentration of 5.00 $\mu g\ l^{-1}$ and a corresponding concentration in ditch water of 0.49 $\mu g\ l^{-1}$.

TABLE 1. Analytical results summary

(Water concentration figures are number of samples with certain concentration. Figures in parentheses are total number of samples taken from that source.)

Slowly permeable clay soil	Autumn 1990	Spring 1991	Autumn 1991	Spring 1992	Autumn 1992	Spring 1993
$\geq 0.1 \mu g l^{-1}$ below root zone	0(8)	2(4)	2(6)	3(6)	5(7)	3(4)
$\geq 0.1 \mu g l^{-1}$ in drain /ditch water	0(35)	3(6)	0(8)	5(6)	14(21)	4(7)
% AI lost in run-off [5]	0	NL[1]	<0.08	0.07-0.25	0.008	0.004-0.006
Freely draining sandy soil	Autumn 1990	Spring 1991	Autumn 1991	Spring 1992	Autumn 1992	Spring 1993
$\geq 0.1 \mu g l^{-1}$ below root zone	0(8)	0(4)	6(6)[2]	2(4)	4(7)	3(4)
% AI lost in run-off [5]	0	0	0.68	0.10	0.002	0.003
$\geq 0.1 \mu g l^{-1}$ in stream water	0(11)	0(1)	3(10)[3]	-	1(7)[4]	0(4)

[1] Run-off produced and concentrations measured but no 'loadings' produced

[2] Faulty installation suspected for leaching to depth

[3] Contamination of stream by un-sprayed alachlor suspected

[4] Highest concentration was 0.1 $\mu g\ l^{-1}$

[5] Values calculated for 5.5 m^2 run-off traps within the field boundary and do not necessarily reflect amounts lost from the field as a whole

CONCLUSIONS

Alachlor was detected in soil water below the rooting zone sampled from both very permeable sandy soils and slowly permeable clayey soils. Leaching of solutes in sandy textured soils is often considered to be greater than in the clayey soils, however similar concentrations were found at the greatest sampling depth in both soils types emphasising the contribution of by-pass flow which is prevalent in these clay soils and can lead to significant herbicide concentrations at depth. Alachlor concentrations in drainage water were influenced by the effectiveness of the drainage systems with the more modern drains with gravel back-fill (often to the base of the topsoil) allowing greater and more rapid movement of water and chemical to surface waters. Concentrations of alachlor in run-off were very variable as was run-off generation on the different soil types. More run-off can often be produced on the sandy soil types after 'rain capping' of the surface whereas generation in the clayey soil types was often limited due to the long lasting cloddy seed-bed. Some high concentrations of alachlor were occasionally detected in run-off usually when very heavy rainfall occurred shortly after application. In many cases surface run-off is unlikely to enter surface waters directly due to presence of headland buffer strips and these were seen to be effective at minimising surface water contamination. Mid-field run-off may possibly cause zones of pesticide enrichment in some fields leading to increased likelihood of transfer to drains in those areas. Alachlor residues were found intermittently in drainflow and surface waters the highest concentrations being attributed to a contamination event during the spraying process. The increased temperature of the late spring application generally allows a more rapid bio-degradation of the alachlor in the topsoil but run-off and leaching events can be significant if antecedent conditions are moist and intensive rain storms occur within two to three weeks of herbicide application. The laboratory calculated half-life of alachlor in the subsoil of the sandy sites was up to 415 days (A. Walker pers. comm.) and indicates a potentially greater degree of persistence for leached material.

This study has shown that the extent to which alachlor leaches through the soil or is transported in run-off is dependent on a whole range of factors including weather conditions, soils properties and crop and soil management conditions. Contamination of surface and groundwaters is as likely to be controlled by individual field conditions and incident weather as the broad physico-chemical properties. Comparative data from the Spring 1993 study will interpreted to support this hypothesis. A range of soil and climatic conditions have been characterised during the study and these are providing input data for predictive model validation. Leaching and runoff model validation is being carried out with the intention that a probabalistic risk assessment can be derived for all potential usage areas in Europe. In order that the environmental fate of alachlor can be compared with the behaviour of other herbicides, used under similar agro-climatic conditions, a comparative study with atrazine and pendimethalin was carried out in Spring 1993. The modelling data and the comparative study will be reported elsewhere when results have been fully evaluated.

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REFERENCES

Beard G.R. 1984, *Soil Survey Record No.* **81**, Soils in Warwickshire V, Sheet SP27/37 (Coventry South).

