Session 4
Poster Presentations

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FACTORS INFLUENCING THE MODELLING OF PESTICIDE DEGRADATION IN SOIL AND THE ESTIMATION OF HALF-LIFE (DT_{50}) AND DT_{90} VALUES

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ABSTRACT

One of the primary objectives of environmental fate studies in soil under both laboratory and field conditions is to determine the rate of pesticide degradation. Quantification of pesticide concentration at various time intervals enables calculation of a rate constant for the decay of parent compound and, where appropriate, metabolites. The term disappearance time for 50%(DT_{50}) and 90% (DT_{90}) of the initial pesticide is frequently quoted and has become established as a trigger to more extensive testing. Traditionally, first-order degradation kinetics have been used for estimating DT_{50} and DT_{90} values. The complexity of the soil environment means that for some compounds first-order kinetics provide a gross over-simplification. This paper considers a number of approaches utilising a variety of curve-fitting mathematical programs, including compartmental models. Results show that, in some circumstances, a wide variety of results can be obtained from the same data set. In general, the compartment model approach provides superior fitting criteria, as expected.

INTRODUCTION

In conducting an environmental safety assessment on a novel pesticide the transformation of the compound in soil is first studied under controlled laboratory conditions and then, once a method of residue analysis has been devised, is investigated under a range of field conditions.

In laboratory studies the effects of various environmental parameters such as soil type (% sand, silt and clay, organic matter), pH, water content and temperature on degradation rate and products are determined. If the molecule is rapidly mineralised under a wide range of laboratory conditions to, for example, CO_2 and H_2O without the formation of persistent metabolites, then only limited field studies may be necessary. However, some pesticides may persist as such or may be readily transformed into more or less active metabolites (Bewick, 1986). Parent compound and metabolites may persist in the soil for some time.

Persistence is the general term which is used to describe how long the molecule or its metabolites remain untransformed and not dissipated in the soil environment. The term "half-life" is used to provide a numerical indication of relative persistence. The use of half-life in this context causes a number of difficulties because the transformation or dissipation may not be linear; therefore the time for 50% of the initial material to be transformed or dissipated will not be the same as that taken to go from 50% to 25%. In this paper the term 'transformation' is used to describe any structural change to a pesticide molecule, *ie.* addition or loss of a

moiety or stereo-specific changes. 'Dissipation' is used to describe loss or transfer from one environmental compartment *eg.*, soil, water and air, to another.

Clearly, pesticides can be both transformed and dissipated simultaneously and the combination of both factors is summarised as persistence. In the environmental assessment of a novel pesticide, it is therefore necessary to determine the rate of persistence from scientific experiments and to determine rate constants. Such data then enable an environmental impact assessment to be conducted and, in combination with fixed regulatory trigger values, may generate requirements for more rigorous higher-tier testing. The purpose of this paper is to focus attention on the scientific principles used to quantify this rate of persistence.

MATHEMATICAL TREATMENT OF PESTICIDE DECLINE DATA

Pesticide decline data are derived from transformation and dissipation processes and therefore are derived from a combination of all the processes acting on a treated area. Various mathematical approaches have been taken to model such data and to obtain a quantification of persistence. Timme *et al.*, 1986 have established an evaluation program using extensions of the simple first order rate equation approach to include first order, 1.5th order, 2nd order and the root function of each.

Table 1 Adapted from Timme *et al.*, 1986

Reaction Type	Co-ordinate transformation		
	Abscissa	Ordinate	Equation
	[X]	[Y = f(R)]	
A 1st Order	None	Log R	Log R - a+bt
B 1.5th Order	None	$1/\sqrt{R}$	$1/\sqrt{R}$ = a+bt
C 2nd Order	None	1/R	1/R = a+bt
D RF 1st Order	$\sqrt{t}$	Log R	Log R = a+b$\sqrt{t}$
E RF 1.5th Order	$\sqrt{t}$	$1/\sqrt{R}$	$1/\sqrt{R}$ = a+b$\sqrt{t}$
F RF 2nd Order	$\sqrt{t}$	1/R	1/R = a+b$\sqrt{t}$

RF = Root function Y = a + bx where a = intercept on the ordinate at x = 0 and b = slope, t = time and R is the residue value.

The underlying assumption of this and other approaches is that the data can be adequately expressed by linearising. Experience shows that this is a 'brittle' system, very sensitive to minor variations in the data such that it forces DT_{50} and DT_{90} values where the fitting criteria are relatively low. It is, however, used by some regulatory authorities.

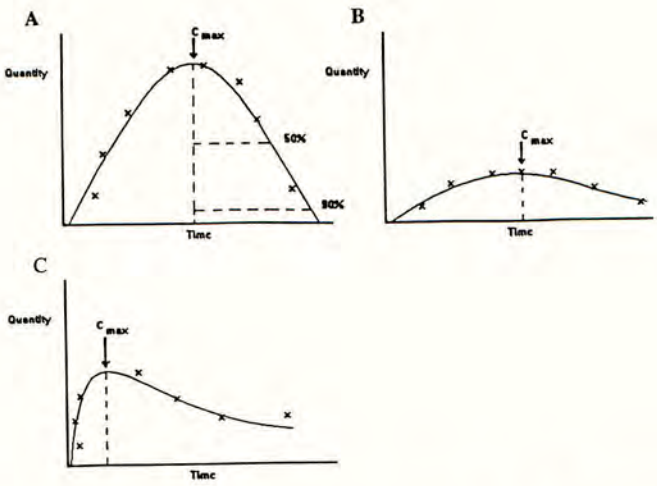
Given the variability of the active processes in pesticide decline, it would appear that no pre-defined order of reaction necessarily fits a given data set. Therefore, the general power rate equation of Hamaker, 1972 may be used in which the order can take any positive value, not limited to whole numbers. The use of such a non-linear function can improve the quality of fit to decline data.

$$\frac{dC}{dt} = KC^n$$

Where C = concentration, K = rate constant, t = time and n = reaction order.

The overall objective of improving the quality of fitting is to provide a more accurate estimation of the rate of decline and hence the decay constant for a particular compound. Predictive environmental models include detailed input data such as daily temperature and rainfall though their weakness often lies in the oversimplification of the pesticide rate of decay constant. In addition to the accurate determination of the DT_{50} and DT_{90} from the parent compound there is also a need to obtain the same values for transformation products. This is more complicated in that there is a formation phase reaching a peak followed by a decline phase.

Figure 1 Formation and decline of transformation products



The shape of the formation and decline curve can be very different depending upon the kinetics and in order to establish the decline kinetics it is necessary to obtain the C_{max}, the point of maximum occurrence. This is fairly straightforward for case A but, however, more difficult for case C. Once C_{max} is obtained then curve fitting will readily provide DT_{50} and DT_{90}.

Four data sets for different parent molecules and a fifth set for a metabolite formation and decline, were chosen for study.

The data sets were subjected to a series of curve fitting programs FIT2, CRVPLOT, CURVEFIT (Excel Macro), SIMSTAT, Timme-Frehse, 1986 model from Bayer AG and KIM compartmental model with power rate equation from Schering AG.

RESULTS

The results are summarised in Table 2.

Table 2 DT_{50} and DT_{90} values for each data set according to curve or model used.

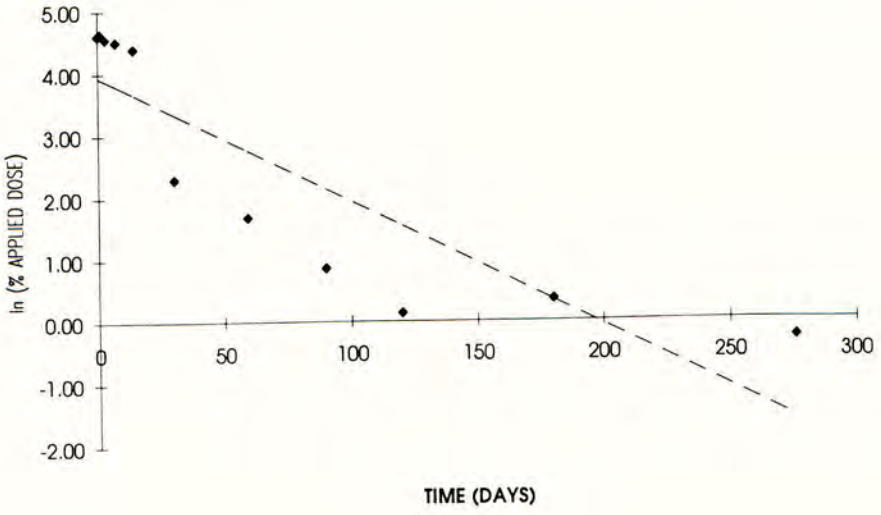
		Time in Days			
Curve/Model		Data Set 1	Data Set 2	Data Set 3	Data Set 4
FIT2	DT_{50}	93	186	180	176
Linear	DT_{90}	167	335	317	318
	Correlation	0.506	0.580	0.887	0.841
FIT2	DT_{50}	38	142	102	64
3rd order polynomial	DT_{90}	79	391	411	241
	Correlation	0.829	0.599	0.979	0.983
CRVPLOT	DT_{50}	24	95	95	80
3rd order polynomial	DT_{90}	53	372	403	379
	Correlation	0.967	0.996	0.991	0.991
CURVE FIT. Excel	DT_{50}	30	110	95	119
Exponential	DT_{90}	120	NA	390	384
	Correlation	0.707	0.986	0.986	0.965
SIMSTAT	DT_{50}	24	100	107	180
Cubic	DT_{90}	54	380	409	321
	Correlation	0.967	0.996	0.991	0.917
Timme/Frehse	DT_{50}	4	111	117	80
	DT_{90}	99	NA	NA	NA
	Best Fit Order	$\sqrt{1}$	1st	1st	1.5
	Significance	0.421	0.526	0.4545	NA
KIM	DT_{50}	16	101	107	93
1 compartment	DT_{90}	54	336	354	308
	Fitting criteria	0.9751	0.9978	0.9943	0.9917
KIM	DT_{50}	16	96	101	80
2 compartments	DT_{90}	54	373	402	698
	Fitting criteria	0.9725	0.9981	0.9947	0.9944
KIM	DT_{50}	16	96	103	79
3 compartments	DT_{90}	54	362	374	399
	Fitting criteria	0.9751	0.9980	0.9945	0.9943
KIM	DT_{50}	18	96	103	80
Power rate	DT_{90}	32	366	377	378
	Fitting criteria	0.9901	0.9980	0.9945	0.9939

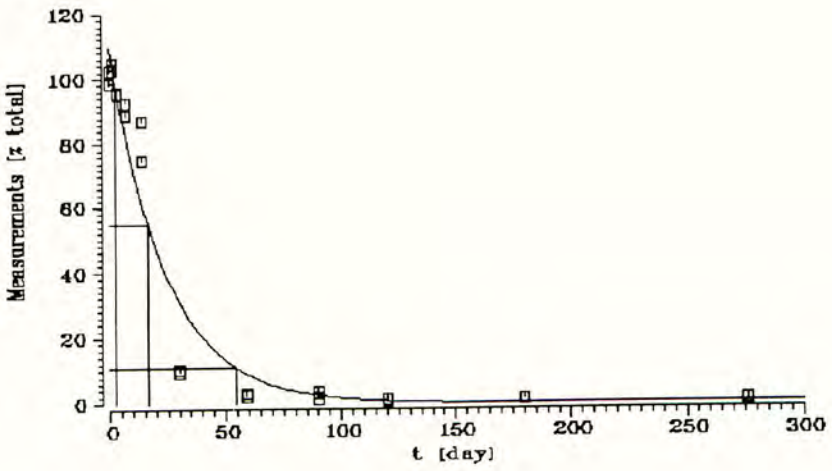
Table 3 Summary of results

	Time in Days			
	Data Set 1	Data Set 2	Data Set 3	Data Set 4
DT_{50} range	4-93	95-186	95-180	64-176
DT_{90} range	32-167	335-391	317-411	241-698

Results therefore show a wide variation according to the curve fitting program or model selected. In general, however, the compartment model gave superior fitting criteria to the data (although direct comparison using the output correlation cannot be made as the mathematical functions are different). This is best illustrated by data set one with a plot of the simple first-order rate kinetics and KIM three compartment model.

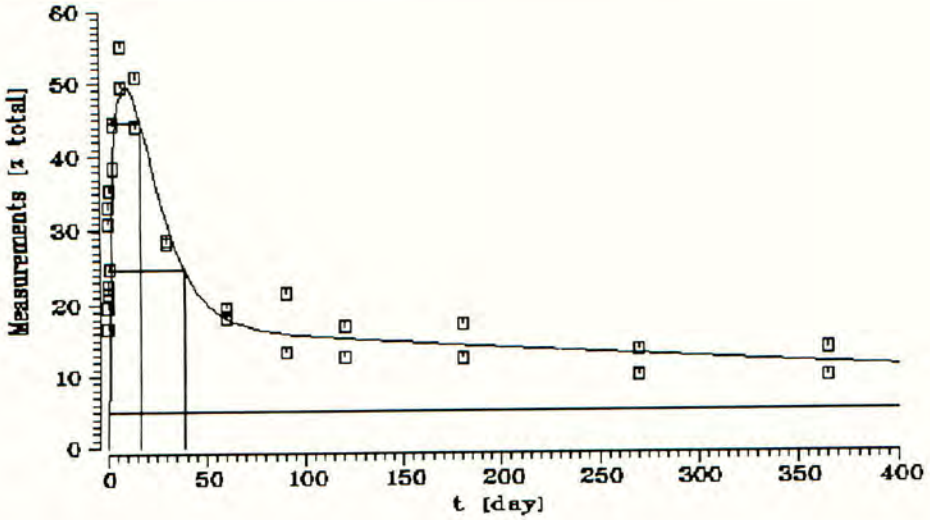
Figure 2 Comparison of data set 1 plot of simple first order rate kinetics and KIM three compartment model





The use of the compartment model for obtaining a C_{max} and then the DT_{50} and DT_{90} for metabolites is illustrated in Figure 3.

Figure 3 Three compartment model fitting for a metabolite (KIM).



CONCLUSION

Given the complexity of pesticide transformation and dissipation in the soil environment and the increasing use of sophisticated predictive environmental models it is apparent that curve/model fitting of measured decline data from both laboratory and field is critically important to the process. This paper has outlined the weakness of the simple first order kinetic approach and shown the superior fitting of compartmental models.

ACKNOWLEDGEMENTS

The authors are grateful to Bayer AG and to Schering AG for the use of the Timme-Frehse and KIM programs. FIT2, CRVPLOT, CURVEFIT, Excel Macro and SIMSTAT were obtained from Libris Britannia 4 CDROM published by PDSL (Public Domain Software Ltd. of Crowborough, West Sussex, England). Grateful thanks to Plant and Soil Metabolism personnel from Rhône-Poulenc Agriculture for the use of their data.

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SPECTROSCOPIC DEMASKING OF SOIL ORGANIC MATTER BOUND ANILAZINE BY ^{13}C NMR TECHNIQUES

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ABSTRACT

Soil-bound residues of organochemicals and their metabolites can be partly extracted together with the humic and fulvic acid fraction. These residues are only detectable by using radioactive labelling, e.g. ^{14}C. An analysis of the character of the bonding can be achieved by means of ^{13}C-NMR spectroscopy. A prerequisite is a specific ^{13}C-enrichment of the observed molecule and, if possible, a ^{13}C-depletion of the humic substances. The fungicide anilazine forms large amounts of soil-bound residues within a few days. High resolution solution ^{13}C-NMR spectra of extracted humic acids of two different soils and different soil horizons as well as of an artificially prepared soil from humified, ^{13}C-depleted maize straw show ester or ether bonds of anilazine to the humic acids. CP/MAS solid-state ^{13}C-NMR spectra of non-humified ^{13}C-depleted maize straw show these bonds as well, but to a large extent the main metabolite dihydroxy-anilazine was found.

INTRODUCTION

Bound residues of pesticides in the environment and their metabolites in soil are characterized by not being extractable with organic solvents under moderate conditions (KHAN, 1982; ROBERTS ET AL., 1984). They may be partly extractable together with the humic matrix, e.g. with dilute sodium hydroxide (FÜHR, 1987). Using ^{14}C-labelled compounds the distribution of the bound residues can be detected by measuring the ^{14}C-radioactivity of the extracted soil organic matter fractions and the humin residue. It is believed that the pesticides, their metabolites or other organic compounds are bound to the humic matrix either by covalent bonds, hydrogen bonds, van der Waals' forces, hydrophobic sorptions or enclosures into suitable molecular gaps of the humic substances in the form of host-guest complexes (CHIOU, 1989; SCHNEIDER, 1991).

^{13}C-NMR spectroscopy offers the possibility of observing the specific chemical environments of carbon atoms. Because the concentrations of pesticides and other organics in the environment are generally in the lower ppm range compared to the soil organic matter, some assumptions have to be made when using the technique of ^{13}C-NMR spectroscopy (WAIS ET AL., 1993). One possible approach is an enrichment by ^{13}C of those carbon atoms of the organic molecules at positions responsible for possible bonds by selective synthesis. This should result in increased signals of the bound residues above those of the humic background in the NMR experiment. Furthermore, an artificial soil with humic substances derived from, for example, humified, ^{13}C-depleted maize straw will lead to even lower background signals of the humic substances.

For all experiments the active ingredient anilazine of the fungicide Dyrene® was used, which forms large amounts of bound residues within a few days. Binding to the humic matrix may occur after a mostly abiotic substitution of one or both chlorine atoms of the triazine ring for reactive functional groups of the humic substances, e.g. acidic hydroxyl or carboxyl groups (MITTELSTAEDT ET AL., 1987; HAIDER ET AL., 1993).

The aim of this study is to investigate how radioactive labelling in combination with the application of stable isotopes can be of assistance in gaining further knowledge about bound residues. ^{13}C-NMR spectroscopy, however, should show that there are changes in chemical shifts due to the fact of different chemical environments of free and bound anilazine (WAIS ET AL., 1995; WAIS ET AL., 1993; HAIDER ET AL., 1993).

MATERIALS AND METHODS

Anilazine, (2-chlorophenyl)-(dichloro-(1,3,5)-triazine-2-yl)-amine, was applied as [triazine-U-^{13}C]anilazine, 90 - 99 % ^{13}C-enrichment, and [phenyl-U-^{14}C]anilazine. The ^{14}C-labelled anilazine was used to record the extraction yield. MITTELSTAEDT ET AL. (1987) showed that there were no great differences in the extraction results if ^{14}C-radiolabels were used either in the triazine or in the phenyl ring of the anilazine. As NMR standards for the detection of the chemical shifts the dihydroxy derivative, (2-chlorophenyl)-(dihydroxy-(1,3,5)-triazine-2-yl)-amine (main metabolite) and the dimethoxy derivative, (2-chlorophenyl)-(dimethoxy-(1,3,5)-triazine-2-yl)-amine (reference for alkoxy bonds) were used. The chemical shifts of their ^{13}C NMR spectra are shown in TABLE 1.

TABLE 1 *Differences in chemical shifts for anilazine, dihydroxy-anilazine and dimethoxy-anilazine using different NMR techniques. C-1: phenyl-bridge C-atom of the triazine ring; C-2 and C-3: other C-atoms of the triazine ring.*

Compound	^{13}C-NMR Method	δ C-1	δ C-2 and C-3
Anilazine	high resolution solution	164.1	170.6/171.5
Dihydroxy-anilazine	high resolution solution	155.5	150.5/153.7
Dimethoxy-anilazine	high resolution solution	167.3	172.3
Anilazine	CP/MAS solid-state	177	163
Dihydroxy-anilazine	CP/MAS solid-state	154-158	
Dimethoxy-anilazine	CP/MAS solid-state	168	172

TABLE 2 *Characteristics of the orthic luvisol (Parabraunerde) from Merzenhausen (MER), North Rhine-Westphalia and the gleyic cambisol (Pseudogley Braunerde) from Overhetfeld (OHF), North Rhine-Westphalia.*

Soil	Horizon	pH ($CaCl_2$)	$C_{org.}$ / %	Sand / %	Silt / %	Clay / %
MER	A_p	7.2	1.2	6.4	78.2	15.4
MER	B_{t2}	6.7	0.3	0.8	74.1	25.1
OHF	A_p	6.9	0.9	74.1	21.7	4.2

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The important characteristics of the two horizons of the orthic luvisol from Merzenhausen (MER) and the gleyic cambisol from Overhetfeld (OHF) are shown in TABLE 2. The artificial soil (AS) was prepared by an aerobic humification of finely milled, ^{13}C-depleted maize straw as described by WAIS ET AL. (1995). The soil samples were incubated with 200 mg/kg or twice with 200 mg/kg of ^{13}C- or ^{14}C-anilazine for 6 to 18 weeks at 20 or 25°C in the dark (after ANDERSON, 1975). The non-humified straw was incubated with ^{13}C-anilazine by shaking for 2 weeks in chloroform at room temperature in the dark.

After incubation the samples were extracted with a mixture of isopropanol/water (1:1), followed by isopropanol (twice) and dichloromethane. The soil residue therefore only contained the non-extractable or bound residues of anilazine. The humic acids (HA) and fulvic acids (FA) were extracted with 0.5 M sodium hydroxide solution. After centrifugation the supernatant was acidified with dilute hydrochloric acid to pH < 2 to precipitate the humic acids. They were centrifuged, redissolved in sodium hydroxide solution (0.5 M), dialysed against water (HPLC quality) and freeze-dried. For ^{13}C-NMR measurements the HA were dissolved in 0.5 M deuterated sodium hydroxide solution and measured by inverse gated decoupling with dioxan as external standard, $\delta = 67.4$ ppm using an AMX 400 Bruker NMR spectrometer at 100.6 MHz (WAIS ET AL., 1995). The CP/MAS NMR spectra of the non-humified straw material were measured using a Bruker CXP 200 NMR spectrometer at 50.3 MHz with hexamethylbenzene as secondary standard, δ(methyl) = 17.0 ppm. All chemical shifts refer to tetramethylsilane.

RESULTS AND DISCUSSION

The fractionations of the bound and the extractable residues of [phenyl-U-^{14}C]anilazine (FIGURE 1) from the different soil samples shows that to the point of extractability and fractionation into FA, HA and humin, it does not matter, whether there is an initial concentration of 200 or 400 mg/kg (MER A_p and OHF A_p). While the extractable fraction of the deeper soil layer, MER B_{t2} (18 % of the radioactivity (r.a.)), is not significantly higher compared to that of the A_p-horizon (13 - 14 % of the r.a.), there is a difference in the concentration of radioactivity in the FA compared to the MER A_p samples. The large amount of extractable radioactivity in the AS may result from the fact that there is still a lot of not completely humified straw material in the sample. This can also contribute to very low concentrations of radioactivity in the FA, because the FA fraction did not build up properly during the 10 weeks of humification of the straw (WAIS, 1994).

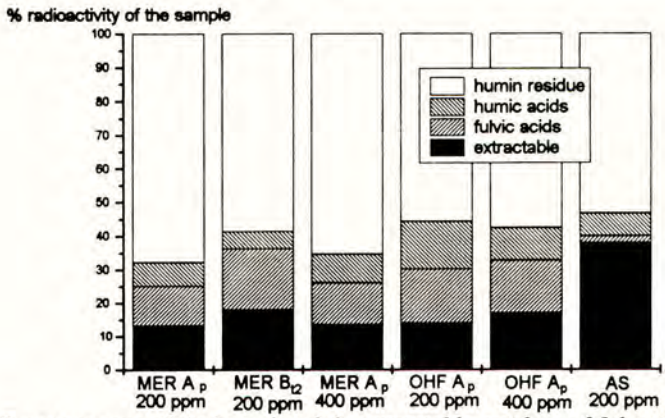

FIGURE 1 *Fractionations of the bound and the extractable residues of [phenyl-U-^{14}C]anilazine from different soil samples. The ppm values indicate the initial concentrations of ^{14}C-anilazine in mg/kg. MER: orthic luvisol from Merzenhausen (see TABLE 2); OHF: gleyic cambisol from Overhetfeld (see TABLE 2); AS: artificial soil prepared from ^{13}C-depleted maize straw in quartz sand.*

^{13}C-NMR experiments were not only carried out to investigate the binding process of the anilazine, but also to examine the reliability of using HA from AS as a model. FIGURE 2 indicates that there are no essential differences in the spectra of the HA either originating from MER A_p or AS prepared from maize straw with natural carbon abundance. So there is actually no limitation in using the HA from AS for qualitative investigations as they are described in this study. The HA spectra of AS from ^{13}C-depleted straw even show the expected decrease in signal heights compared to the background of the spectra.

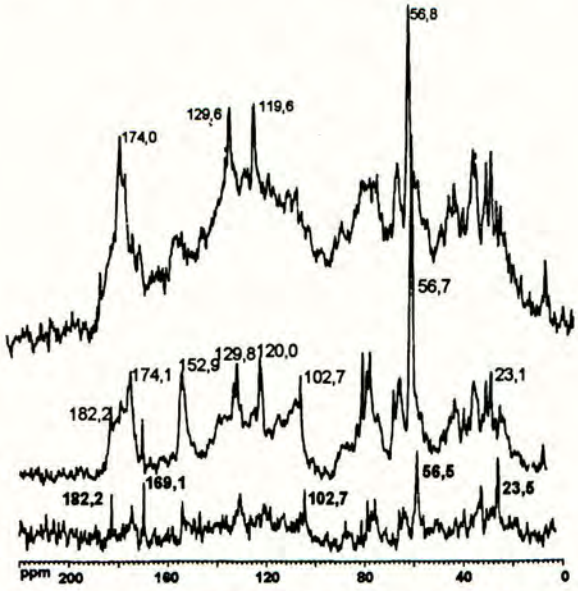

FIGURE 2 *^{13}C-NMR spectra of HA extracted from MER A_p (top), AS from straw with natural carbon abundance (centre) and AS from ^{13}C-depleted straw (bottom)*

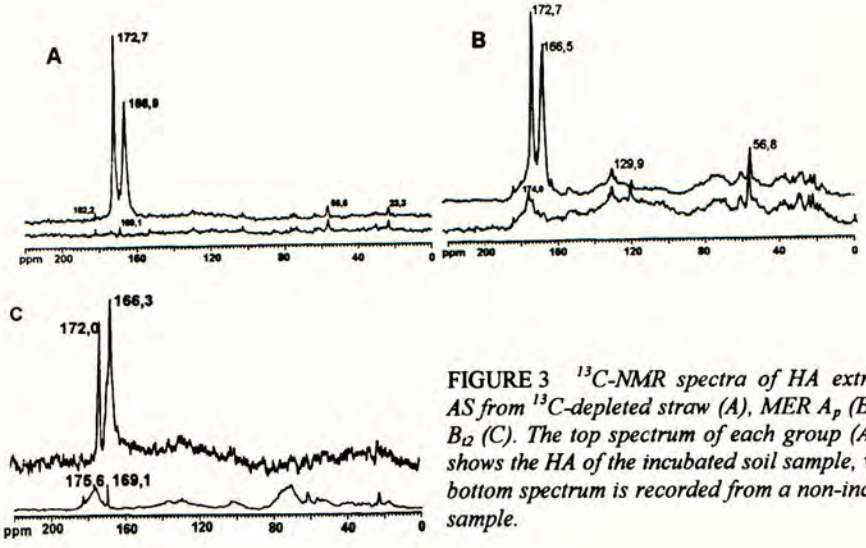

FIGURE 3 *^{13}C-NMR spectra of HA extracted from AS from ^{13}C-depleted straw (A), MER A_p (B) and MER B_{t2} (C). The top spectrum of each group (A, B and C) shows the HA of the incubated soil sample, whereas the bottom spectrum is recorded from a non-incubated soil sample.*

All HA ^{13}C-NMR spectra of the ^{13}C-anilazine incubated soil samples either from the AS, MER A_p or MER B_{t2} (FIGURE 3) show additional signals in the range of those of the dimethoxy derivative as indicated in TABLE 1. So it can be concluded that ester or ether bonds of the triazine carbon atoms of the anilazine to the HA are formed. Since this also occurs in the soil sample of the B_{t2} horizon, there should be a permanent detoxification by a strongly reduced bioavailability even if the anilazine would be transported into deeper soil layer e.g. by preferential flow.

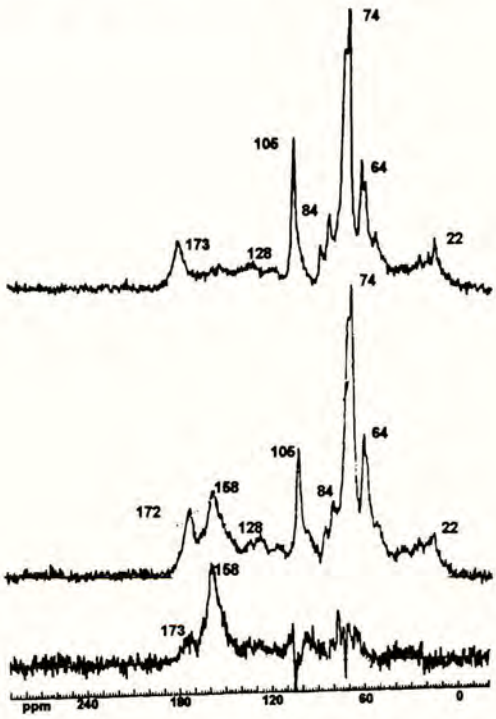

FIGURE 4 *^{13}C CP/MAS NMR spectra of the non-humified straw material. Non-incubated sample (top), sample containing 66 ppm of ^{13}C-anilazine (centre) and difference spectrum (bottom).*

The CP/MAS NMR spectra in FIGURE 4 of the non-humified, ^{13}C-depleted maize straw underline this fact in one point, because the difference spectrum resulting from the incubated and the non-incubated sample shows a signal at $\delta = 173$ ppm belonging to dialkoxy-anilazine. But there is interference with signals of aliphatic amides or those of carboxyl groups of the straw bearing the same chemical shifts (HIMMELSBACH AND BARTON, 1980). The main signal in the difference spectrum at $\delta = 158$ ppm can be regarded as originating from the main metabolite dihydroxy-anilazine, which was found in several laboratory degradation and lysimeter studies (e.g. MITTELSTAEDT, 1994).

CONCLUSIONS

For concentrations of up to 400 mg/kg of anilazine no clear diffenreces in the results of the fractionation into extractable radioactivity and radioactivity bound to the FA, HA and humin is observed. Even the results of the lower soil horizon (B_{t2}) are nearly the same as those for the comparable A_p horizon. All non-extractable residues of ^{13}C-anilazine soil samples show dialkoxy bonds of the triazine carbon atoms to the humic acids. These considerably strong chemical bonds will lead to a partial

immobilization of the compound itself and, therefore, to a detoxification of the soil by a greatly reduced bioavailability. On the other hand the CP/MAS spectrum of the non-humified straw material shows a strong signal of the dihydroxy metabolite. The question may therefroe be posed, whether the alkoxy bonds to the humic acids are partly a result of the extraction procedure using strong alkaline solutions. Further investigations to demonstrate the fact of dialkoxy bonds to soil organic matter as well as further investigations of the behaviour of the dihydroxy-derivative in the B_{t2} horizon seem to be necessary.

The use of humic acids of AS from ^{13}C-depleted straw is not limited to qualitative observations concerning the binding mechanisms, but fractionation into extractable and non-extractable radioactivity shows more extractable radioactivity than in the native soil samples after just 10 weeks of humification.

ACKNOWLEDGEMENTS

For experimental help we are grateful to Miss S. Rosellen and Mr M. Meyer (both KFA Jülich). Further thanks are due to Dr. R. Körmeling (Bayer AG) for synthesis and supply of the labelled compounds and to Prof. H.M. Helal and Mrs H. Lemke (both F.A.L. Braunschweig) for helping to grow the ^{13}C-depleted maize. We also acknowledge that this study is part of cooperation with Bayer AG, Germany.

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MICROCOSM EXPERIMENTS TO STUDY MECOPROP DEGRADATION IN THE CHALK AQUIFER OF HAMPSHIRE.

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ABSTRACT

Pesticide degradation in groundwater and aquifer material has received relatively little attention compared to the behaviour in surface soils. The widely used herbicide mecoprop can be readily leached from soils and has been detected in some groundwater sources, it has been shown to degrade slowly in topsoils, but little work has been done on its transformation in the subsurface. This paper describes a series of microcosm experiments undertaken to establish whether degradation of mecoprop occurs in the unsaturated zone. Results show that the microbial population in groundwater from the study sites has the ability to degrade mecoprop and this degradation is enhanced by the presence of core material.

INTRODUCTION

Determining the persistence of herbicides in soil is an important part of the herbicide registration process, but much less information exists about their persistence in groundwaters or aquifers. Compounds which leach to the subsurface and eventually to the groundwater are expected to encounter a different set of environmental conditions, such as lower oxygen concentrations, lower levels of nutrients and smaller microbial populations.

Aquifer microorganisms have the capability to degrade many organic pollutants but the rate of degradation is much slower than found in soil. Whilst the relative persistence may be similar in aquifers to that in soil, the actual rates of degradation are likely to be slower and cannot be predicted from soil data. With previously uncontaminated soils, a lag period may occur whilst the microbes adapt to a new food source (Bromilow, 1992).

The objective of the study was to investigate the microbial degradation of mecoprop in the unsaturated zone. Groundwater and core material from two sites in Hampshire, referred to as ASM and AWC, were collected. Core material was kept chilled prior to the experiments starting, the depths referred to are for the core material measured from the surface and ground water was collected from the same borehole as the core material when required.

EXPERIMENTAL

A series of microcosm experiments were set up (Table 1) to determine the disappearance of mecoprop in groundwater when core material is present. The microcosms consisted of a slurry of chalk core in groundwater (1:25) with mecoprop added at 50µg/l. Samples were taken in duplicate at pre-determined intervals. The mecoprop was extracted using Waters

C18 Sep-Pak cartridges and determined using High Performance Liquid Chromatography (Table 2).

TABLE 1. Microcosm conditions

1. Sterile groundwater.
2. Non-sterile groundwater.
3. Sterile groundwater with non-sterile core.
4. Non-sterile groundwater with sterile core.
5. Sterile groundwater with sterile core.
6. Non-sterile groundwater with non-sterile core.

TABLE 2. Chromatography conditions

Column	Spherisorb C8 5µm 250mm x 4.6mm i.d.
Eluant	60% HPLC-Grade methanol.
	40% 0.1M acetic acid in HPLC-Grade water.
Flowrate	1.2ml/min.
Injection size	100µl

RESULTS

A pilot experiment using fresh groundwater spiked at different concentrations of mecoprop showed a 72% disappearance of mecoprop in 14 days. This was used to establish a spiking concentration for the microcosm experiments of 50 µg/l as being appropriate.

An initial experiment based on the pilot was established using groundwater and core material from the ASM site. This was run over a 14 day period. No significant disappearance of mecoprop was observed in any of the microcosms (Figure 1.). This may be explained as a lag period due to microbial acclimatisation to the new food source. Insufficient microcosm material remained to continue with this experiment.

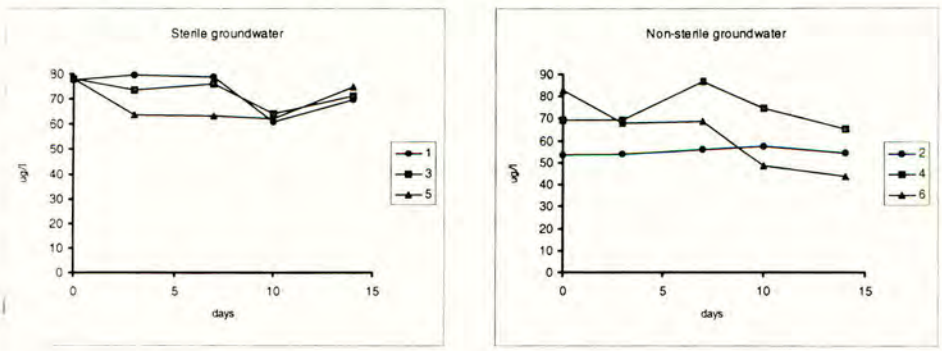

Figure 1. Concentrations of mecoprop in solution in the microcosms from ASM, core material from 2.78m. (The legend numbers refer to the microcosm numbers in Table 1.)

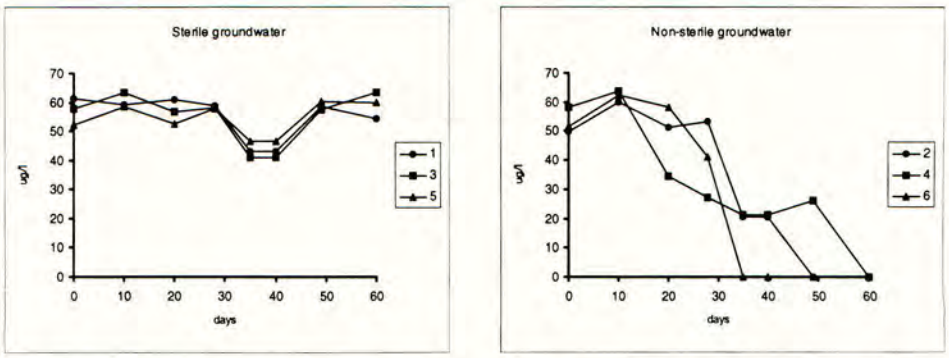

Figure 2. Concentrations of mecoprop in solution in the microcosms from AWC, core material from 2.88m. (The legend numbers refer to the microcosm numbers in Table 1.)

Further experiments were established using groundwater and core material from the AWC site, run over a 60 day period sampling at about 10 day intervals. These experiments used core material from two different depths to see whether depth influenced the disappearance of mecoprop. Generally, the results for the two depths show the same trend for mecoprop disappearance (Figures 2 & 3) i.e. that microbial activity in the groundwater is necessary for mecoprop degradation, with this degradation rate being enhanced by activity in the core material.

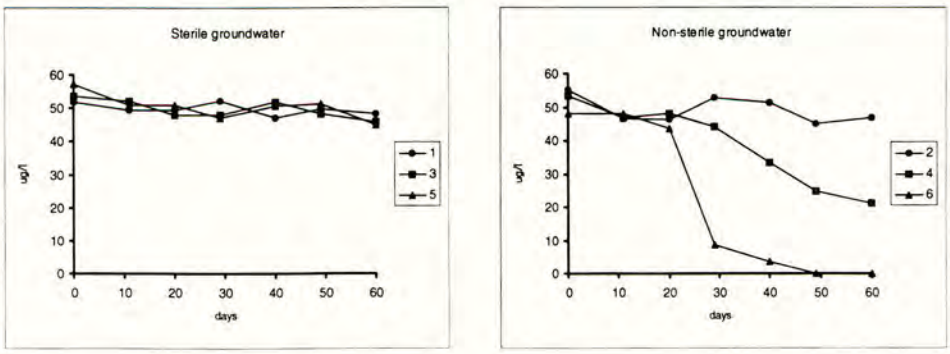

Figure 3. Concentrations of mecoprop in solution in the microcosms from AWC, core material from 5.07m. (The legend numbers refer to the microcosm numbers in Table 1.)

The observed differences in the results from the two depths could be explained by differences in sample handling prior to the start of experiments. Groundwater for the 5.07m microcosms was collected and stored at room temperature for a period of two weeks, whilst the 2.88m experiment was run using groundwater collected the day prior to setting up the microcosms. It is thought that this storage of the groundwater may have affected the microbial potential to degrade mecoprop. To test this theory an experiment using fresh and stored groundwater from two sites was carried out. The stored groundwater had been stored for several months at 4°C and the fresh groundwater was pumped the same day as the start of the experiment.

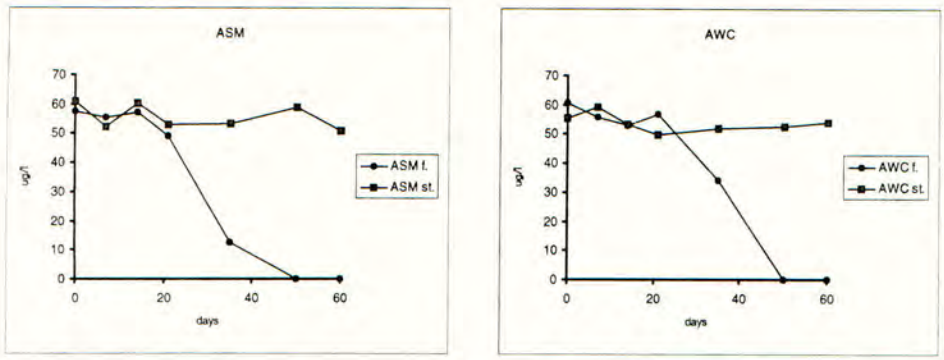

Figure 4. Concentrations of mecoprop in solution in groundwater from two sites used to compare the degradation potential of fresh versus stored groundwater.

The fresh groundwater showed complete degradation of the mecoprop in 50 days (Figure 4) with no change in concentration in the stored groundwater, indicating that for this type of experiment freshly collected groundwater is essential.

DISCUSSION

The results indicate that microbial populations of the Chalk at these two sites have the ability to degrade mecoprop. Degradation is enhanced by the addition of subsurface core material. There are two possible explanations for this observation. Firstly, that the microbial population in the groundwater forms a symbiotic association with a second population in the core material, achieving a combined effect resulting in enhanced degradation, and secondly, that the core material contributes support, increased surface area and better availability of nutrients, also with the result of stimulating microbial activity. Microbial degradation of mecoprop was more effective with recently collected groundwater. Results indicate a period of microbial adaptation before degradation began, confirming similar results obtained in earlier studies on mecoprop degradation in soil (Bromilow, 1992).

ACKNOWLEDGEMENTS

This paper is published with the permission of the Director of the British Geological Survey, a component institute of the Natural Environment Research Council (NERC). The work was part of a commissioned research project financed by the National Rivers Authority.

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THE FATE OF [BENZENE-U-^{14}C-]BENAZOLIN-ETHYL IN A LYSIMETER STUDY SUPPORTED BY DETAILED LABORATORY EXPERIMENTS AND MODEL CALCULATIONS

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ABSTRACT

An outdoor lysimeter study with the herbicide ^{14}C-benazolin-ethyl applied to two soil types was started in Februrary 1994. Sampling of the plough layer between March and August 1994 showed that 43 % of applied radioactivity was still present in both soil types in August, with the majority located in the upper 0-2.5 cm soil layer. Only traces of radioactivity could be detected in soil below 15 cm depth. Benazolin-ethyl was not detected at any sampling interval. After six months, benazolin in soil was found to account for 2.7 % and 6.8 % of applied radioactivity for of the gleyic planosol and orthic luvisol, respectively. Total radioactivity in drainage water was ‹1 %. Mathematical modelling showed that simulations using parameters for the hydraulic functions derived from pedo-transfer functions could not predict all terms of the soil water balance correctly. However, in the case of the gleyic planosol, the volume of leachate and soil moisture in the top soil layer was calculated accurately. The amount and movement of ^{14}C-benazolin in the plough layer was overestimated by the model in both cases.