Boorman D.B. and Hollis J.M. 1990, Hydrology of soil types: a Hydrologically based classification of the soils in England and Wales. *Proceedings of the MAFF conference of river and coastal Engineers, Loughborough University 10-12 July 1990.*

Hollis J.M. and Carter A.D. 1990, A comparison of laboratory, lysimeter and field study techniques to determine environmental fate of pesticides in the UK. *Brighton Crop Protection Conference - Pests and Diseases 1990,* **3**, 1005- 1010.

Williamson A.R., and Carter A.D. 1991, Field studies to determine the potential risk of contamination of ground and surface waters by an autumn and spring applied herbicide in oilseed rape and fodder maize. *Brighton Crop Protection Conference - Weeds 1991,* **2**, 477- 484.

SUSPENDED AND COLLOIDAL MATTER IN THE LEACHATE FROM LYSIMETERS: IMPLICATIONS FOR PESTICIDE TRANSPORT AND LYSIMETER STUDIES

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ABSTRACT

As part of a study of possible transport mechanisms for pesticides in the unsaturated zone, arrays of mini-lysimeters were set up at ADAS Rosemaund (Hereford and Worcester, UK) and at Reading University and the leachates analysed for volume, pH, dissolved organic carbon content and suspended matter concentration. The results suggested that:

(i) the concentration of suspended matter is independent of the volume of the leachate;
(ii) the concentration of the suspended matter decreases over the winter period;
(iii) the suspended matter may have a distinct mineralogical composition;
(iv) the suspended material affects the pH of the leachate; and
(v) the dissolved organic matter content (DOC) is independent of the suspended matter, but exerts a control on the pH of the leachate.

If these results reflect real soil processes then they have important implications for suspended/colloidal matter as possible media for transporting pesticides. If they only reflect processes present in a lysimeter, then they suggest that lysimeter studies of pesticide mobility could give misleading results.

INTRODUCTION

This project was initiated as part of a study of pesticide run-off in agricultural catchments by the Agrohydrology group of the Institute of Hydrology, in order to give a better understanding of the physics and chemistry of pesticide mobility within soils.

The fieldwork is based at ADAS Rosemaund (Hereford and Worcester, UK). Mini-lysimeters have been set up using the Rosemaund soil (typic brown earth, Bromyard series; silty loam, 16% clay, 66% silt, 18% sand), and operated at both Rosemaund and at PRIS (Reading University) throughout the winter of 1992/93 (October to March).

As well the pesticide concentration of the leachate (not reported here), the suspended matter and aspects of the water chemistry were also measured in order to investigate whether suspended and colloidal matter were possible media for pesticide transport within the soil profile.

METHODOLOGY

The mini-lysimeter design (Figure 1) was chosen for ease of construction and handling, making it possible to set up and monitor a relatively large number of lysimeters in a very short space of time. The lysimeter soil core is taken by hammering into the soil a 15x20 cm section of uPVC drainpipe, cut with a bevelled lower edge to facilitate insertion into the ground so that it is flush with the field surface. The core is then carefully extracted and placed on top of the collector device. The collector device is housed in a 15x30 cm section of uPVC drainpipe and consists of a gauze stretched over a glass funnel which feeds into a 0.5 l glass bottle. The two sections of pipe are then glued and taped together so as to prevent water entering through the join, and left free-standing at the field-site to operate and be observed. Five lysimeters were situated at Rosemaund and two at PRIS. To avoid the problem of shrinkage away from the walls of the lysimeter, the experiment was run only during the winter months when the soil was most likely to remain above field capacity and therefore suffer less from shrinkage.

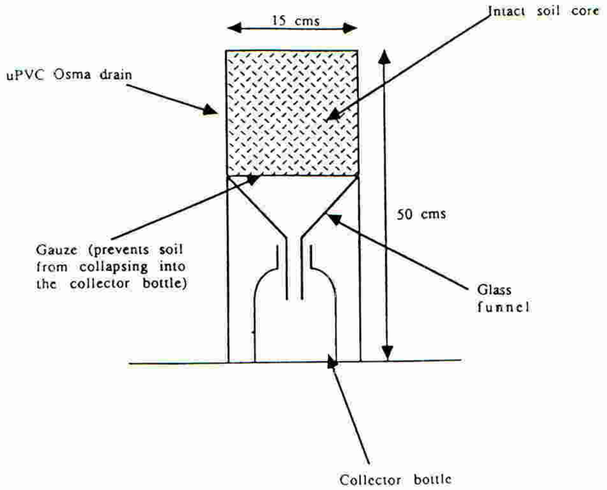

Figure 1: The mini-lysimeter design used in this study.