INTRODUCTION

Results presented in this paper are part of the current status of the EU-project '*Critical Parameters Governing the Mobility and Fate of Pesticides in Soil/Aquifer Systems*'. The general objectives of this project are the identification and quantification of important parameters governing the mobility of test compounds in order to define suitable input parameters for model scenarios at field and regional scales (Vereecken *et al.*, 1995). To meet these objectives, experimental research and modelling activities are needed and the experiments have to be designed to match the needs of the models used. In February 1994, an outdoor lysimeter study with the herbicides ^{14}C-benazolin-ethyl and atrazine was undertaken. In order to monitor water flow in the lysimeters, deuterated water, potassium bromide and methylene blue were applied simultaneously with the herbicides. Lysimeter experiments were conducted as described by Steffens *et al.* (1992). In this paper, experimental results of the fate of benazolin-ethyl in lysimeters will be presented. The general behaviour of benazolin-ethyl in soil is well documented by Leake (1991). Results from this study including detailed laboratory experiments were used as input data for mathematical modelling. Predictions from the model *WAVE* for soil temperature and moisture content, drainage flux at the bottom of the lysimeter and the simulated time course of residue profiles in soil are compared with experimental results.

MATERIALS AND METHODS

Chemicals

Benazolin-ethyl is a broad spectrum herbicide mainly used for weed control in cereals and oil seed rape. Technical grade and [benzene-U-^{14}C-]benazolin-ethyl and metabolites (as reference substances) were supplied by AgrEvo Company. The chemical names of the active ingredient and its metabolites are: ethyl 4-chloro-2-oxobenzothiazolin-3-yl (benazolin-ethyl), 4-chloro-2-oxobenzothiazolin-3-yl acetic acid (benazolin), 4-chlorobenzothiazolin-2-one (BTS 18753), N-methyl-4-chlorobenzothiazolin-2-one (BTS 18564).

Soils

TABLE 1 Characteristics of the gleyic planosol from Krauthausen and the orthic luvisol from Merzenhausen, North Rhine-Westphalia.

Soil	Horizon	pH $_{(CaCl_2)}$	$C_{org.}$ [%]	Sand [%]	Silt [%]	Clay [%]
Gleyic planosol	A_p	7.2	1.3	8.8	73.3	17.9
Orthic luvisol	A_p	7.2	1.2	6.4	78.2	15.4

Lysimeter experiments

In February 1994, ^{14}C-benazolin-ethyl was applied to four lysimeters (1 m^2 surface area, undisturbed soil monoliths of 1.1 m depth) at rates of 0.68 kg/ha for the gleyic planosol and 0.75 kg/ha for the orthic luvisol. No crop was planted. Soil samples from lysimeter of each soil type were collected monthly from March to August 1994. At each one, six soil cores of 3.5 cm diameter and 30 cm depth were taken and divided into seven soil layers. Pooled soil samples were extracted with simulated soil solution (0.01 M $CaCl_2$ solution) for 24 h, followed by an extraction with acetone for 1 h and ethylacetate for 1 h (rotary shaker at 120 rpm, soil/solution ratio 1:2). Radioactivity in the extracts was measured by liquid scintillation counting and extracts were further analysed by radio-thin-layer chromatography with co-chromatography of non-labelled reference compounds. Residual radioactivity in soil was combusted for $^{14}CO_2$ determination. Two lysimeters, one of each soil type, were equipped with devices to measure soil moisture content by time domain reflectrometry (depths of 15, 30, 45, 65, 80, 105 cm). Soil temperature sensors were installed at depths of 5, 10, 20, 30 and 60 cm.

Degradation studies

The degradation study was carried out using Erlenmeyer flasks with 100 g dry soil each and one replicate (Anderson, 1975). The concentration of benazolin-ethyl was 0.1 mg a.i./100 g dry soil. The flasks were incubated in the dark at different temperature (6, 15, 25 °C) and moisture (20, 40, 60 % WHC) regimes. Soil was sampled at days 0, 2, 6, 11, 25, 39 and 91 and samples were extracted as described above. The linear soil-water distribution coefficients (K_d) were calculated from the partitioning of the pesticide into the soil solution and organic solvent phases during extraction. For each moisture content the DT_{50}-value was determined according to first-order kinetics. Fitting to other kinetics was also applied according to Timme & Frehse (1986). A linear regression analysis of the log-values for gravimetric water content and the respective DT_{50}-value led to the parameters A and B which describe the effect of soil moisture content on pesticide degradation (Walker, 1987).

Model calculations

WAVE is a mechanistic-deterministic model for simulating water flow and solute transport in heterogeneous cropped soils (Vanclooster *et al.*, 1993). Water flow is simulated using Richards' equation and the convection-dispersion equation describes solute transport. Pesticide sorption is accounted for with a constant linear isotherm. Degradation rate is corrected for the effects of soil moisture content according to the model of Walker (1987) and the effects of soil temperature are accounted for by an Arrhenius approach. Parameters for soil hydraulic functions were derived from pedo-transfer functions (Vereecken *et al.*, 1989; 1990), resulting in parameters for the $\theta(h)$ relationship according to Van Genuchten (1985) and the K(h) equation of Gardner (1985). Potential evapotranspiration is a necessary input.

RESULTS AND DISCUSSION

Six months after application of the herbicide, most of the radioactivity was located in the top 2.5 cm of both soil monoliths. Only traces of penetration below 15 cm were measured (Figure 1). Results of Leake (1991) support these data. The amount of radioactivity in the drainage water (data not shown) was below 1 % of that applied (AR). More than half of the residual radioactivity was not extractable, a finding also presented by Leake (1991). Characterisation of radioactivity in the extracts for two

sampling dates (5/94, 8/94) are shown in Table 2. In May, an average of 45-50 % of AR was benazolin and 3-6 % BTS 15758 from a total residue of 85-90 % of AR (see Figure 1). In August, only 43 % of AR was left in both monoliths, possibly as a result of losses by mineralisation to $^{14}CO_2$ during the summer when temperatures were high (Figure 3). This has to be seen in combination with total irrigation of 88.5 mm which prevented drying of the soil (see Table 4). Also, detectable quantities of benazolin (4-9 % of AR) and BTS 15785 (ca. 5 % of AR) decreased profoundly at the later sampling interval. Benazolin-ethyl could not be detected at either sampling interval and this can be explained by its rapid hydrolysis to benazolin. Leake *et al.* (1987) reported a half-life for benazolin-ethyl in soil of <1d. Therefore in this case as basis for half-life determination and modelling benazolin was taken.

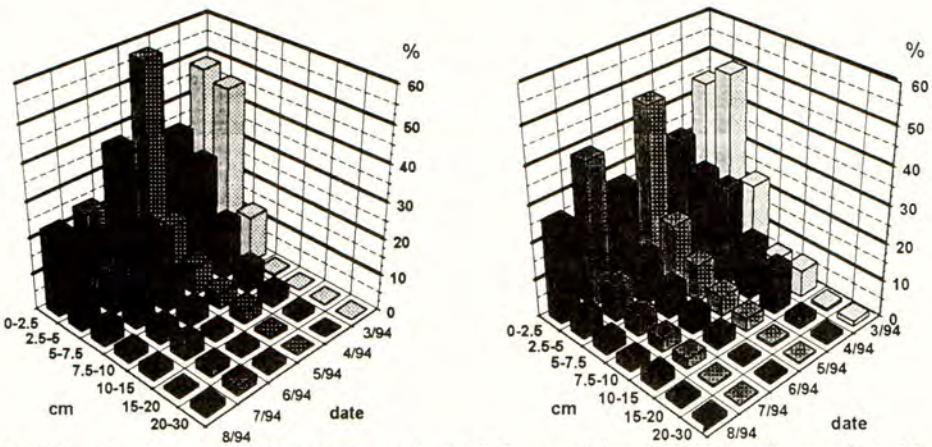

FIGURE 1 Distribution of residual radioactivity in different soil layers of both soil types from March until August 1994. Applied radioactivity = 100 %. (left gleyic planosol, right orthic luvisol)

TABLE 2 Characterization of radioactivity in desorption solutions and acetone extracts from different soil layers of both soil monoliths at sampling dates 05/08/94 and 08/09/94. Applied radioactivity = 100 %.

	Desorption solution						Acetone extracts					
	Benazolin %		BTS 18753 %		BTS 18564 %		Benazolin %		BTS 18753 %		BTS 18564 %	
Gleyic plan.	5/94	8/94	5/94	8/94	5/94	8/94	5/94	8/94	5/94	8/94	5/94	8/94
0 - 2.5 cm	25.2	2.8	n.d.	n.d.	n.d.	n.d.	7.5	1.2	3.0	2.5	0.3	n.d.
2.5 - 5 cm	4.9	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	0.1	1.4	1.1	n.d.	n.d.
5 - 7.5 cm	2.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.8	0.1	1.0	0.5	n.d.	n.d.
7.5 - 10 cm	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	0.6	0.2	n.d.	n.d.
10 - 15 cm	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	0.6	n.d.	n.d.	n.d.
Total	**35.1**	**2.8**					**10.5**	**1.4**	**6.6**	**4.4**	**0.3**	
Orthic luvisol												
0 - 2.5 cm	20.8	6.4	n.d.	0.3	n.d.	n.d.	5.8	1.6	1.5	2.3	0.2	0.1
2.5 - 5 cm	10.6	0.4	n.d.	0.1	n.d.	n.d.	2.9	0.1	0.8	1.1	n.d.	n.d.
5 - 7.5 cm	4.8	n.d.	n.d.	n.d.	n.d.	n.d.	1.3	n.d.	0.4	0.7	n.d.	n.d.
7.5 - 10 cm	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	n.d.	0.2	0.6	n.d.	n.d.
10 - 15 cm	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	0.2	n.d.	n.d.	n.d.
Total	**39.7**	**6.8**		**0.4**			**11.0**	**1.7**	**3.2**	**4.7**	**0.2**	**0.1**

Limit of reliable determination in soil segment is 0.05 % of AR, n.d. = not detected

Benazolin had an average half-life of 50 d in the orthic luvisol and of around 56 d in the gleyic planosol. Although the fitting of the residue data to first-order kinetics was never the 'best-fit', this procedure led to reasonable results (Table 3). It was not possible to set up a linear regression equation at a significant level to determine the parameters A and B of the Walker equation. However, the parameters A and B derived in this statistical analysis were used as input for the model calculations.

TABLE 3 Average DT_{50}-values determined from laboratory experiments at 25 °C under different soil moisture conditions (WHC = water holding capacity).

	orthic luvisol		gleyic planosol	
WHC [%]	DT_{50} value[d]	R^2_{mod}	DT_{50} value[d]	R^2_{mod}
20	51	0.76	54	0.79
40	48	0.85	38	0.93
60	53	0.80	37	0.88
Parameter A	47.3		147.9	
Parameter B	0.02		0.45	

From February to August, 105.9 l and 87.8 l leachate were collected from the two orthic luvisol lysimeters, representing an average of 18.5 % of the total precipitation and irrigation applied during this period (Table 4). Drainage of the gleyic planosol lysimeters gave 103.8 l and 107.5 l of leachate, respectively, representing an average of 20.2 % of the total precipitation and irrigation. The predicted leachate flux and total volume was in good accordance with the experimental data for the gleyic planosol. *WAVE* overpredicted drainage for the orthic luvisol by around 50 % (Figure 2).

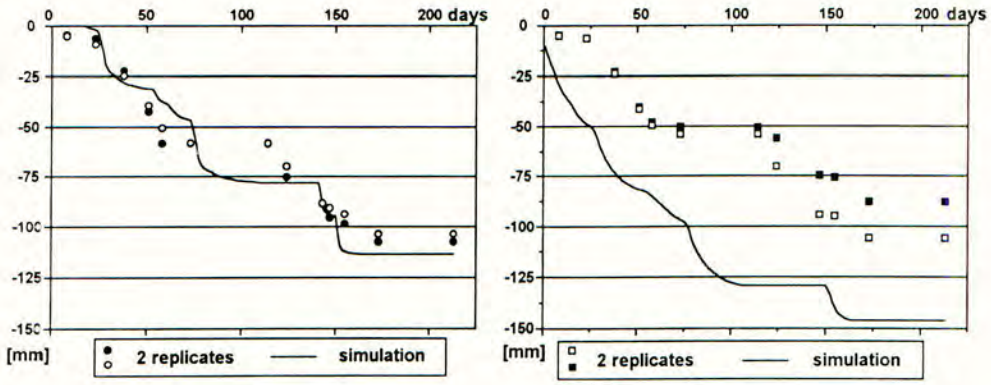

FIGURE 2 Measured and simulated accumulated drainage water flux at the lower boundary of the lysimeters of both soil types. (left gleyic planosol, right orthic luvisol)

A soil water balance has been calculated at the end of the experiment according to Eq. 1 (Table 4). *WAVE* was not able to predict these terms accurately for either soil type. The simulation of water movement in the orthic luvisol overpredicts the leachate volume due to a large degree of drying which did not actually occur in the experiments. Although the gleyic planosol calculation gave good agreement between measured and calculated leachate volumes, the change in the soil moisture storage was not well predicted.

TABLE 4 Simulated and measured values for the soil water balance of four lysimeters.

	Precipitation	Irrigation	drainage	ΔΘ	Evaporation
Gleyic planosol a	431.7	88.5	107.5	-74.6	487.3
Gleyic planosol b	431.7	88.5	103.8	-74.6	491.0
Simulation	431.7	88.5	113.0	-2.7	409.9
Orthic luvisol a	431.7	88.5	87.8	-52.3	484.7
Orthic luvisol b	431.7	88.5	105.9	-52.3	466.1
Simulation	431.7	88.5	146.1	-82.9	457.1

$$ET = prec. + irrig. - drain - \Delta\Theta \qquad \text{Eq. (1)}$$

ET: evapotranspiration [mm]
prec.: precipitation [mm]
irrig.: irrigation [mm]
drain.: drainage at the bottom of the lysimeter [mm]
ΔΘ: change in soil moisture contents over the monolith [mm]

In order to interpret the simulation results for solute transport, it is necessary to check whether the soil moisture content and temperature are calculated properly because of their strong effect on pesticide degradation. The predicted soil temperatures are in excellent agreement with the measured data (Figure 3). The applied parameters for the hydraulic functions derived from pedo-transfer functions are not able to simulate the soil moisture content in the top 15 cm of the orthic luvisol. The simulation for the gleyic planosol is in better agreement with the recorded data (Figure 3). It is planned to use hydraulic parameters based on measurements of soil samples to improve the performance of *WAVE*.

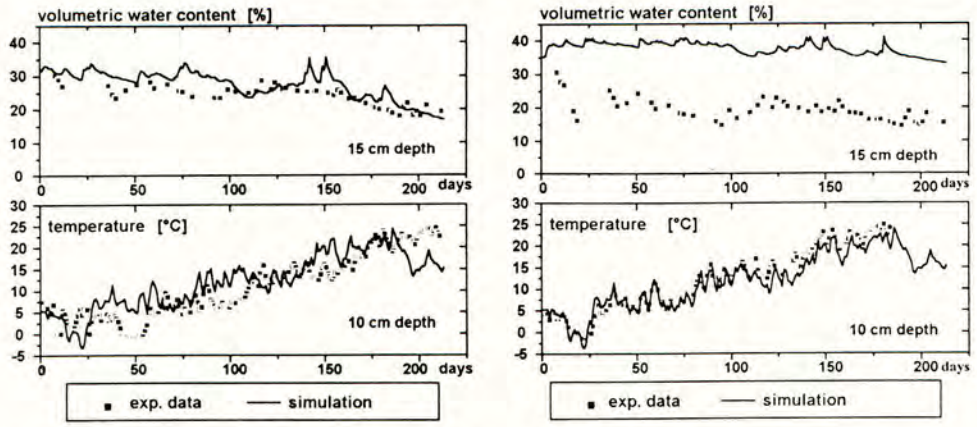

FIGURE 3 Measured and simulated soil moisture content at 15 cm depth and soil temperature at 10 cm depth. (left gleyic planosol, right orthic luvisol)

In both simulations, the model predicts leaching of benazolin to deeper soil layers than occurred in the experiments (Figure 4). The total amount of benazolin is overestimated by 25 % in May. In August, *WAVE* predicts residues around 3.7 and 2.4 times higher than the measured data in the orthic luvisol and gleyic planosol, respectively (see Table 2). Evaluation of further results from the laboratory degradation study will result in a more site-specific set of parameters for future use.

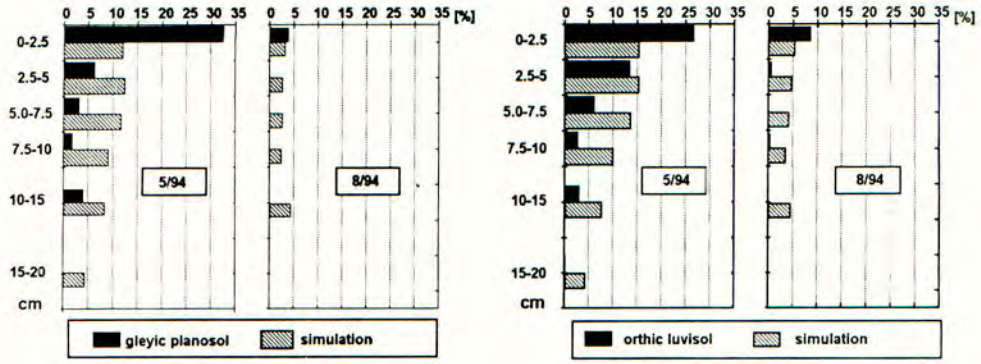

FIGURE 4 Measured and simulated residues of benazolin in May and August 1994 in the top soil layer (0-30 cm). Applied radioactivity = 100 % (left gleyic planosol, right orthic luvisol)

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions of colleagues working on this project, especially A. Steffen, J. Noël, M. Neumann and T. Combach. We are grateful to AgrEvo Company for supply of the test and reference compounds.

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LEACHING OF HERBICIDES IN SOIL MACROPORES AS A POSSIBLE REASON FOR GROUNDWATER CONTAMINATION

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ABSTRACT

An experimental setup was constructed to investigate leaching of herbicides (chlorotoluron and isoproturon) and a tracer in undisturbed small-scale lysimeters. A lysimeter with sieved and repacked soil was used as a reference. A comparison of water and solute flow after high intensity irrigation showed clear differences between undisturbed and disturbed samples. Chlorotoluron, isoproturon and the tracer were analysed in the first effluent of the undisturbed soil. In contrast, there was no breakthrough of herbicides or tracer from the disturbed sample. This difference in leaching behaviour can be explained by preferential flow in macropores, giving rapid movement of water and solutes down the soil profile. The consequences for groundwater contamination are discussed.

INTRODUCTION

The application of pesticides to agricultural sites may give rise to contamination of surface and groundwaters. Since 1980 the number of studies monitoring for pesticides in groundwater increased (Pestemer *et al.*, 1993; Pionke *et al.*, 1989). For example, Spalding *et al.* (1989) reported the occurrence of 17 different pesticides in Nebraska`s groundwater.

What is the reason for such contamination? - To reach ground water, pesticides have to pass through the unsaturated soil profile. This flow process is influenced by a variety of factors such as degradation, sorption, volatilisation and plant uptake. The transport of water and solutes is also greatly influenced by the soil pore system. In particular, macropores (e.g. earthworm and root channels, shrinking cracks) may be a major factor influencing hydraulic conductivity and leading to a bypass transport of water. In comparison to matrix flow, relatively little adsorption of pesticides is possible and, as a result of high intensity rainfall, transport of normally highly adsorbed pesticides may take place below the root zone.

In the past, the description of flow processes in soil profiles considered only matrix flow. However, the results of transport experiments cannot be explained by the convective-dispersive theory in all cases (Beven & Germann, 1982; Isensee *et al.*, 1990). The presence of preferential pathways may explain fast vertical transport. The phenomenon of macropore flow is summarised by Van Genuchten *et al.* (1990).

The present small-scale lysimeter studies describe the transport of water, tracer and selected herbicides in a well-structured, water unsaturated loess soil.

METHODS AND MATERIALS

The experiments were carried out with a loess soil (soil type: parabrownearth) located near Braunschweig. The most important soil parameters are shown in Table 1. It is a highly-

structured soil with continuous earthworm-channels down to a depth of 1 m. The high silt content causes a stable primary and secondary pore system. Undisturbed soil samples were taken in soil column cylinders (diameter 30 cm, length 100 cm) from the described site.

Soil sampling was carried out using a hydraulic pressure equipment (for details see Nordmeyer & Aderhold, 1994). This procedure allows the sampling of soil monoliths with minimum disturbance to the soil.