The leachate was collected at regular intervals, at least every two weeks starting from the 19 November, and its volume and pH were recorded immediately. Samples were then transported to the lab where they were filtered through a Buchner funnel using a 0.45 µm cellulose-nitrate filter. For the purposes of this study suspended matter is defined as larger than 0.45 µm and the colloidal matter as less than 0.45 µm.

After filtration, the pH of the leachate was measured again and the dissolved organic carbon (DOC) content analysed using an Astro 2001 dissolved-carbon analyser (the DOC content is taken as a proxy measure of the colloidal matter content of the leachate, as very few mineral particles have sizes below 0.45 µm). The residue from the filtration process was dried and weighed in order to calculate the concentration of suspended matter. If the size of the sample allowed, it was dispersed, and the less than 20 µm fraction was collected by pipette for analysis by x-ray diffraction to determine its clay mineralogy. The less than 20 µm fraction was used in order to include the larger kaolinite particles found in the soil matrix.

RESULTS

The concentration of suspended matter appears to be independent of the volume of leachate from which it is collected (Figure 2). The lack of correlation shown by all the lysimeters seems to suggest that the amount of matter released to the leachate is not constant with time, nor is its release solely due to water movement in the soil core, since either of these possibilities would give either inversely or directly proportional relationships between the suspended matter concentration and the volume of leachate. If suspended matter concentrations are measured with time, we can see that they tend to decrease. Ideally, as the results from one lysimeter show (Figure 3), this decrease can be modelled as an exponential decay. Any such decay process can be given a half-life and in this case it is 8.8 days. The implication of this result is that there is a set amount of material available for release and so the concentration of suspended matter in the leachate decreases as the pool of material it draws upon dwindles. The possible sources of this suspended matter are discussed later.

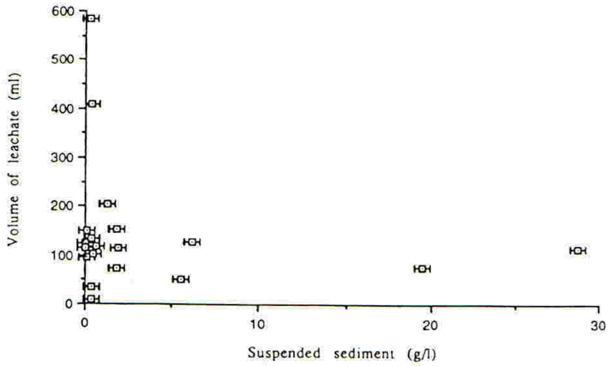

Figure 2: Plot of the volume of leachate against the concentration of the suspended sediment collected from the array of mini-lysimeters, showing the lack of correlation. The error bars are the maximum fixed error in measuring the suspended matter concentration.

When the mineralogy of the suspended matter is examined and compared to the clay mineralogy of three samples of the uppermost soil horizon taken at 15 cm depth, some differences are seen. The suspended matter appears enriched in expandable minerals relative to the Ap horizon (Figure 4). On the x-ray diffraction trace a separate peak due to the expandables becomes visible, separate from the normal peak at 10 Å(although no such peak was distinguishable in the Ap horizon samples). The expandables appear to be a mixed-layer mineral composed of over 80% smectite. The apparent enrichment of the suspended matter in expandable clay minerals, relative to all others, is believed to be due to the smaller size of smectites relative to the other clay minerals.

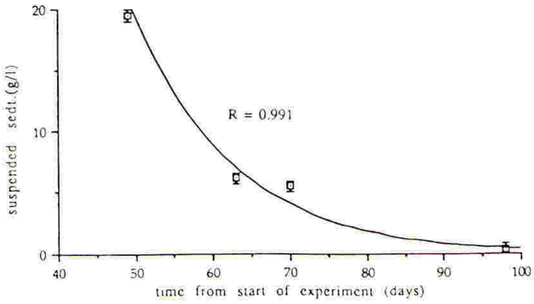

Figure 3: Exponential decay curve (half-life = 8.8 days) of the suspended sediment concentration against time from the start of the experiment (taken from the setting up of the lysimeter) for one of the mini-lysimeters. The error bars are the maximum fixed error in measuring the suspended sediment concentration.

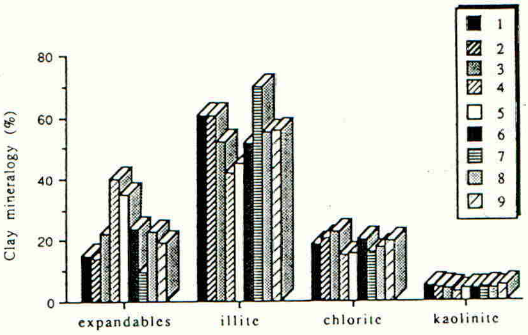

Figure 4: The clay mineralogy of six suspended sediment samples collected from the leachate of the mini-lysimeters (samples 4-9) in comparison to the clay mineralogy of three samples of the Ap soil horizon (1-3).