TABLE 1: Soil characteristics

	TOPSOIL	SUBSOIL	
Soil depth [cm]	0-30	40-70	70-100
Soil texture [%]			
Sand	6.6	4.8	6.9
Silt	85.0	74.2	81.2
Clay	8.4	21.0	11.9
pH-value ($CaCl_2$)	6.8	6.9	7.7
Organic carbon [%]	1.3	0.3	0.2
Bulk density [g/ cm^{-3}]	1.58	1.55	1.6
CEC [mmol/100 g]	6.12	7.87	8.45

After sampling, the monoliths were installed in the experimental setup (Fig. 1). A sprinkling device was set onto the top of the lysimeter. The irrigation water dripped out from 87 hypodermic needles, ensuring a good spatial distribution.

An end-cap was put on the bottom of the lysimeter, from which the outlet ended in a low pressure chamber. Suction was applied during the experiments to simulate the natural soil moisture tension and to avoid water saturation in soil. A fraction collector was used to sample the percolating water at high resolution.

An air-impermeable and water-permeable layer was put in the end-cap. This microporous diaphragm acts in the same way as a ceramic plate. Three tensiometers with electronic pressure transducers were installed horizontally (5 cm above the bottom). The data were monitored continuously on a personal computer with A/D-interface card. The experiments were carried out in an lysimeter station (Nordmeyer & Aderhold, 1994) at a controlled temperature of 10°C (+/- 2°C).

Reference lysimeters were prepared by sieving (2 mm) and repacking soil from undisturbed soil samples. The resulting bulk density was slightly lower than in the undisturbed soil.

Before starting leaching experiments, all soil samples were irrigated (5 mm/d until outflow occurred) to ensure the same initial water content. After that, the lysimeters drained for one week to reach field capacity. Two herbicides, chlorotoluron and isoproturon, were applied at 10 kg A.I./ha. Additionally a tracer (bromide) was applied at 75.7 kg/ha. The solute was pipetted in a fine grid to get a good spatial distribution. Two irrigations (intensity 20 mm/h) were made with 24 h between them and a third irrigation followed after three weeks. This represents the intensity of a heavy rainfall. Percolate collection was carried out at

30-minute intervals and soil water tension was recorded at 5-minute intervals. Finally the percolate was analysed for herbicides and tracer.

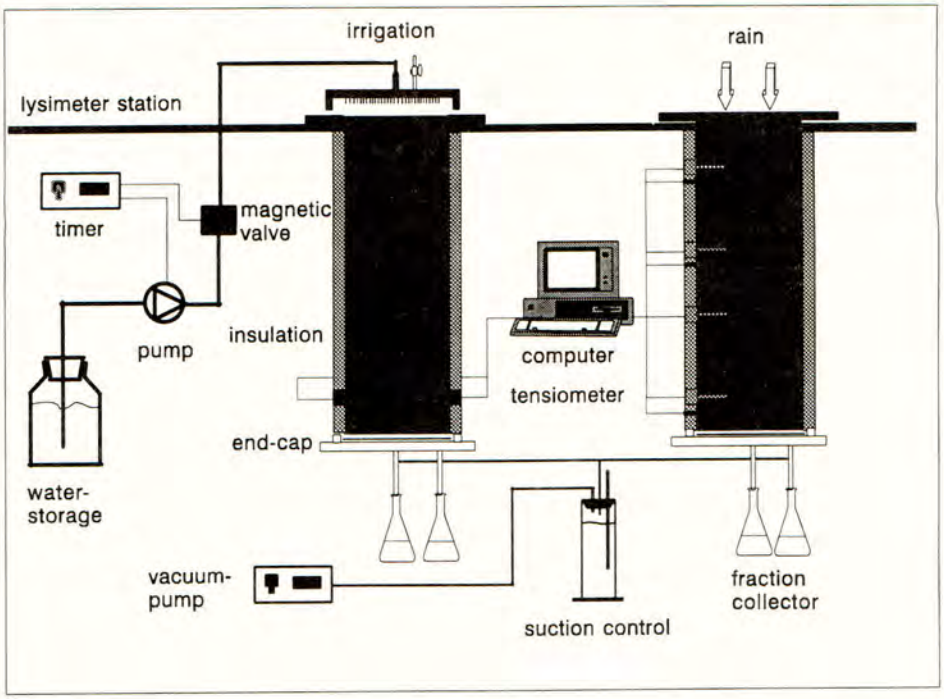

FIGURE 1: Experimental setup for testing leaching behaviour of herbicides in unsaturated, structured soil.

The herbicides were extracted and enriched from 10 ml percolate by using a BAKER-10-Extraction-System (C_{18}-Solid phase extraction, SPE). After elution, herbicides were analysed using high performance liquid chromatography (hplc) with UV-detector. Bromide was analysed by ion exchange chromatography after filtering the water samples (membrane filter, 0.45 µm).

RESULTS AND DISCUSSION

The measured breakthrough curves of water, tracer and herbicides at 1 m soil depth show clear differences between disturbed and undisturbed soil samples. Figure 2 presents data for the undisturbed soil. The breakthrough curves of tracer (bromide) and herbicides (chlorotoluron and isoproturon) are shown in Figures 2A and 2B. The first irrigation did not produce any percolate. After the second irrigation, chlorotoluron, isoproturon and the tracer could be detected in the first effluent (after exchange of 0.02 pore volume water). It may be concluded that some amounts of the herbicide moved through the soil with very little adsorption to the matrix. Despite this, the breakthrough curves show different herbicide concentrations. This can be explained by adsorption to the channel walls, with greater adsorption, giving lower concentrations in the effluent.

The third irrigation after 3 weeks gave relatively stable concentrations of chlorotoluron and increasing concentrations of isoproturon. Bromide could not be detected (detection limit 0.1 mg/l). A possible reason for this observation is the bypassing of bromide-free irrigation water with only slight interaction with the soil solution and the much higher detection limit for bromide in comparison to herbicides.

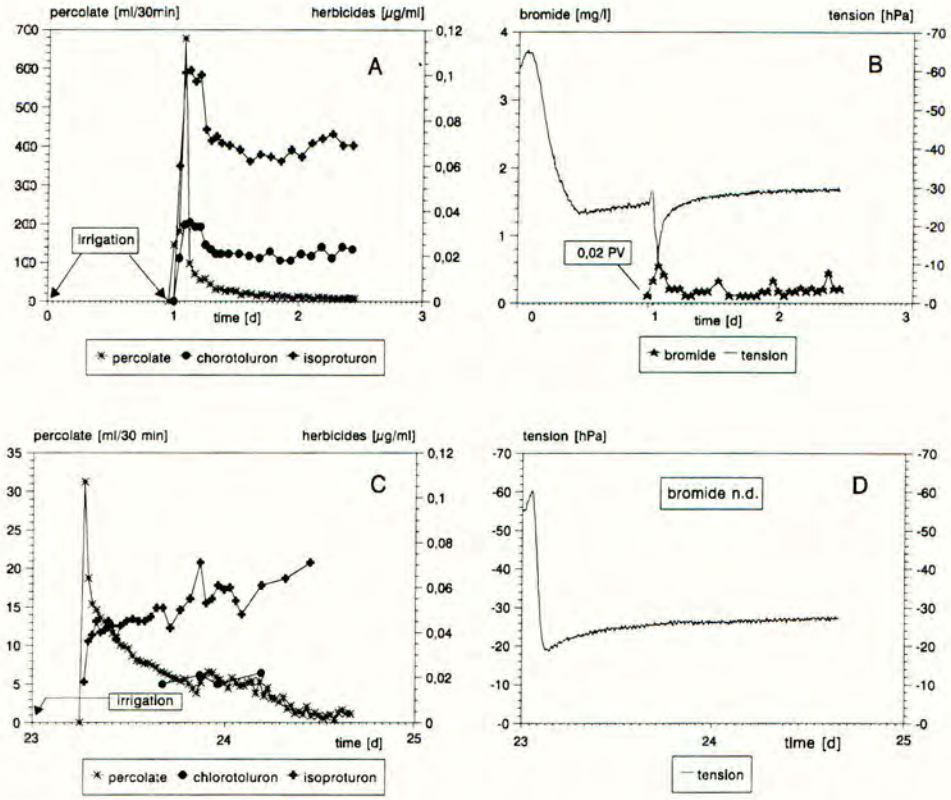

FIGURE 2: Soil water tension, percolate and breakthrough curves of bromide, chlorotoluron and isoproturon. Irrigation 1 and 2 (A, B). Irrigation 3 after 3 weeks (C, D). (n. d. = not detectable, PV = pore volume).

Figures 3A and 3B show water flow, tracer and herbicide behaviour in the homogeneous, repacked soil and an identical irrigation scheme. There was no breakthrough of applied substances and neither herbicides nor tracer were leached out of the soil. The lysimeter showed immediate response to irrigation. The first effluent could be measured 4 hours after the first irrigation started. Because the effluent contained no bromide, it can be assumed that it was displaced soil water. It is to be assumed that water and solutes moved down homogeneously as a wetting front according to a typical 'chromatography' transport. No evidence for preferential flow was observed.

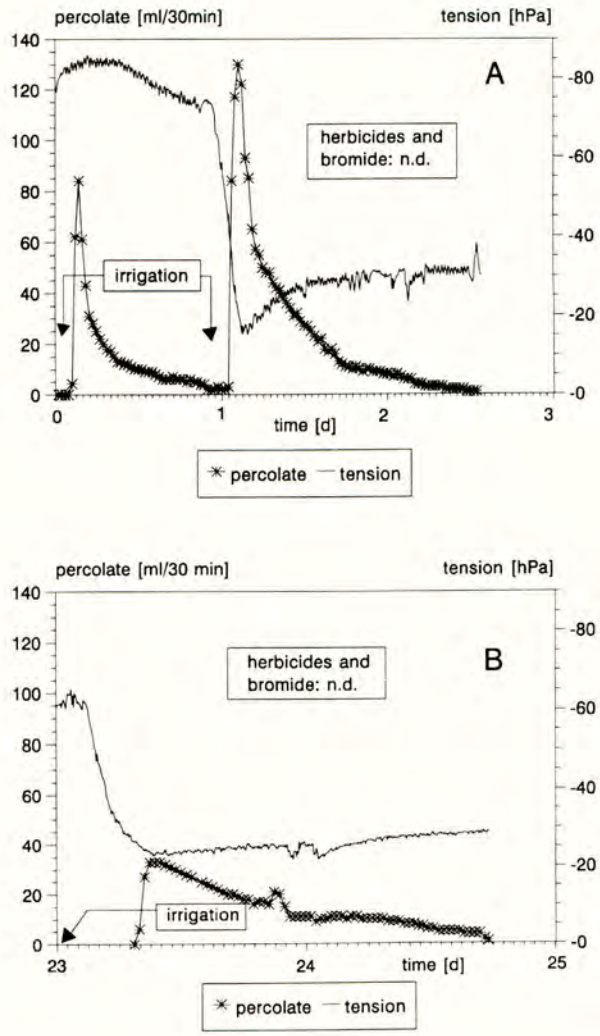

FIGURE 3: Soil water tension and percolate for repacked soil. Irrigations 1 and 2 (A) and irrigation 3 (B). (n. d. = not detectable)

The experiments show that the transport of water, tracer and herbicides is greatly influenced by the pore system of the soil. Macropores may lead to a rapid transport of water and solutes due to decreased filter and buffering capacity of the soil. The consequences of such bypass flow are obvious: contamination of aquifers from the surface may occur much earlier than in the case of convective-dispersive transport. This can be of great importance for the prognosis and assessment of pesticide transport in soils with regard to groundwater contamination.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the Volkswagen Foundation for their financial support of this study.

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THE MOBILITY OF TRICLOPYR UNDER LABORATORY AND FIELD CONDITIONS

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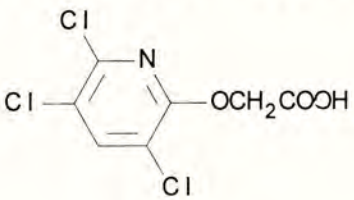
ABSTRACT

Laboratory studies are used to provide data to support the registration of pesticides. Whilst these experiments give some indication as to the environmental fate of a molecule, they do not always predict the results seen under field conditions. For example, the herbicide triclopyr was shown from sorption and column leaching studies to have high leaching potential, which triggered the need for a lysimeter study under field conditions. However, the results from the lysimeter study were contrary to the laboratory work indicating little or no leaching potential. The likely reason for this is that triclopyr degrades more rapidly in the field than in the laboratory, significantly reducing the availability of any residues for leaching. One factor contributing to the increased degradation of triclopyr is sunlight, which promotes ring-cleavage and mineralisation to carbon dioxide.

INTRODUCTION

Laboratory studies provide data to support the registration of pesticides. Whilst these experiments give some indication as to the environmental fate of a molecule, they do not always predict the results seen under field conditions. One example of this is described.

3,5,6-Trichloro-2-pyridinyloxyacetic acid, common name triclopyr (as the butoxyethyl (EB) ester), is the active ingredient of 'Garlon'* herbicides which are active against woody and perennial broad-leaved weeds. They are used in the control of weeds around field margins and farm buildings without harming the existing grass species.



Triclopyr

To support the registration of triclopyr a number of laboratory studies have been carried out to help make an assessment of its likely environmental impact (mobility, persistence). These studies have included sorption, column leaching, soil degradation and photolysis. In addition, field studies and a lysimeter study have been carried out.

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LABORATORY STUDIES

Adsorption/desorption

The sorption characteristics of [^{14}C]-triclopyr EB ester were investigated using one standard (Speyer 2.2 loamy sand) and three agricultural (sandy loam, sandy clay loam and sandy clay) soils (Reeves and Mackie, 1994), according to OECD Guidelines (1981). As part of the preliminary tests, some hydrolysis of the ester occurred to give triclopyr (*ca* 20%), and so [^{14}C]-triclopyr was subsequently used as the test material.

The adsorption test was carried out in the dark using [^{14}C]-triclopyr at a concentration of 4 9 mg/l in aqueous 0.01M $CaCl_2$. This is below its water solubility of 440 mg/l (Worthing and Hance, 1991). The results showed that *ca* 6-16% of applied radioactivity adsorbed to the soils. Of this, *ca* 70-77% was recovered following two desorption steps showing that adsorption was largely reversible. The adsorption Kd and Koc values are shown in Table 1.

TABLE 1. Adsorption Kd and Koc values for triclopyr in four soils

Soil type	% AR adsorbed	Kd (ml/g)	Organic carbon (%)	Koc (ml/g)
Speyer 2.2 (Loamy sand)	11	0.88	2.1	42
Sandy loam	6	0.45	1.1	41
Sandy clay loam	12	1.01	1.7	59
Sandy clay	16	1.32	2.7	49

The results showed that triclopyr had little affinity for any of the soils used. The Kd values calculated would classify triclopyr as a mobile chemical which would be expected to have high leaching potential.

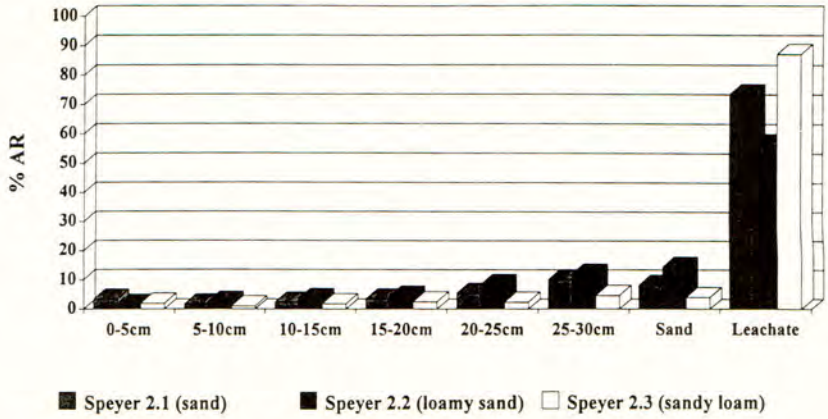
Column leaching studies

Column leaching studies (Reeves and Haq, 1993) were carried out using [^{14}C]-triclopyr EB ester as non-aged and aged pesticide, according to BBA Guidelines (1986) using standard soils. The application rate was equivalent to 1.44 kg a.e./ha, which is the recommended use rate for brush control. The results from the leaching studies would supplement the sorption study, and help to decide whether a lysimeter study was required.

Non-aged leaching

The non-aged leaching study was carried out using columns (30 cm long x 5 cm i.d.) of Speyer 2.1 (sand), 2.2 (loamy sand) and 2.3 (sandy loam) soils, to which [^{14}C]-triclopyr EB ester (as EC formulation) was applied. The columns were leached with 200 mm water equivalent in the dark over a two day period and the leachate collected. The distribution of radioactivity in the soil columns and leachate after non-aged leaching are shown in Figure 1.

FIGURE 1. Distribution of radioactivity after leaching with non-aged triclopyr

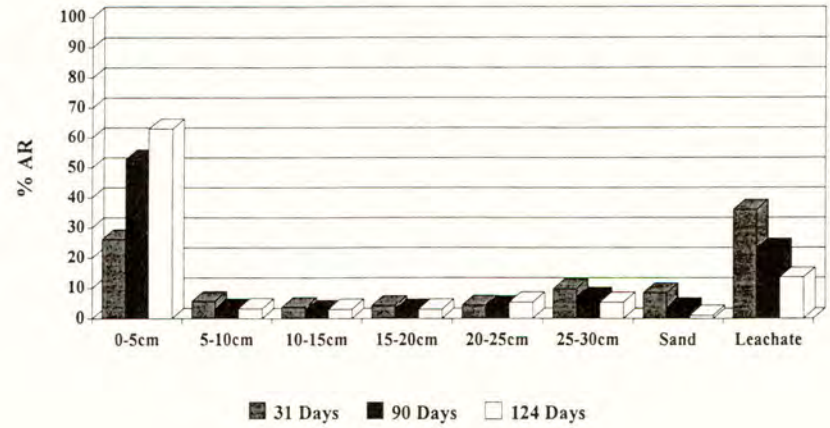


Between 57 and 87% of applied radioactivity was found in the leachate which largely comprised triclopyr, showing that degradation of the ester had occurred during leaching. These results confirmed those from the sorption study, indicating that triclopyr would have high potential to leach. Furthermore, the findings triggered the need for a lysimeter study because, based upon BBA requirements, greater than 5% of the applied radioactivity leached.

Aged leaching

[^{14}C]-Triclopyr EB ester (non-formulated) was applied to Speyer 2.1 soil (sand) at 40% moisture holding capacity and maintained in the dark at 20°C under aerobic conditions. Aged soil at 31, 90 and 124 days was then applied separately to columns of Speyer 2.1 soil and leaching carried out as for the non-aged experiment. The distribution of radioactivity in the soil columns and leachate after aged leaching are presented in Figure 2.

FIGURE 2. Distribution of radioactivity after leaching with aged triclopyr



The aged test gave less radioactivity in the leachate. That from 31-day aged soil (*ca* 36% of applied) consisted of triclopyr (30%) and 3,5,6-trichloro-2-pyridinol (6%). This decreased to *ca* 23% from 90-day aged soil (10% triclopyr, 5% pyridinol, 8% unknown), and further decreased to *ca* 15% from 124-day aged soil (7% triclopyr, 3% pyridinol, 5% unknown).

The results confirmed those from the non-aged experiment, indicating that triclopyr would have high potential to leach, although its mobility was significantly decreased by ageing. This demonstrated the important effect that residence time in soil has upon leaching. The extent to which leaching occurred confirmed that a lysimeter study would be necessary because, based upon BBA requirements, greater than 2% of the applied radioactivity leached. In addition, the 3,5,6-trichloro-2-pyridinol soil metabolite was also shown to have some leaching potential.

Aerobic soil degradation

The aged leaching experiment demonstrated that residence time in soil can affect leaching potential. This is an important consideration for triclopyr because of its relatively short half-life in soil, which ranged from 6-52 days in the laboratory, depending upon soil type. This was determined under standard conditions in an aerobic soil degradation study (Reeves, 1994) carried out to BBA Guidelines (Schinkel *et al*, 1986). The degradation products were principally 3,5,6-trichloro-2-pyridinol and carbon dioxide.

Photolysis

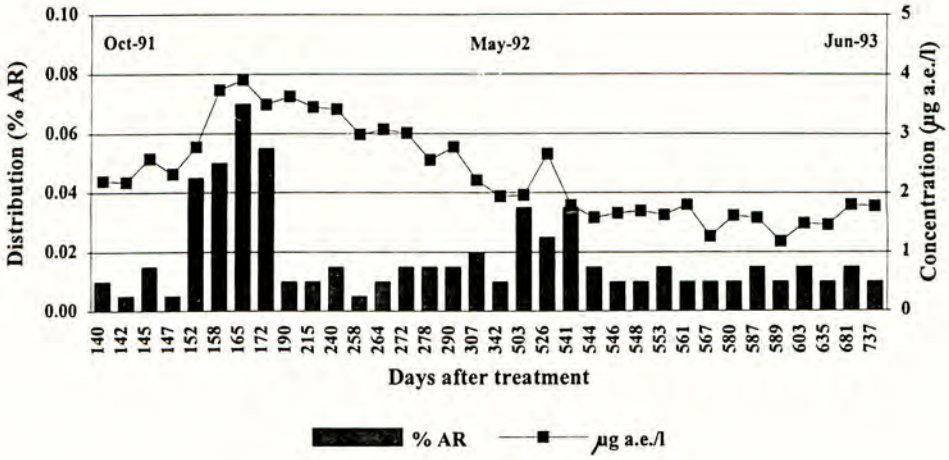
Photolysis under aqueous conditions (Woodburn *et al*, 1990) has been shown to be an important degradation route for triclopyr, where ring-cleavage rapidly occurs to give short-chain organic acids. Examples of these include oxamic, oxalic, pyruvic and maleic acids. Therefore, the likely effect of any exposure of triclopyr residues to sunlight and moist conditions would be to facilitate the degradation in soil. This would reduce its half-life in the environment even further from the values indicated in the aerobic soil degradation study, which like the other laboratory studies are carried out in the dark.

FIELD STUDIES

Lysimeter study

The lysimeter study to BBA Guidelines (Führ *et al*, 1990) was carried out using two lysimeters (0.5 m^2 x 1 m deep) containing sandy soil and sown with rough grass to mimic brush control use (Reeves, 1993). Application was made in June 1991 with [^{14}C]-triclopyr EB ester (as EC formulation) at a rate equivalent to *ca* 2 kg a.e./ha (slightly in excess of the recommended field rate). The lysimeters were then maintained under outdoor conditions, according to normal farming practice, for two years until June 1993. Leachate was collected when available and the results of analysis throughout the two year study are given in Figure 3.

FIGURE 3. Distribution and concentration of radioactivity in lysimeter leachate (mean of two replicates)



The results showed that over the two year period of the study, the total amount of radioactivity found in the leachate was only 1% of that applied, which is very much less than predicted from the laboratory column leaching studies. This radioactivity corresponded to a mean concentration of *ca* 2 µg a.e./l, of which only small amounts (0.07 µg a.e./l each) were attributed to either triclopyr or 3,5,6-trichloro-2-pyridinol. The remainder comprised dissolved carbon dioxide (up to 40%) together with large amounts of polar, acidic material.

Upon study completion, the non-leaching radioactivity was predominantly found on the lysimeter in the top 30 cm of soil (*ca* 85% of applied) with little significant movement seen below this depth. The majority of this radioactivity was non-extractable using acidic aqueous acetonitrile, indicating strong adsorption of any residues to the soil. These results have therefore shown little or no potential for triclopyr to leach under field conditions.

CONCLUSIONS

The results from the lysimeter study have clearly indicated that the use of the herbicide triclopyr for brush control will not pose a contamination threat to groundwater. This is because triclopyr was not detected at concentrations greater than 0.1 µg a.e./l, which is the limit of the EC Drinking Water Directive (1980) for single pesticides. This is also true for the soil metabolite, 3,5,6-trichloro-2-pyridinol. These findings contradict initial results from the laboratory studies (sorption and column leaching), which predicted high leaching potential.

One factor which can affect the mobility of a pesticide is its half-life in soil, with less persistent compounds generally having lower potential for leaching. This is an important consideration for triclopyr because of its relatively short soil half-life in the laboratory of between 6 and 52 days. Any factors present in the field which could accelerate this

degradation would therefore be expected to further reduce leaching potential. One such factor is suggested to be exposure to sunlight. This is because aqueous photolysis is an important degradation route for triclopyr, where ring-cleavage rapidly occurs to give short-chain organic acids. Further mineralisation of these acids in soil to carbon dioxide, and/or subsequent conjugation/binding to soil components could dramatically reduce the leaching potential. The results from the lysimeter study supported this.

In conclusion, experiments carried out using the herbicide triclopyr have shown that laboratory studies should not be relied upon solely to predict the environmental fate of a pesticide, and that they should be considered in conjunction with field studies when making an assessment of the impact of a pesticide upon the environment.

ACKNOWLEDGEMENTS

The author would like to thank Dr. J.A. Mackie of Inveresk Research International Ltd., Tranent, Scotland for carrying out the sorption study, and Dr. D.A. Yon of DowElanco Europe for initial work on the lysimeter study.

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ASSESSMENT OF THE BEHAVIOUR OF THE HERBICIDE BENTAZONE IN SOIL

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ABSTRACT

In the upper soil layer, the herbicidal active ingredient bentazone is quickly degraded, microbially and aerobically, via the intermediary and instable products 6-OH-bentazone, 8-OH-bentazone and AIBA. These are immediately bound to the organic matter fraction. Additionally, a considerable part (24 - 50 %) is mineralized to CO_2. Half-lives in laboratory studies averaged 45 d. Half-lives in field soils ranged from 3 to 21 d with an average of 12 d. The nature of bound (non-extractable) residues of bentazone and/or its degradation products was further investigated and the bioavailability assessed for plants and earthworms. The bound residues were not bioavailable and were thus of low environmental relevance. Besides the metabolic degradation, abiotic degradation processes (e.g. photolysis) also contribute to the disappearance of bentazone in the environment.

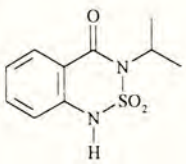
INTRODUCTION

The purpose of this review is to summarize and update research information considering the fate of bentazone in soil covering soil metabolism, soil degradation half-lives under laboratory and field conditions, bioavailability studies of the bound residues for plants and earthworms, and photolysis.

IDENTITY OF THE ACTIVE INGREDIENT

Name (common name):	bentazone
Chemical name (IUPAC):	3-isopropyl-1H-2,1,3-benzo-thiadiazine-4(3H)-one-2,2-dioxide
CAS:	25057-89-0
EC no.:	613-012-00-1

Structural formula:



Bentazone

RELEVANT PHYSICAL-CHEMICAL DATA

Solubility in water:	570 mg/l
K_D value:	from 0.18 - 3.06 cm^3/g
K_{OC} value:	from 13.3 - 175.6 cm^3/g
Mean log P_{OW} value:	- 0.456 at pH 7, 22°C
Vapor pressure:	1.7 x 10^{-6} hPa at 20°C
pKa:	3.3 at 24°C

BEHAVIOUR IN SOIL

The structural formulae of the metabolites are given in Figure 1.

Soil metabolism

The first step in the aerobic, microbially induced degradation of bentazone is a hydroxylation of the active ingredient molecule on the phenyl ring in the 6- or 8-position. As could be shown in cell suspension cultures, several fungal species carry out the hydroxylation of bentazone to 6-OH-bentazone and 8-OH-bentazone. It has not been possible, however, to detect 6-OH-bentazone and 8-OH-bentazone directly in the soil, because both are further metabolized microbially more rapidly than they can be produced from bentazone by hydroxylation. During earlier metabolism studies with "BBA-standard soils"[1], which due to storage had a less than optimal degradation capacity, it was possible to find traces of 2-amino-N-isopropyl-benzamide (anthranilic acid isopropylamide, AIBA). However, when using fresh field soils, i.e. soils microbially at an optimum, this metabolism product was also degraded more rapidly than it was formed from bentazone and was no longer detectable.

Metabolically, the metabolite AIBA is known to be important for the degradation of bentazone such that as degradation continues, the natural substance anthranilic acid evolves. Anthranilic acid is known to be an intermediate stage in microbial intermediary metabolism and therefore has to be considered an ubiquitous natural substance (Lehninger, 1975). For example, it is incorporated catabolically into the citric acid cycle or utilized anabolically in the synthesis of the amino acid, tryptophan.

The primary path of transformation for bentazone lies in the incorporation of the three reactive metabolites, 6-OH-bentazone, 8-OH-bentazone and AIBA (or anthranilic acid), into the organic soil matrix.

The final stage of bentazone degradation in soil then occurs via humification and mineralization.

This incorporation of ^{14}C activity from the active ingredient during the formation of new humus has been shown to result from the action of aerobic microorganisms in the case of bentazone. Under anaerobic (e.g. under N_2) and sterile conditions, the degradation process practically ceased.

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[1] Request of the Federal Biological Research Centre for Agriculture and Forestry, Federal Republic of Germany

Bollag (1991) was able to show that many crop protectants are metabolized to unstable intermediates (phenols and aromatic amines), which frequently are incorporated covalently into the organic soil matrix. Oxido-reductive enzymes and anorganic agents ubiquitously present in the soil play a major role in the process. The phenols and anilines, or for bentazone the 6-OH-bentazone, 8-OH-bentazone and AIBA (or anthranilic acid), occurring as intermediate products in the degradation process give rise to free radicals that readily bind or polymerize onto reactive groups of humins and so themselves become part of the humus structure.

Additions of both OH-metabolites to soil verify this finding: within a few hours they can no longer be extracted from the soil, because they are rapidly integrated biotically and abiotically into the organic soil components.

It has been shown that the humification products possess no biological relevance and that they are not bioavailable, for example, to maize plants (Lee, Führ and Mittelstaedt, 1988) or to earthworms (Ebert, 1992).

The ^{14}C activity incorporated in the humins does not remain there forever as a stable residue. In the medium term, these residue forms are eliminated from the soil at the rates characteristic of CO_2 mineralization for these fractions (humins, humic and fulvic acids).

Studies on the metabolism of bentazone in soil show that only the active ingredient itself should be targetted for environmental analysis, since intermediate stages in the degradation process cannot be detected analytically because of their rapid conversion rates.

The metabolism process is outlined in Figure 1.

Half-lives in laboratory and field soils

Extensive laboratory and field trials have been made concerning the degradation behavior of bentazone in soil.

In the laboratory, at the tested temperature range of 20 - 23°C, the average DT 50 value for bentazone was about 45 d (see Table 1). No significant correlations were found between the measured DT 50 values and the pH values or moisture contents of soil at the tested ranges. As can be seen in the column "Measurement of biomass" in Table 1, the biological activity of the soils was not checked until 1987. A mean DT 50 value of about 41 d is calculated for the soils which have been checked for biomass.

In the field, the mean DT 50 value for an average annual precipitation level of 762 mm was 12 d, on the basis of results from Germany and the USA (see Table 2). A DT 50 value of 14 d was found for an average soil temperature in Germany of about 12.4°C during the months of March to December and for an average precipitation of 543 mm. The corresponding values in the USA were 11 d at 15.7°C and 981 mm. DT 90 values averaged 44 d (ranging from 10 to 69 d).

The difference observed between laboratory and field values maybe explained by the fact that under field conditions degradation takes place under conditions with alternating wetness and dryness of the upper soil instead of at a constant soil moisture level. Contrary to

the prevalent opinion, a partial drying of the upper soil strongly stimulates microbial activity by improving the supply of oxygen all the way to the finest pores and this is also important for bentazone degradation. This stimulation has been shown to lead to an accelerated degradation of Xenobiotics and an increased mineralization level (Ottow, 1990).

Abiotic degradation processes

The film of active ingredient left on the plant or soil surface after application of the product is subject to the abiotic degradation process of photolysis. The UV spectrum of bentazone shows an absorption band above 290 nm with a maximum between 330 and 335 nm. Position and intensity of this maximum ($\varepsilon = 3 \times 10^3$ l/mol cm) are constant in aqueous solution between pH 4 and pH 9. This means that the ultraviolet part of the sunlight reaching the earth's surface is absorbed by bentazone, so that a direct photodegradation is possible under normal conditions in the environment. The measured quantum yield for bentazone degradation in aqueous solution ($\phi = 4 \times 10^{-4}$ mol/Einstein) leads to a calculated degradation half-life of about 1.6 d for exposure in central Europe in the month of May.

Experiments exposing bentazone solutions to light sources similar to sunlight for several days generally confirmed the predicted figures. There was a rapid degradation of the active ingredient, with a half-life of several days. A series of intermediate metabolites and the final mineralization product, CO_2, were found in the studies. It is to be expected that the photosensitizers in natural surface waters strongly accelerate the photolytic degradation of bentazone.

Based on these results, photodegradation can be viewed as a very effective sink for bentazone in the environment.

The preceding information indicates that the active ingredient bentazone applied as a crop protection measure is degraded not only by metabolic processes in the soil and in the plant, but also by photolysis. Hydrolysis evidently plays a subordinate role in the degradation of bentazone in the environment.

FIG. 1 Proposed metabolic pathway of bentazone in soil

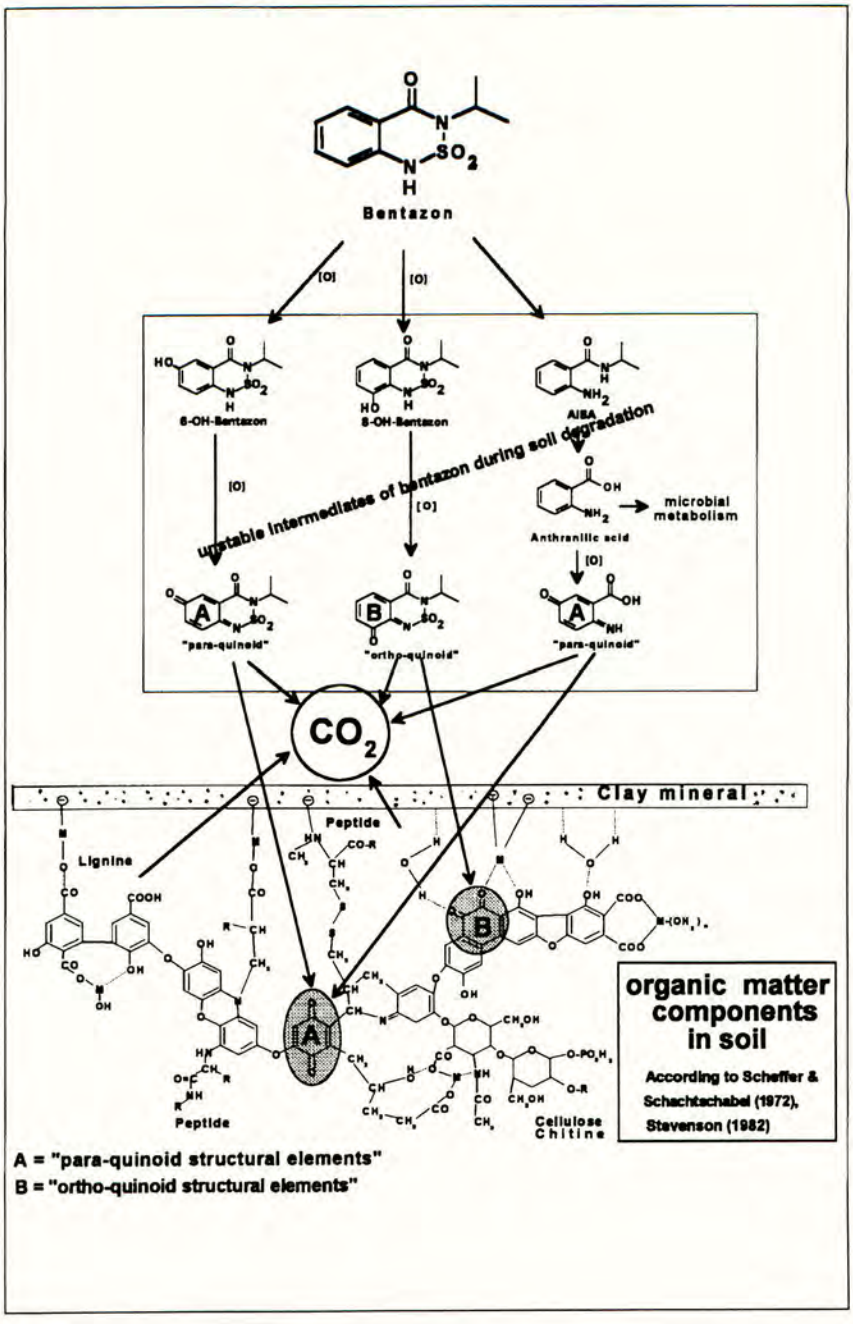

TABLE 1 Half-lives of bentazone in various laboratory soils

Year	Soil type	Biomass checked	Soil origin	pH (KCl)	Temp. ° C	Moisture % MWC	Appl. rate mg/kg	Half-lives (days)
1972	loamy sand	no	Sandhofen	4.6	23	42	2	32
1973	loamy sand	no	Sandhofen	4.6	23	42	3.4	42
1973	loamy sand	no	Sandhofen	4.6	23	42	3	46
1973	loamy sand	no	Sandhofen	4.6	23	42	3	47
1987	loamy sand	yes	US	4.6	23	40	10	45
1972	sandy loam	no	Niedereschbach	5.1	23	72	2	102
1972	loamy sand	no	standard soil 2	5.2	23	40	6	29
1972	loamy sand	no	Sandhofen	5.5	23	42	2	32
1988	loamy sand	yes	Lufa Speyer	5.8	23	40	2	14
1987	sandy loam	yes	US	6.1	20	40	10	65
1972	loamy sand	no	Sandhofen	6.4	23	42	2	42
1972	sandy loam	no	Limburgerhof	6.7	23	54	2	12
1972	sandy loam	no	Limburgerhof	6.7	22	54	5	25
1972	sandy loam	no	Limburgerhof	6.7	22	23	2	34
1972	sandy loam	no	Limburgerhof	6.7	23	36	2	34
1972	sandy loam	no	Limburgerhof	6.7	23	42	2	35
1972	sandy loam	no	Limburgerhof	6.7	23	54	2	42
1972	sandy loam	no	Limburgerhof	6.7	23	36	3	60
1972	sandy loam	no	Limburgerhof	6.7	22	36	3	60
1988	loamy sand	yes	Limburgerhof	6.7	23	40	2	50
1974	loamy sand	no	standard soil 1	6.8	20	40	5	53
1988	sandy loam	yes	Limburgerhof	7.1	23	40	2	78
1988	loam	yes	Ruchheim	7.2	20	40	2	14
1972	silty loam	no	Bruchfeld	7.5	23	72	2	56
1973	silty clay loam	no	Bruchfeld	7.5	23	42	3	70
1973	silty clay loam	no	Bruchfeld	7.5	23	42	3	84
1987	clay	yes	US	7.7	23	31	10	24
							Average of half-lives (days) in laboratory soils:	45
							Average of half-lives (days) in laboratory soils with proven bioactivity:	41

TABLE 2 Soil half-lives of bentazone in field soils in Germany and USA

Year	Field site	Soil type	Climatic data (Mar - Dec) Average Soil Temp., rain	DT50-values (half-lives) days	DT90-values days
1990	FRG Holzen	sandy loam	10.8 ° C 715 mm	11	38
	FRG Stetten a. H.	silty clay	11.8° C 596 mm	21	69
1989	FRG Goch-Nierswalde	sandy loam	14.4° C[1] 413 mm	18	61
	FRG Havixbeck	loamy silt	11.7° C 525 mm	17	56
	FRG Limburger-hof	loamy sand	13.2° C 467 mm	4	43
Germany:	Average half-life (days) of bentazone in field soils:		12.4° C 543 mm	14	53
1987 - 1988	US Hollandale (MN)	loam	10.0° C 879 mm	11	37
	US Geneso (IL)	silt loam	12.8° C 869 mm	19	63
	US Greenville (MS)	silt loam	19.4° C 1062 mm	14	47
1988	US Chico (CF)	silty clay loam	17.3° C 1153 mm[2]	6	20
	US Madera (CF)	sandy loam	18.9° C 944 mm	3	10
USA:	Average half-life (days) of bentazone in field soils:		15.7° C 981 mm	11	35
Grand average: Half-life of bentazone in different countries in field soils:			14.0° C 762 mm	12	44

[1]climatic data collected from May - Nov, only

[2]including irrigation during Mar - Dec

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OUTDOOR LYSIMETER STUDIES ON ^{14}C-BENTAZONE - RESULTS FROM DIFFERENT CLIMATIC SITES

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ABSTRACT

The fate of the ^{14}C-labelled herbicide bentazone (Basagran^{R} - 480 g AI/ha) was investigated in undisturbed sandy soil lysimeters exposed and cultivated under different climatic conditions. The lysimeters (1.2 m depth, 1 m^2 surface area) were taken from agricultural land and installed in outdoor testing facilities at the Fraunhofer-Institute in Schmallenberg and at the BASF AG, Limburgerhof. The formulated product was applied at both study sites post-emergence to cereals (1 kg AI/ha). Despite different climatic conditions and therefore varying amounts of leachate the total radioactivity in the leachate was very similar two years after a single application. A repeat application of ^{14}C-bentazone in the second year led to an expected increase of total radioactivity in leachate. Nevertheless, the annual mean concentration of ^{14}C-bentazone was still below 0.1 μg/l. The relative amounts of total radioactivity in the soil cores two years after the second application were nearly identical (about 49% of the applied radioactivity) and corresponded approximately to the results obtained two years after the single application. No significant displacement of radioactive material into deeper soil layers was observed. 1-2% of the applied radioactive material was incorporated into the crop.

INTRODUCTION

Bentazone is a widely used post-emergence herbicide that provides excellent control of dicotyledonous weeds in e.g. winter and summer cereals and maize (Anonymous, 1990a). It is the only active ingredient in the product, Basagran^{R} (BAS 351 32 H). The application rate for bentazone depends on the weed species to be controlled, but does not exceed 1 kg/ha in Germany. As laboratory column leaching studies showed considerable leaching potential, outdoor lysimeter studies had to be conducted. Lysimeter experiments are designed in particular to simulate actual field conditions regarding climate, cultivation and vegetation of the soil (Kubiak *et al.*, 1988; Bergström, 1990; Kördel *et al.*, 1991a; Hance & Führ, 1992). The objective of this project was to elucidate the leaching potential of ^{14}C-bentazone after single and repeated application on undisturbed lysimeters maintained under different natural climatic conditions. The experiments were performed according to the German guideline for outdoor lysimeter studies (Anonymous, 1990b; Schinkel, 1991).