The colloidal matter content was found to be independent of the suspended matter content and showed no decay with time. However, the DOC content does exert a control on the pH of the leachate (Figure 5). The DOC content, from all the lysimeters over the whole of the sampling period,correlates well with the pH of the leachate before filtration ($R^2 = 0.699$), suggesting that the colloidal matter is largely basic and thus adsorbs the available protons. A pH effect can also be seen with the suspended matter. The average change in pH upon removal of the suspended matter was +1.26 pH units. The average pH of the leachate before filtration was 6.74 (standard deviation = 0.39) and after filtration was 7.94 (standard deviation = 0.30). This suggests that the suspended matter is also removing protons and thus creating a more basic solution.

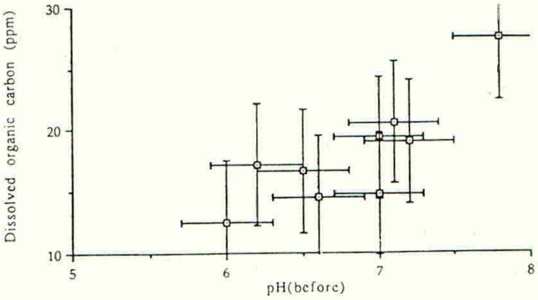

Figure 5: Plot of the dissolved organic carbon content against pH measured in the leachate from the array of mini-lysimeters before filtration. The error bars give the maximum fixed error in the instrumental measurements of the pH and the DOC.

DISCUSSION

It is possible that the movement of suspended and colloidal matter provides a mechanism for pesticide transport down the soil profile. This mechanism works by the removal of matter in the soil solution whilst pesticide is adsorbed to it. The pesticide may thus be transported and later desorbed into the solution proper. In the case of the DOC, the pesticide may be better thought of as complexed with the molecules than adsorbed to them (Madhun et al. 1986). Our results shed some light on this process. The suspended matter appears to come from a limited reservoir and thus any effect will die away with time, but so would the concentration of pesticide from a single application: at the same time that the threat of pesticide pollution diminishes, therefore, so does the likelihood of suspended matter as a possible transport mechanism. However, the decline of the soil pesticide levels and the suspended matter in the leachate are not necessarily in phase with each other. The pesticide concentration falls away from the time of spraying, but from what events the suspended matter decays away is unclear. The time-scale on Figure 3 is the number of days from the setting up of the lysimeter, yet it could be any date of our choice. The question of what is an appropriate starting date depends on the mechanism that generates the pool of available suspended matter. Two possibilities are: the pool of suspended matter is either generated by the mechanical disturbance of cultivation or by the setting up of the lysimeter itself. If it is due to the setting-up of the lysimeter alone then this possible mechanism for pesticide transport could prove to be a major problem in lysimeter studies of pesticide mobility in the soil. It may be possible that the reservoir of available material is added to by the action of frost on the soil core. A qualitative analysis of our lysimeter data with meteorological data (number of days frozen, taken as percentage of the length of the collection period for any particular sample) for both the Reading and the Rosemaund sites showed no apparent significant correlations.

The significance of suspended or colloidal matter to pesticide pollution will also depend on where the source of the material is in the soil. If the source is dominantly at the soil surface, then the material will carry more pesticide than if it comes from lower soil horizons. If the soil surface is the source, then the most likely release mechanism is rainsplash rather than overland flow and not necessarily the mechanical disturbances mentioned above (wetting and drying cycles or freeze/thaw). If this is the primary mechanism then the flow of suspended and colloidal matter will be largely down the macropores, with the possibility of some direct transport of material to water courses by overland flow.

The implications of the pH data are uncertain. If the suspended material adsorbs protons then it will be doing so in competition with some pesticides, and even if this is not the case it will be affecting the surface acidity of the non-mobile adsorbents which in turn affects pesticide adsorption/desorption mechanisms.

Experiments for the next season will investigate questions about the source and nature of the suspended and colloidal matter, its mechanism of release and its relation to pesticide transport in lysimeters and the soil profile.

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REFERENCES

Madhun, Y.F.; Long, J.L.; Freed, V.H. (1986) Binding of herbicides by water-soluble organic materials from soils. *Journal of Environmental Quality*,**15**,64-68.

Quansah, C. (1985) The effect of soil type, slope, flow rate and their interactions on detachment by overland flow with and without rain. In: *Soils and Geomorphology*, Jungerius (Ed.), Catena supplement 6, pp. 19-29.

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