LYSIMETER EXPERIMENTS

Undisturbed, sandy soil lysimeters (1.2 m depth, 1 m^2 surface area) were taken from agricultural land near Hannover (soil type A) and Speyer (soil type B). The lysimeters were embedded in the grounds of the outdoor testing area of the Fraunhofer-Institute (FhG) in Schmallenberg (soil type A) and about 300 km south of this at the BASF AG, Limburgerhof (soil types A & B). The collection procedure for lysimeters and the

experimental equipment are described in detail by Traub-Eberhard *et al.* (1992) and Spiekermann (1994). The soil characteristics corresponded to the requirements of the German Federal Biological Research Centre for Agriculture and Forestry ($\geq$ 70% sand, $\leq$ 10% clay, $\leq$ 1.5% OC; Anonymous, 1990b). Characteristic soil data are given in Table 1. Cultivation of the lysimeter soils and application of the active ingredient were performed according to agricultural practice. ^{14}C-labelled bentazone (spec. radioactivity 1.62 MBq/mg) was applied as formulated product BAS 351 32 H post-emergence to cereals (1 kg AI/ha). Leachate was collected regularly and analysed immediately. The lysimeter soils were sectioned into horizontal 10 cm layers (Traub-Eberhard *et al.*, 1992; Steinhanses & Kördel, 1993) two years after single or repeated application. Experimental details of the lysimeter studies are given in Table 2.

TABLE 1. Characteristic data for the lysimeter soils. Origin of soil type A: Borstel, Neustadt am Rübenberge, Lower Saxony, Germany; origin of soil type B: Schifferstadt, Rhineland-Palatinate, Germany.

	Soil type A, depth (cm)				Soil type B, depth (cm)			
	0-30	30-50	50-80	80-120	0-35	35-60	60-80	80-100
Sand (%)	73.8	81.2	89.8	98.2	75.8	76.3	87.5	90.1
Silt (%)	23.3	14.2	7.1	1.0	16.6	14.1	5.3	6.3
Clay (%)	2.9	4.6	3.1	1.0	7.7	9.7	7.3	3.6
OC (%)	1.5	1.3	0.3	0.2	0.9	0.4	0.1	0.2
pH	6.2	6.3	5.9	5.5	5.7	6.3	6.5	6.8

TABLE 2. Experimental details of outdoor lysimeter studies on ^{14}C-bentazone.

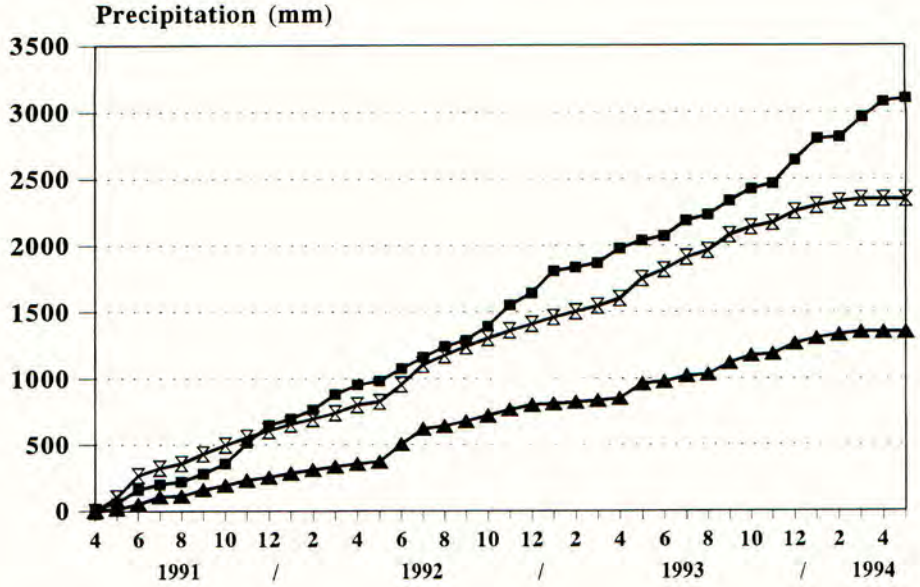
Study site:	FhG, Schmallenberg		BASF, Limburgerhof	
Lysimeter no.[a]:	S-A(I)	S-A(II)	L-A(I)	L-B(II)
Soil type:	A	A	A	B
Application rate:	1 kg AI/ha	1 kg AI/ha	1 kg AI/ha	1 kg AI/ha
Time of application:	18/04/91	18/04/91 05/05/92	22/04/91	22/04/91 17/03/92
Cultivation:	winter wheat winter barley winter rye	winter wheat winter barley winter rye winter rape	summer wheat winter barley winter rye	winter wheat winter barley winter rye winter rape
Sectioning of lysimeters:	21/04/93	11/05/94	13/05/93	17/05/94

[a] S: Schmallenberg, L: Limburgerhof; A, B: soil type; I, II: single or repeated application

Due to low natural precipitation at Limburgerhof compared to Schmallenberg, additional irrigation of the lysimeters was carried out at this site to meet the required annual total of 800 mm rainfall (Anonymous, 1990b). The amount of precipitation during

the three-year experimental period is given in Figure 1. The annual mean air and soil temperatures of both sites differed by about 1-3°C and 2°C respectively.

FIGURE 1. Cumulative amount of precipitation at study sites Schmallenberg (-■-, natural rainfall) and Limburgerhof (-▲-, natural rainfall; -⧖-, natural rainfall plus additional irrigation).



RESULTS AND DISCUSSION

Leachate

There was significantly higher evapotranspiration and lower amounts of leachate in Limburgerhof (Figures 2 & 4) because of increased air temperatures during the summer period and less natural rainfall compared to the Schmallenberg site.

In spite of the different climatic conditions and the varying water budget of the lysimeters, the total amounts of radioactive material in leachate were very similar. Two years after the single application, 3.0 and 2.4% of the applied radioactivity occured in the leachate of lysimeter S-A(I) and L-A(I) (Figure 3), respectively. At both study sites the annual mean concentration of ^{14}C-bentazone was below the threshold value of 0.1 μg/l.

Repeat application of ^{14}C-bentazone resulted in the expected increase of total radioactivity in the leachate of lysimeter S-A(II) and L-B(II) (Figure 5). Comparing soil types A and B, the appearance of radioactive material in leachate varied over the course of the study, but the total amounts of radioactivity were nearly identical. About 2.6% of the applied radioactivity was detected in the leachate at both study sites during the three-year testing period. The annual mean concentration of ^{14}C-bentazone in the leachate was still below 0.1 μg/l.

Preferential flow processes such as side-wall flow or macropore flow, mainly described for loamy soils (Bergström, 1990, 1992; Kördel *et al.*, 1992), did not occur in the lysimeters at either study site.

FIGURE 2. Cumulative amount of leachate during the two-year experimental period. Lysimeter S-A(I): soil type A, study site Schmallenberg (-■-); lysimeter L-A(I): soil type A, study site Limburgerhof (-⧖-).

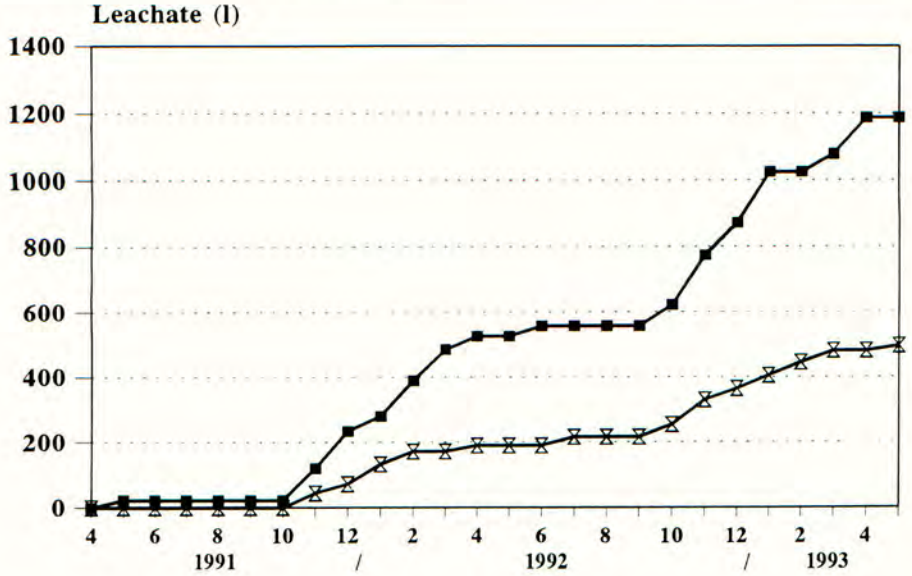


FIGURE 3. Cumulative amount of total radioactivity in leachate after a single application of ^{14}C-bentazone in spring 1991. Lysimeter S-A(I): soil type A, study site Schmallenberg (-■-); lysimeter L-A(I): soil type A, study site Limburgerhof (-⧖-).

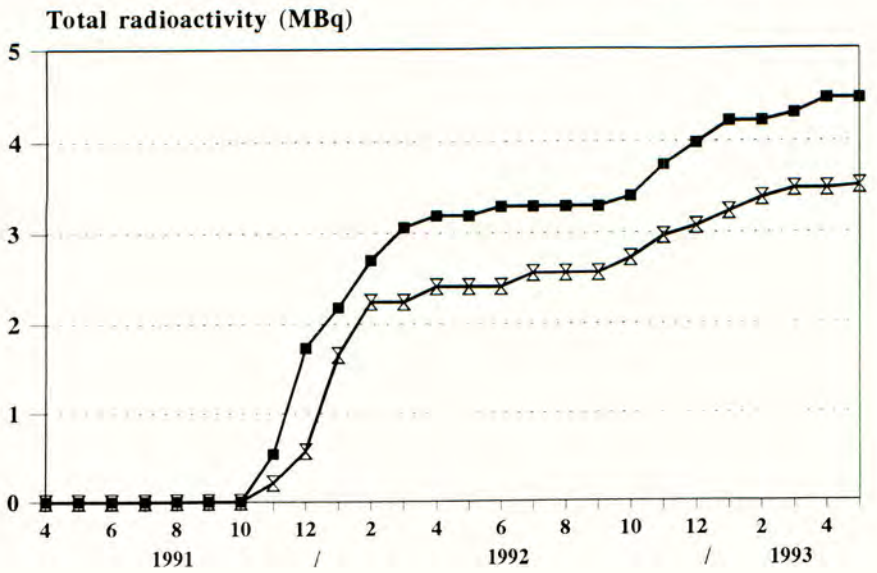


FIGURE 4. Cumulative amount of leachate during the three-year experimental period. Lysimeter S-A(II): soil type A, study site Schmallenberg (-■-); lysimeter L-B(II): soil type B, study site Limburgerhof (-⧖-).

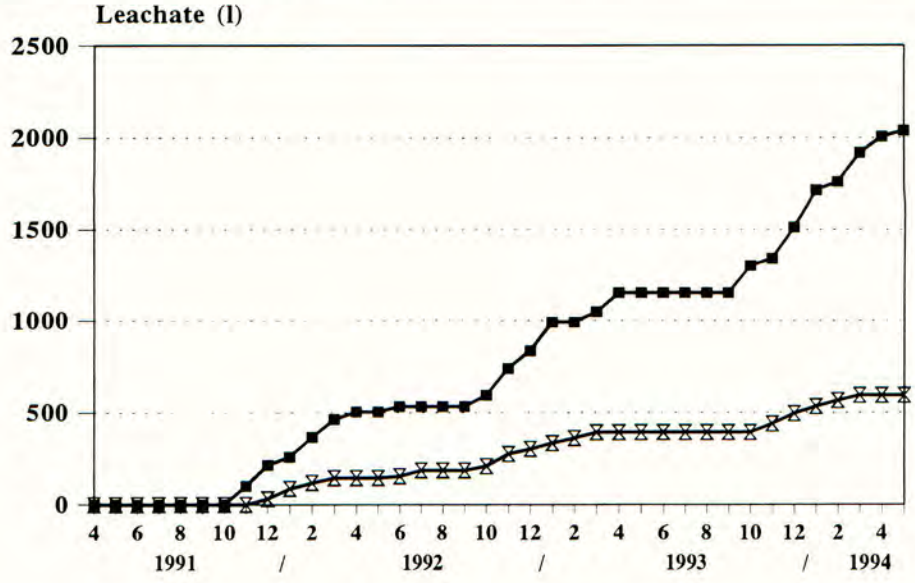
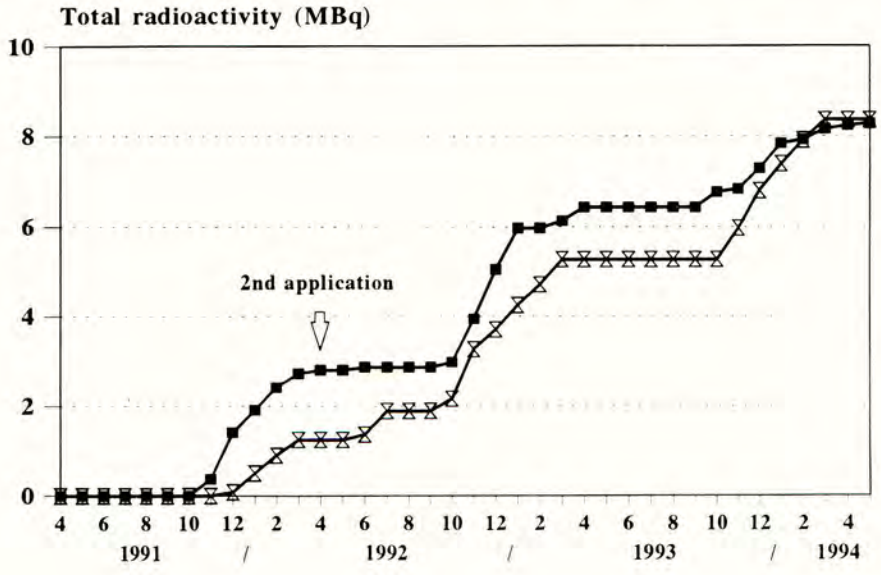


FIGURE 5. Cumulative amount of total radioactivity in leachate after the first and second application of ^{14}C-bentazone in spring 1991 and 1992. Lysimeter S-A(II): soil type A, study site Schmallenberg (-■-); lysimeter L-B(II): soil type B, study site Limburgerhof (-⧖-).



Soil

Two years after the single application, 58.9 and 48.1% of the applied radioactivity was still present in the soil from lysimeters S-A(I) and L-A(I) (Table 3). About 49% of the initial radioactivity was detected in lysimeters S-A(II) and L-B(II) two years after the second application. Most of the radioactivity was found in the topsoil.

TABLE 3. Total radioactivity in the lysimeter soils A and B two years after single (I) and repeated (II) application; n.d. = not detectable.

Soil depth	Lysimeter S-A(I)	Lysimeter L-A(I)	Lysimeter S-A(II)	Lysimeter L-B(II)
(cm)	(% of applied radioactivity)			
0-10	37.2	23.7	28.0	41.0
10-20	11.1	15.0	12.6	5.5
20-30	5.5	5.6	3.5	0.9
30-40	1.7	1.4	1.2	0.3
40-50	1.0	1.3	1.0	0.2
50-60	0.9	0.5	0.7	0.2
60-70	0.7	0.4	0.5	0.1
70-80	0.2	0.2	0.3	0.1
80-90	0.2	n.d.	0.3	0.2
90-100	0.2	n.d.	0.2	0.1
100-110	0.2	n.d.	0.2	0.1
110-120	n.d.	n.d.	n.d.	n.d.
Total	58.9	48.1	48.5	48.7

TABLE 4. ^{14}C-bentazone in the lysimeter soils A and B two years after single (I) and repeated (II) application; n.d. = not detectable.

Soil depth	Lysimeter S-A(I)	Lysimeter L-A(I)	Lysimeter S-A(II)	Lysimeter L-B(II)
(cm)	(% of applied radioactivity)			
0-10	0.20	0.06	0.08	0.15
10-20	n.d.	0.03	0.04	0.02
20-30	n.d.	n.d.	0.01	n.d.
30-40	n.d.	n.d.	< 0.01	n.d.
40-50	n.d.	n.d.	< 0.01	n.d.
50-60	n.d.	n.d.	n.d.	n.d.
60-70				
70-80				
80-90				
90-100				
100-110				
110-120	n.d.	n.d.	n.d.	n.d.
Total	0.20	0.09	0.15	0.17

Detailed investigations of the soil profiles revealed that only negligible amounts of ^{14}C-bentazone remained in the soil ($\leq$ 0.2%), mainly in the upper soil layers (Table 4). The major part of the radioactive material was incorporated into organic matter as bound residues.

Crop

The grain yields of the harvested cereals at both study sites were comparable and within the scope of agricultural practice; less than 0.1% of the applied radioactivity remained in the grain fractions (Table 5). 1-2% of the applied radioactivity was detected in the stalks.

TABLE 5. Grain yields and total radioactive material in the grain fractions after harvest.

Crop	Lysimeter S-A(I)		Lysimeter L-A(I)		Lysimeter S-A(II)		Lysimeter L-B(II)	
	(dt/ha)	(%)[a]	(dt/ha)	(%)[a]	(dt/ha)	(%)[a]	(dt/ha)	(%)[a]
Wheat[b]	50	0.02	34	0.02	62	0.03	46	0.03
Winter barley	81	0.02	67	< 0.01	69	0.02	54	0.01
Winter rye	-	-	-	-	21	< 0.01	28	< 0.01

[a] % of applied radioactivity
[b] Lysimeter L-A(I): summer wheat; lysimeters S-A(I), S-A(II) and L-B(II): winter wheat

CONCLUSION

The results for both study sites were in good agreement despite different climatic conditions and they clearly demonstrate the suitability of outdoor lysimeter studies to assess the mobility, degradation and distribution of radiolabelled substances in cultivated soils. A potential contamination of deeper soil layers and/or groundwater by bentazone at an application rate of 1 kg/ha, which was predicted by standardized laboratory experiments, can be discounted, even after repeat application on soils of various origin. These results confirm previous lysimeter studies on ^{14}C-bentazone which were conducted under another experimental set-up, i.e. different application rates, cultivation and soil type (Kördel *et al.*, 1991b).

ACKNOWLEDGEMENT

The authors gratefully acknowledge Ch. Deimel, S. Hobbold, Ch. Lehmann, N. Roth, C. Schäfer and Ch. Than for their excellent technical assistance.

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EVALUATION OF HERBICIDE MOBILITY IN SOIL USING FIELD LYSIMETERS IN THE MEDITERRANEAN AREA

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ABSTRACT

A lysimeter experiment is in progress in Italy for a period of 4 years. The aim is to evaluate herbicide mobility in the soil profile (1 meter) and the leaching to the groundwater in Mediterranean pedoclimatic conditions. The results in this first year show the different behaviour of the herbicide metolachlor, linuron, fenoxaprop and diflufenican. Leaching is more evident for metolachlor than linuron. Diflufenican and fenoxaprop, including its main metabolites, were not detected in water leachate. There is evidence that in preferential flow herbicide residues may easily move to the bottom of the lysimeter mainly when they are persistent and applied in higher labelled doses. A protocol of use of the lysimeter in these conditions must be performed.

INTRODUCTION

Many scientists confirm the importance of lysimeter studies to evaluate pesticide mobility in soil (Bergström, 1990; Hance&Führ, 1991). This is recently increased because for environmental hazard assessment must be suitable tools better representing reality. The EC Directive 91/414 considers the use of lysimeters essential for water risk assessment when active ingredients are persistent and mobile.

In Italy and in the Mediterranean area, few lysimeter studies on pesticides have been carried out, some only in the recent past (Marucchini *et al.*, 1992; Businelli *et al.*, 1993) and using containers of soil exposed to external natural conditions.

In 1993 a 4-year lysimeter experiment was set up to evaluate the risk of groundwater contamination by many herbicides used in the Mediterranean area. Expected informations include the development of a lysimeter protocol useful for these conditions and the evaluation of models predicting mobility in soil.

MATERIALS AND METHODS

Tor Mancina lysimeter station (42.03°; 12.36'; 50 m - Roma) has been described in previous papers (Tombesi *et al.*, 1989; Capri *et al.*, 1994). Lysimeters are concrete cylinder 1.5 m depth and 1.6 meter in diameter; they were groved in to the soil and filled with sieved soil in 1987. Soil is loam (pH 7.7, organic matter 2.0 %). Water percolating to the bottom of the lysimeters is weekly collected. Sediment is separated from water sample through filtration and analyzed separately. Water sample are extracted with Empore Disk® and the herbicides analyzed by HPLC-UV, GLC-ECD and GLC-MS.

The whole study is planned for four years using different crops in a rotation soyabean, wheat, maize, broad bean, soyabean, wheat. Different herbicides are applied at different growth stages of the crop. Some of those are reported in Table 1. Treatments are set out using doses

reported on the label and all crop management has been done using good agriculture practices of the region. Crop management inside the lysimeter is the same in the surronding field (6000 mq).

Table 1 - Residues analysed in the leachate.

Formulation	Herbicide	Dose (g/ha)	Application
Dualin SP®	metolachlor (40 %)	1231	27/05/93
	linuron (10 %)	308	
WHIP®	fenoxaprop-ethyl (12.5 %)	300	8/07/93
QUARTZ®	diflufenican (4.6%)	200	14/02/94
BrNa	Br^-	100000	27/05/93

RESULTS

In this paper results from the first year (27 May 1993 to 3 June 1994) for analysis of metolachlor, linuron, fenoxaprop-ethyl and diflufenican residues are reported (Table 2).

Leaching

Lysimeters began to discharge water on the 8th July. 380 mm of the 417 mm (total) discharged from the lysimeter were concentrated in December and in January. In the first four months from the metolachlor and linuron application only 1.4 mm was collected and analysed while 22 mm of percolation characterized the lysimeter after diflufenican application. Total rainfall from 27 May 1993 to 3 June 1994 was 764 mm; irrigation about 278 mm (Fig. 1).

Herbicide behaviour showed in the first year of the experiment was different for the different compounds. Linuron was measured in the collected water sample 41 and 83 days after treatment but not in the following sampling. Metolachlor has been measured for a large number of samples than linuron. Total fenoxaprop as ester, acid and main metabolite was never detected. The same also for diflufenican (Table II).

On the basis of the minimum environmental properties of these substances we can say that these results are as aspected.

Metolachlor is much more mobile than linuron because of its low Koc (Koc=200 ml/g) and high solubility (530 mg/l). These also confirm results obtained by Businelli *et al.* (1993). Metolachlor is weakly adsorbed in soil and being very soluble in water it may be tranported towards the deeper soil layers. This herbicide is also of low persistence in Italian conditions (Capri *et al.*, 1993). This characteristic associated with the increasing water percolating during the days after the first sampling, causes its disappeareance 130 days after application (Table II).

Linuron was measured only in the first sampling after application . This behaviour is anomalous because we expect a very low mobility when observing its Koc which is high (400 ml/g and its solubility which is low (75 mg/l). Its behaviour was variable between the different lysimeters.

Fenoxaprop as ester is quickly hydrolized to acid form: the former has a half-life of 1-2 days while the latter 2-17 days and a Koc=0.143 m3/kg (Hoechst, 1994). These properties give a low probability that residues will reach deeper soil layers. In this experiment no residues were detected.

Diflufenican is a herbicide with low solubility (<0.05 mg/l) and high persistence (DT50=11-20 months) (Stork *et al.*, 1994). No residues were detected in the four months monitored (from Febrary to June)(Table 2).

Table 2 - Results obtained in the lysimeter study (27 May 1993 to 30 June 1994).

	lysimeter			
	L 11	L 12	L 13	L 14
Total water discharged (mm)		413.9	416.8	416.7
Average concentration in the leachate ($\mu g\ l^{-1}$)				
metolachlor	0.03	0.03	0.02	0.02
linuron	ND	ND	ND	ND
fenoxaprop *	ND	ND	ND	ND
diflufenican	ND	ND	ND	ND
Highest concentration ($\mu g\ l^{-1}$)				
metolachlor	22.9	2.1	0.2	0.2
linuron	ND	< 0.1	ND	<0.1
fenoxaprop *	ND	ND	ND	ND
diflufenican	ND	ND	ND	ND
Time to reach the highest concentration (days)				
metolachlor	122	133	133	133
linuron	ND	41	ND	83
fenoxaprop *	ND	ND	ND	ND
diflufenican	ND	ND	ND	ND
Time to reach the bottom of lysimeter (days)				
metolachlor	111	122	63	133
linuron	ND	41	ND	83
fenoxaprop *	ND	ND	ND	ND
diflufenican	ND	ND	ND	ND
Br^-	129	129	122	129
Range of time when water samples were contaminated (days)				
metolachlor	111÷133	122÷133	63÷133	133
linuron	ND	ND	ND	ND
fenoxaprop *	ND	ND	ND	ND
diflufenican	ND	ND	ND	ND
Total residues in water (μg)				
metolachlor	12074.5	12073.6	7881.0	10407.9
linuron	ND	23	ND	13
fenoxaprop *	ND	ND	ND	ND
diflufenican	ND	ND	ND	ND
Recovery (%)				
metolachlor	6.13	6.13	4.00	5.28
linuron	ND	0.48	ND	0.27
fenoxaprop *	ND	ND	ND	ND
diflufenican	ND	ND	ND	ND

* total; ND less than quantification limit always <0.1 µg/l.

Preferential flows

Preferential flow may occur during the experiment, increasing the mobility of the herbicide. This phenomenon is evident during the season characterized by heavy rains after a dry period. In Figure 1 these occur mainly in spring. In this period collected water was rich in sediment. Preferential flows is also suggested because linuron, metolachlor and bromide do not reflect a chromatographic trend in leaching. This is shown in the breakthrough curve reported in Figure 2.

In the spring, during seed bed preparation, some cracks on the soil surface and deeper in the profile were already visible inside and outside the lysimeters. These cracks were produced by the dry climate which came before. During the summer the cracks were not evident because of irrigation applied to the crop. Cracks developed in winter caused by dry climate.

We may exclude formation of preferential flow patways during packing of the lysimeters because soil was sieved and left undisturbed for 6 years. There is no edge effect as demonstred in trials carried out before the experiment (Capri *et al.*, 1994).

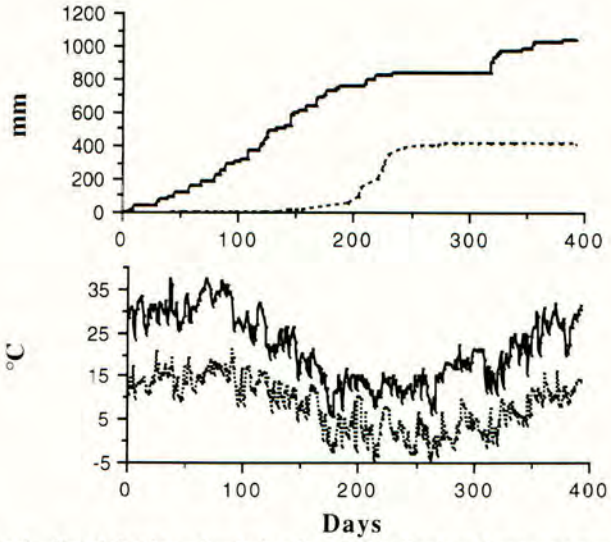

Figure 1 - Precipitation plus irrigation (thick line) and average water discharged (dotted line) from lysimeters in the top picture; temperatures in the picture below. The days are from 27/05/93 to 3/06/94.

DISCUSSION

Defining how we would evaluate the risk for the groundwater using the lysimeters.

The EC Directive defines contaminated drinking water as that containing pesticide residues greater than 0.1 µg/l. The herbicides investigated show residues less than this limit so they pose no risk for the groundwater. The results with metolachlor however indicate that the average concentration in a year is less than 0,1 µg/l although in the sampling period between 100 to 130 days it is higher than the limit (Table 2). Which value must be used ?

Defining what is the *worst case*

Usually it is a soil poor in organic matter and rich in sand. The effect of the low organic matter is universally known for its effect immobilizing lipophilic herbicide; sand increases mobility. The gap is that no attention is paid on the effect of the preferential flow. In agreement with Jarvis (1994) we believe that there are many situations in agricultural condition of South Europe where vulnerability of the groundwater is caused by preferential flow. This agrees with contamination of groundwater as produced by irregular leaching. In this situation also much adsorbed contaminant could pose a high risk of contamination.

Defining the type of lysimeter: monolithic or repacked.

Considering the occurrence of cracks this choice is difficult and may depend on the effects and importance of the cracks. Dry climates can produce cracks quite indipendently from the structure and the texture of soil (White, 1985). So a loam soil in our climate produces cracks for a large part of the year resulting in loam to clay soils posing a high risk of contamination independently of wheather it is a monolithic lysimeter or packed one.

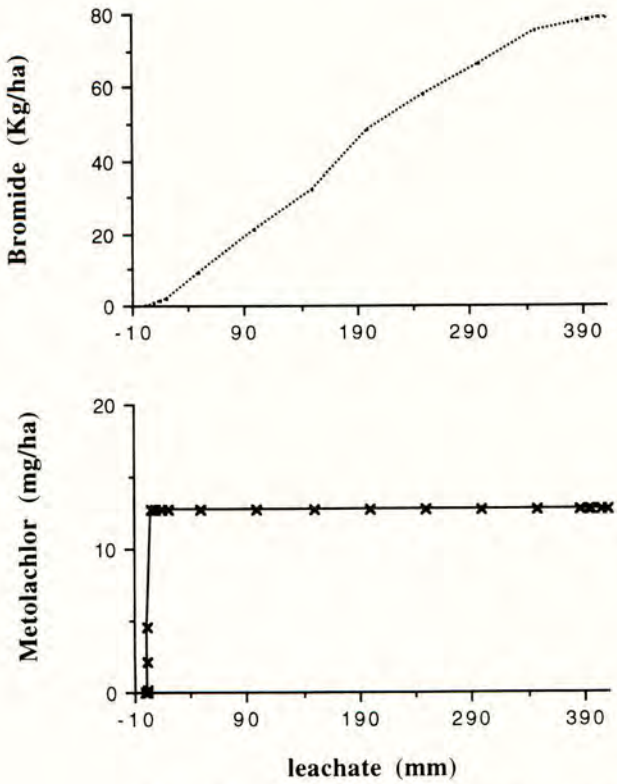

Figure 2 - Metolachlor and bromide breakthrough curves.

Defining the peculiarity for a Mediterranean lysimeter protocol

There is no protocol and no standard in Europe for using lysimeters. Usually the lysimeter protocol edited by BBA(1990) is followed as it is the only one published in Europe. As we can see in the results reported here the meagre rain and its unusual distribution through the year may make our protocol different from those used in Central and Northern Europe. For instance the collection of monolithic lysimeters is difficult because of the dry season, and the time period of the experiments may be different because for a long periods these may be no discharge of water from the bottom.

These observations need a fast answer in order to implement the European Directive. The feeling is that more detailed studies are required before some of these questions can be answered.

ACKNOWLEDGEMENTS

This work was in little part supported by Research National Council, contract number. 94.01003CT06.

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STUDY OF ATRAZINE AND TERBUTHYLAZINE MOVEMENT IN SOIL WATER BY THE MEANS OF THE SUCTION CUP METHOD

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ABSTRACT

Soil water sampled with suction cups and analyzed with enzyme immunoassay contained residues of atrazine at concentrations >0.1 μg/l, even though the last applications were made 2-4 years previously. The longer the periods between application and sampling, the higher were the concentrations due to slow transport with gradually percolating water. Higher concentrations of atrazine during summer (peaks in June/July up to 0.8 μg/l) could be caused by bound residues released by mineralisation of organic matter or concentration effects with decreasing soil water content. Concentrations of terbuthylazine and bromide, which served as a tracer for water movement, increased immediately after application, with maxima (0.35 μg/l and 6.0 mg/l, respectively) seven weeks after spraying. This indicates the existence of macropores and the importance of preferential flow for the rapid transport of herbicides in soil water to depth, bypassing sorption and degradation in upper soil layers.

INTRODUCTION

Leaching of pesticides into groundwater may contaminate drinking water resources. For reasons of public health, several governments have set limits for tolerable concentrations and banned some substances, such as atrazine, from use. To investigate the leaching mechanisms and to gain data for simulation models, it is not sufficient to carry out laboratory experiments with soil columns. Rather, actual leaching must be measured in the field over long periods under natural conditions. The first question which arises is how to obtain representative soil water samples at high spatial and temporal resolutions in a cheap and easy to handle manner. The second question is how to cope rapidly with the analysis of a large number of small volume samples. Our experiences and results with ceramic suction cups and enzyme immunoassay studying the movement of the widely used, but now banned in Germany, maize herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and its substitute terbuthylazine (2-chloro-4-ethylamino-6-butylamino-1,3,5-triazine) may widen the knowledge about the practicability of these methods and the leaching behaviour of these substances.

MATERIALS AND METHODS

Experimental site and treatments

Since 1986, the Bavarian State Institute of Soil Cultivation and Plant Production has conducted a field trial at its agricultural experimental station in Puch near Fürstenfeldbruck (Southern Bavaria) to investigate nitrate leaching from arable land and grassland under dif-

ferent nitrogen-fertilization schemes using the suction cup method. Further investigations concerning the occurrence of atrazine and terbuthylazine residues in soil water after various application frequencies have been initiated on arable plots in 1991 and 1993, respectively. Bromide, which served as a tracer for water movement, was additionally broadcast in 1989 as granular potassium bromide, sprayed in 1993 on the same day as terbuthylazine and sprayed again in 1994 (each time 400 l/ha KBr solution). Different treatments for atrazine are shown in Table 1, and in Table 2 for terbuthylazine and bromide.

TABLE 1. Atrazine treatments (kg AI/ha)

Treatment	Application dates			Suction cups per depth
	11.06.87	27.05.88	02.06.89	
A1	1.0	-	1.0	8
A2	-	1.0	-	8
A3	-	-	1.0	16
A4	-	-	-	16

TABLE 2. Terbuthylazine (kg AI/ha) and bromide (kg/ha) treatments

Treatment	Substance	Application dates				Suction cups per depth
		22.11.89	22.05.90	02.06.93	27.04.94	
TB1	bromide	150	-	-	71	24
	terbuthylazine	-	1.7	-	-	
TB2	bromide	150	-	84	71	24
	terbuthylazine	-	1.7	1.0	-	

The soil type at the site is a Luvisol derived from loess loam over Riss moraine (at 10-14 cm: 23% clay, 67% silt, pH 6.5, 1.09% organic carbon). The mean annual precipitation is 922 mm and the average temperature is 8.0°C.

Soil water sampling and analyses

On the 0.5 ha site, 160 "model Czeratzki (1971)"-ceramic suction cups (20 cm in length, 4 cm in diameter, 0.8 μm mean pore size, manufactured by Laboratoriumsbedarf W.O. Schmidt, Braunschweig) were installed vertically to 60 and 130 cm depth (upper edge) under 8 grassland and 25 arable plots (5 x 5 m) with four and two replicates per depth, respectively. They were connected to glass bottles (located in 1 m deep pits between the plots) with PVC plastic tubes running 40 cm underground to allow regular farming practice. To obtain soil water, a vacuum of 0.5 bar was applied for several hours a number of times a day according to soil moisture content (generally two hours, four times a day). Water samples were collected every two weeks (weekly soon after application) and stored until analysis at 5°C in glass test tubes. The samples were analyzed without further preparation (Riess, 1993).

A sensitive enzyme immunoassay (EIA) has been used for the determination of atrazine on microtiter plates with a detection limit of 0.03 μg/l. The method is based on polyclonal antibodies from sheep. Substantial cross-reactivities were only detected for propazine (116%), which is not used in most European countries, and deethylatrazine (13%). Analysis of water samples with EIA and GC/MS showed good correspondence with a coefficient of determination of $r^2=0.96$. The measuring range of the EIA covered 0.03 to 3 μg/l with

the centre of the test (50% B/B_0) at 0.25 µg/l (Wüst and Hock, 1992; Schewes *et al.*, 1994). Instrumentation and procedure of the EIA are described by Schewes (1993). A monoclonal antibody-based immunoassay made it possible to determine terbuthylazine in the range from 0.05 to 1 µg/l with a 50% B/B_0 value of the test at 0.2 µg/l. Details of the EIA are described by Giersch *et al.* (1993). The assays were run in duplicate. Bromide in soil water samples was analyzed with a Br^- ion-specific electrode (ORION Modell 94-35 SC). An ionic strength adjuster, 5 M $NaNO_3$, was added to the samples at a rate of 2% to reduce ionic interferences (Abdalla *et al.*, 1975; Onken *et al.*, 1975).

Statistical analysis

To create representative time series curves of the concentrations of atrazine, terbuthylazine and bromide in soil water from different treatments, the moving averages over three sampling dates were calculated using the SAS statistics-program (SAS, 1985). Single values which differed by more than two standard deviations from the mean of the corresponding sampling date were considered as outliers, eliminated and the procedure repeated.

RESULTS AND DISCUSSION

As demonstrated for terbuthylazine in Figure 1, concentrations in samples of replicate suction cups from the same treatments and installation depths showed a great variability (coefficient of variance of up to 180%). However, no dependency between equally varying sample volume and concentrations could be found. Spatial variability of soil properties relevant for water infiltration and movement, and herbicide sorption and degradation, are thought to be responsible for this observation and could be measured in the field for soil texture. Samples from 60 and 130 cm depth had very similar concentrations, so that no distinction between installation depths was made in further trial evaluation. Similar results have been obtained for atrazine, bromide and nitrate in previous investigations.

Atrazine concentrations in soil water from treatments which varied in frequency and time from the last application showed seasonal variations on different levels (Fig. 2). Highest concentrations were observed for A1 with applications four (1987) and two (1989) years before sampling started in 1991, followed by A2 and A3 with three (1988) and two (1989) years, respectively. Because the curve of A3 is very similar to the lowest curve of the control A4, which received no application during the experimental period, it is concluded that only the application in 1987 caused the highest concentrations observed for A1 and that the peak from atrazine applied in 1989 has not yet reached the sampling depth. It cannot be ruled out that atrazine was used on the field in the decades before 1983, and this could explain the residues found for the control treatment. Higher concentrations during summer, with peaks in June/July up to 0.8 µg/l, could be caused by bound residues released by mineralisation of organic matter at higher soil temperatures or increases of concentration with decreasing soil water content. The curves are interrupted in the dry summer of 1992 because no water samples could be drawn.

Terbuthylazine and bromide were applied in 1990 and 1989, respectively, to both treatments TB1 and TB2 before being sprayed separately on the same day in 1993 only on TB2. Bromide was applied again to both treatments in 1994. Immediately after application, concentrations of terbuthylazine and bromide increased steadily to maxima (0.35 µg/l and 6.0 mg/l, respectively) seven weeks after spraying in 1993 (Figs. 3 and 4). Bromide concentrations are still increasing at the end of the study period after the 1994 application. This rapid transport with soil water to depth is most probably the result of preferential flow through macropores, which reach into the vicinity of the suction cups, bypassing sorption or degradation in upper soil layers. The fast breakthrough of bromide in lysimeters (1 m^2 x 1.5 m) and the synchronic course of nitrate and ammonium content in soil samples from 0-30, 30-60 and 60-90 cm depth on the same site have previously excluded a methodical error of the suction cup method (e.g. hydraulic shortcut along the refilled boreholes above the

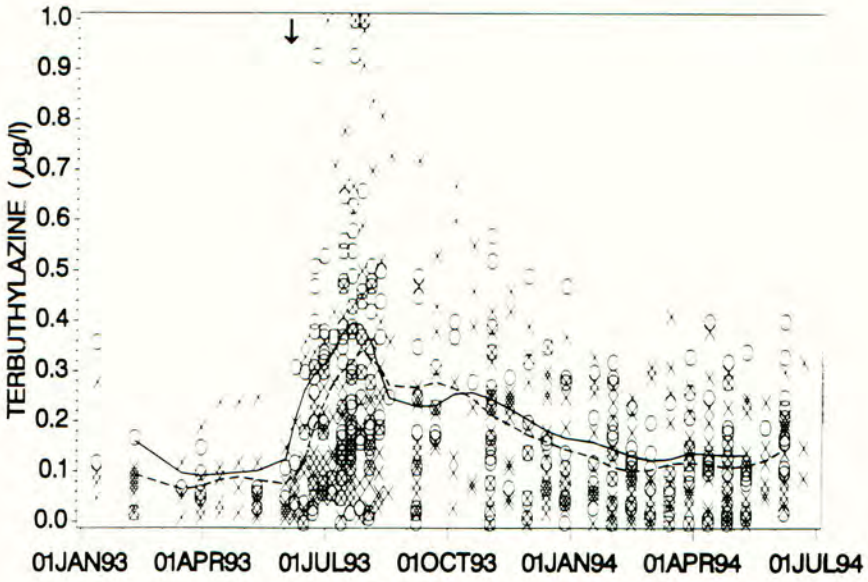

FIG. 1. Terbuthylazine concentration (µg/l) in soil water. Curves of moving average for treatment TB1 over all samples from 60 cm (————) and 130 cm (— — —) depth and single values from 60 (O) and 130 cm (X) depth except outliers. (Arrow marks application date).

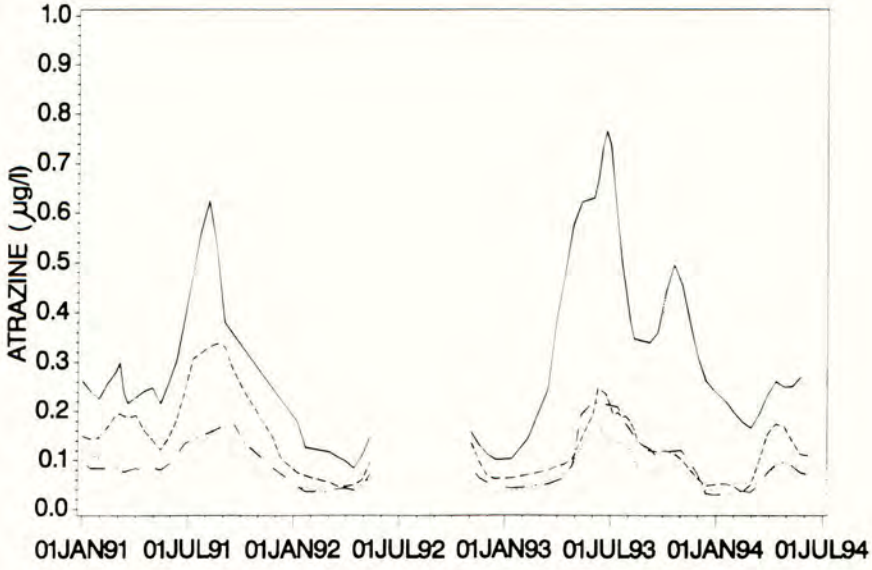

FIG. 2. Atrazine concentration (µg/l) in soil water. Curves of moving average for treatments A1 (————), A2 (— — —), A3 (·····), A4 (—·—·—) over all samples from 60 cm and 130 cm depth except outliers.

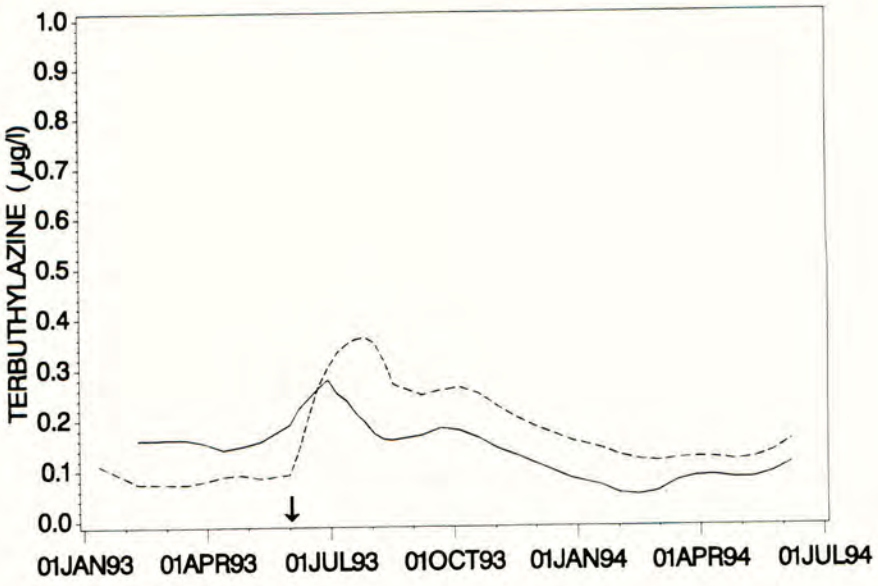

FIG. 3. Terbuthylazine concentration (μg/l) in soil water. Curves of moving average for treatments TB1 (————), TB2 (— — —) over all samples from 60 cm and 130 cm depth except outliers. (Arrow marks application date).

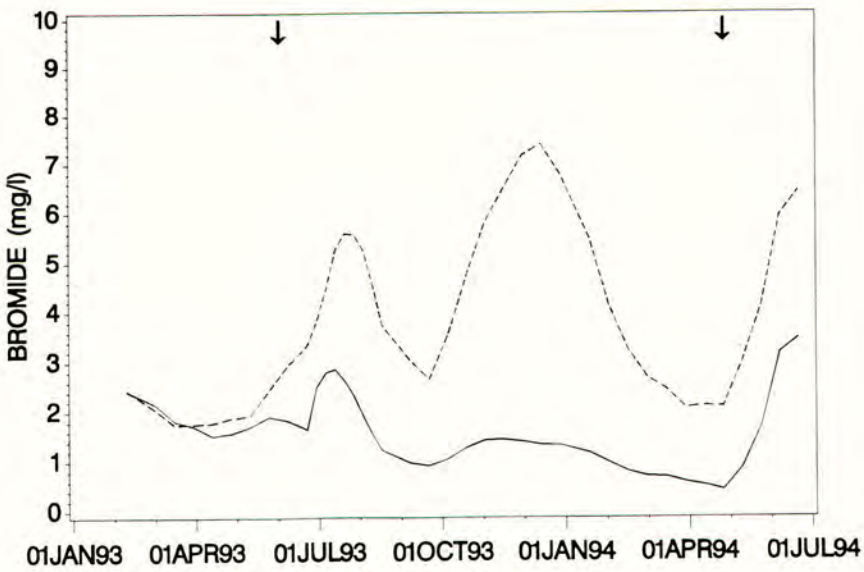

FIG. 4. Bromide concentration (mg/l) in soil water. Curves of moving average for treatments TB1 (————), TB2 (— — —) over all samples from 60 cm and 130 cm depth except outliers. (Arrows mark application dates).

cups) supporting the assumption of naturally high soil permeability. This could also account for the similar concentrations observed at both sampling depths (Riess, 1993). The peaks might be amplified by release of bound residues through mineralisation of organic matter as assumed for observed atrazine peaks during these months. Small simultaneous increases of terbuthylazine and bromide concentration in the control TB2, which can only be caused by previous applications, support this hypothesis. A second, larger bromide peak in the winter of 1993/94 could be caused by bromide not previously transported by preferential flow percolating slowly through the soil matrix. A simultaneous second terbuthylazine peak was not observed perhaps because of sorption and degradation during the intervening period.

From this experiment we conclude that suction cups are useful, easy to handle, and relatively cheap tools to obtain soil water samples in an non-destructive way. Samples can be taken repeatedly from the same points to allow long-term monitoring programs of herbicide leaching. The enzyme immunoassay proved to be a valid, relatively simple, fast analytical method which was especially effective when many small volume water samples had to be analyzed for residues. Preferential flow of soil water transporting terbuthylazine through macropores was observed using suction cups and was demonstrated to be an important leaching mechanism. More than four years after the last application, seasonally varying concentrations of atrazine residues (mostly below 0.5 μg/l) could be found due to slow transport with water moving through the soil matrix.

ACKNOWLEDGEMENTS

Antibodies and enzyme tracers were kindly provided by A. Dankwardt, T. Giersch, B. Hock, S. Wüst, Institute of Botany, Technical University Munich, Freising-Weihenstephan. We thank A. Wurzinger for the bromide analysis and S. Anke, S. Babl, M. Bracker, M. Walser for excellent technical assistance. We are indebted to Ms. T. Kydd for reading the English manuscript. R. Schewes was funded by the Volkswagen-Foundation, Hannover.

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VARIABILITY IN LYSIMETER RESULTS

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ABSTRACT

Six studies have been conducted at Rhône-Poulenc's Manningtree lysimeter facility with contrasting agrochemicals, each with two undisturbed cores of sandy soil 0.5 m^2 x 1 m deep. Leachate volumes differed very little (by 10% or less over the first year) between duplicates. In three studies the composition of the leachate was very similar for the two cores. In the other three, however, there were differences between 2- and 4-fold in the total amount of radioactivity collected. In two of these there were differences of about 20 fold in the amounts of parent material while in the other, primary metabolites were detected in one core but not the other. Cores in two of these studies have been sampled using an inversion and excavation technique which permits examination of the entire cross section of a lysimeter core. This sampling process indicates that holes produced by worms and moles may help explain at least a portion of the observed variability.

INTRODUCTION

During 1991 a lysimeter facility was established at Aldhams Farm, Lawford, Manningtree, Essex, UK. This facility, designed to comply with the German guidelines on lysimeter studies (BBA, 1990 & 1991), has been previously described in some detail (Parsons & Jones, 1993). Since 1992 six lysimeter studies have been initiated and the first of these are nearing completion. Preliminary results have shown significant levels of variability. Cores have been examined in two studies in an attempt to better understand the reasons for this variability. This paper describes the variability and the observations made during examination of the cores.

METHODS

Duplicate lysimeters were used for each study. They consisted of 80 cm diameter (0.5 m^2 surface area) and 1 m deep undisturbed soil cores in GRP (glass reinforced plastic) cylinders. The soil, Cuckney series loamy medium sand to medium sand from Shuttleworth College Farm, Bedfordshire, was provided by the Soil Survey and Land Research Centre, Silsoe. Characteristics are summarised in Table 1. The six test materials were applied and the test crop managed in simulation of typical agricultural practice.

A simple method was devised for sampling the cores at the end of the study. In this the risk of treated surface soil contaminating deeper soil was eliminated, there was no need to use a separate sampling device and the disposal of radioactive soil was facilitated.

TABLE 1. Soil analysis and classification

Sand	89 - 98 %
Silt	6 - 1 %
Clay	5 - 1 %
Organic carbon	1.0 - < 0.05 %
UK Classification	Typical brown sand
FAO Classification	Luvic arenosol
USDA Classification	Sandy, mixed mesic typic udipsamment

The cores are removed from the ground in a process rather similar to the method of collection (Yon, 1992). A 2-metre square hole is dug out to surround each core and shored with timber shuttering. The plumbing is disconnected and a lifting top-plate fitted. The core is lifted out of the shored hole using the loader bucket of a wheeled digger, placed on the soil surface nearby and then inverted. The galvanised pan which is sealed to the bottom of the core is cut off using an angle-grinder.

Soil is removed from the GRP cylinder in 10 cm layers starting with the deepest which is now on the top. The surface of each 10-cm layer is cleaned and the presence of holes recorded by photography and drawing. The cylinder is cut away at intervals with the angle-grinder to facilitate this. Each layer is mixed using a small cement mixer. This is possible because the soil is sandy. Then each layer is sub-sampled for analysis, bagged and weighed before disposal so that the proportion of applied material remaining at each depth can be calculated.

RESULTS

Results are shown in Figures 1 and 2 and summarised in Table 2.

For all six test materials the two lysimeters have yielded very similar amounts of leachate. This is clear when viewed over the course of two seasons with roughly monthly sampling intervals but this view may obscure short term differences in flow rate.

In the case of the three materials shown in Figure 1, there were marked differences in the amounts of radioactivity found in leachate from the cores. The differences in the amounts of important analytes were greater (about twenty-fold for products 1 and 3). Major metabolites were only detected in the leachate from one of the two lysimeters treated with compound 5.

In the case of the other three materials (shown in Figure 2), there has been reasonable agreement between the two lysimeters as far as total radioactivity is concerned. Analysis for the main metabolite of product 2 has also produced similar results for the two lysimeters.

Core sampling has been completed for two studies (materials 1 and 3).

In the study with material 1 (Table 3), lysimeter E proved to have more earthworm burrows than lysimeter D. At 70 cm below the surface there were four times as many. This contrast between the two cores is consistent with the greater amounts of radioactivity and parent compound found in leachate from lysimeter E.

FIGURE 1. Results from three studies showing differences between the two lysimeters for amounts of radioactivity and analytes.

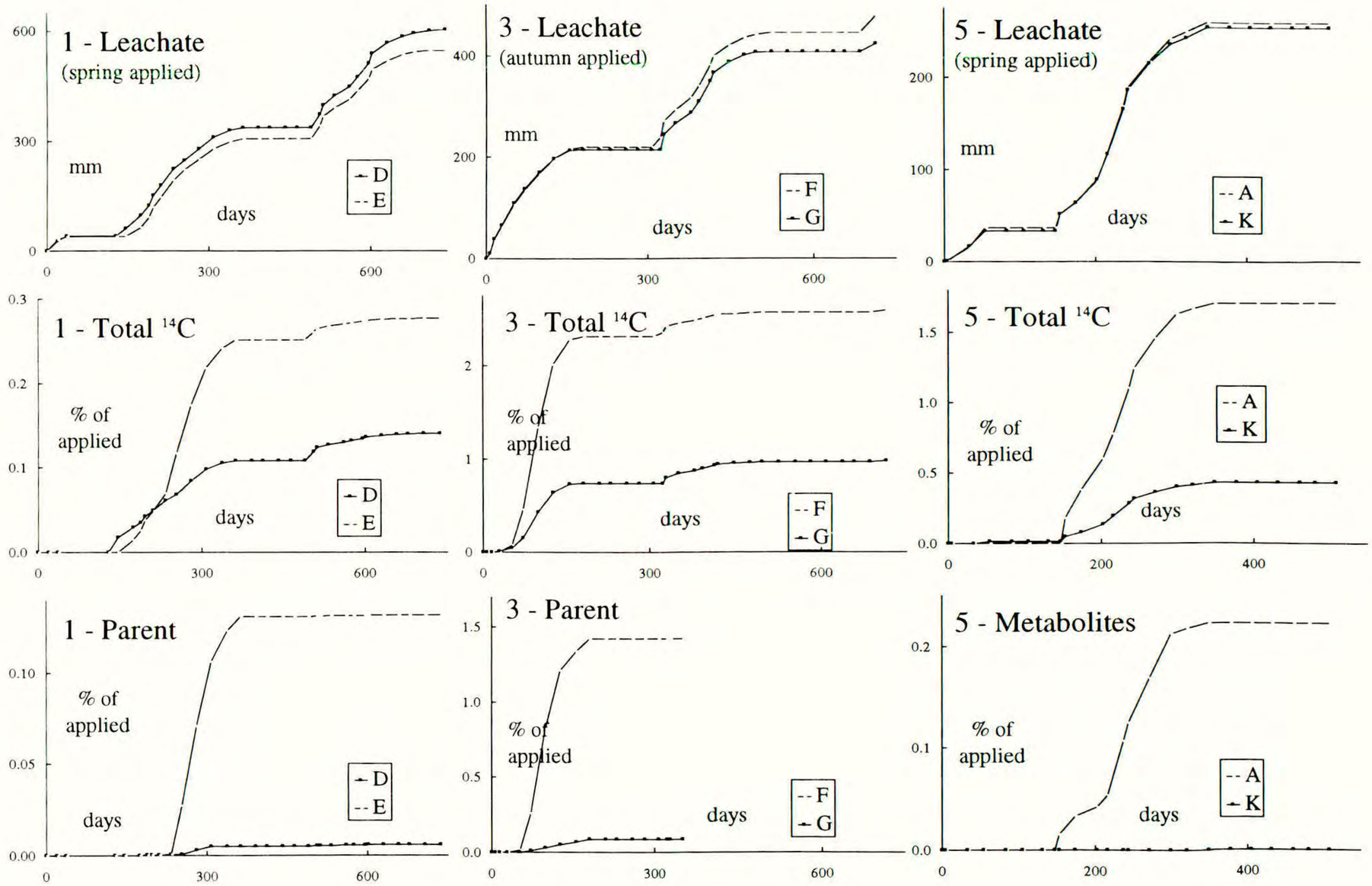
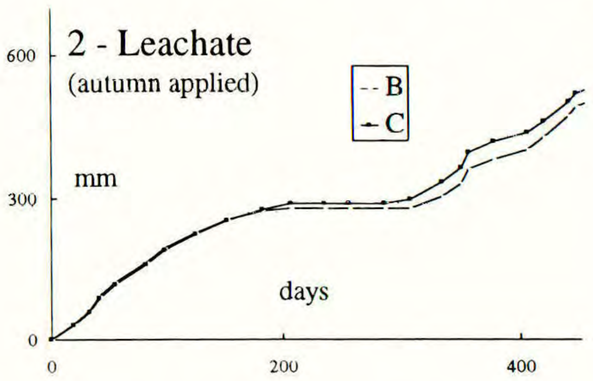
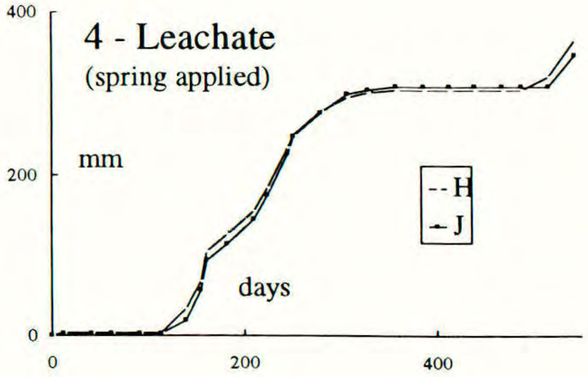
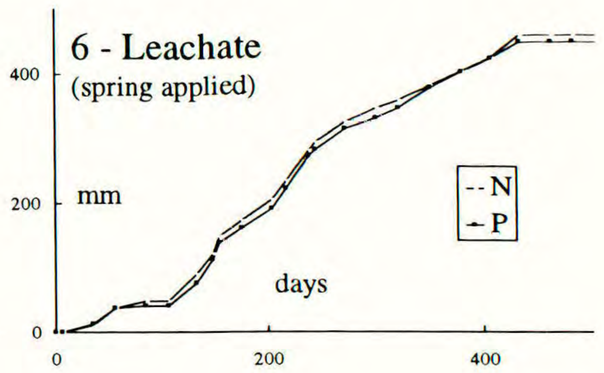
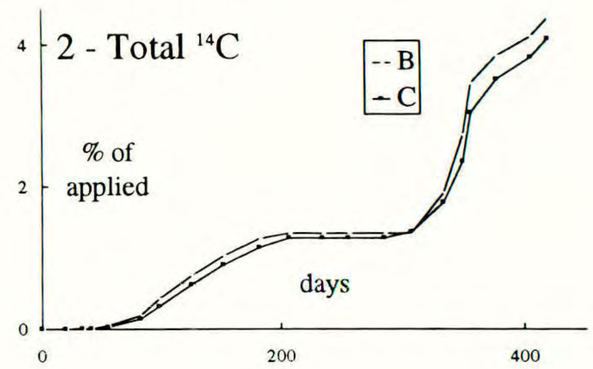


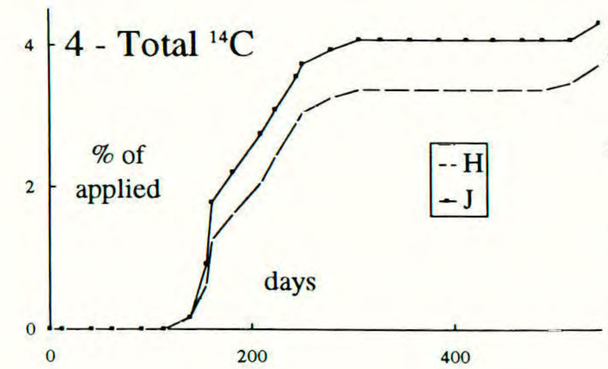
FIGURE 2. Results from three studies showing agreement between the two lysimeters for amounts of radioactivity.

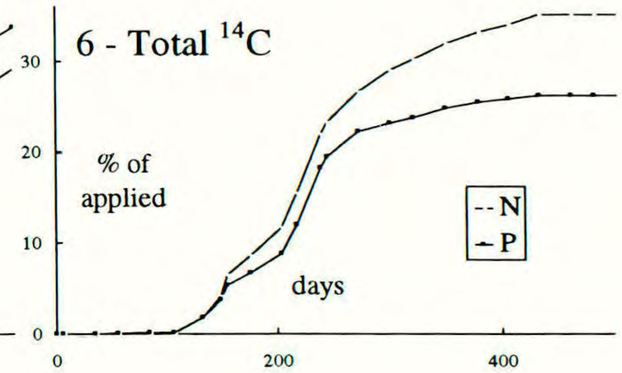












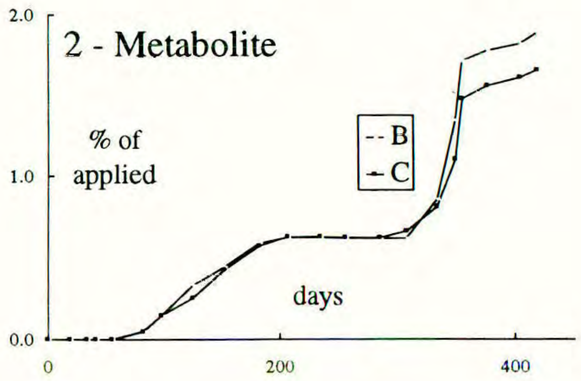


TABLE 2. Summary of first year results
(numbers in brackets provide a measure of variability: the ratio of larger to smaller)

Test material	Application time	Lysimeter	Leachate mm	Total ^{14}C % of applied	Parent or significant metabolite/s % of applied
1	Spring	D	337	0.109	0.005
		E	308	0.252	0.131
			(1.09)	(2.3)	(26)
2	Autumn	B	362	3.46	1.712
		C	397	3.05	1.476
			(1.10)	(1.1)	(1.2)
3	Autumn	F	294	2.46	1.423
		G	267	0.84	0.085
			(1.10)	(2.9)	(17)
4	Spring	H	305	3.37	
		J	310	4.08	
			(1.02)	(1.2)	
5	Spring	A	258	1.71	0.318
		K	253	0.43	<0.049
			(1.02)	(4.0)	(>6.5)
6	Spring	N	403	33.1	
		P	402	25.4	
			(1.00)	(1.3)	

TABLE 3. Worm holes found in lysimeters for test material 1.

			Lysimeter D	Lysimeter E
40 cm deep	Number of worm holes	Small (5 mm)	8	10
		Large (10 mm)	0	1
	Approx. cross-sectional area of holes in cm^2		1.6	2.8
70 cm deep	Number of worm holes	Small (5 mm)	3	10
		Large (10 mm)	0	2
	Approx. cross-sectional area of holes in cm^2		0.6	3.5

In the study with material 3 (Table 4), there were fewer worm holes and they were smaller. Mole (*Talpa europaea*) burrows were found in both lysimeters. Although both worm and mole holes could have affected movement of water and dissolved radioactivity, the physical evidence does not allow a definitive conclusion as to the cause of the difference in leachate compositions between the two cores.

TABLE 4. Worm and mole holes found in lysimeters for test material 3.

Depth	Lysimeter F		Lysimeter G	
	Number of worm holes (3 mm)	Mole holes	Number of worm holes (3 mm)	Mole holes
30 cm	1	0	1	0
40 cm	4	0	2	0
50 cm	1	0	2	0
60 cm	3	1 (32 mm)	4	1 (28 mm)
70 cm	1	0	2	0
80 cm	2	0	4	0
90 cm	0	0	1	0
100 cm	0	0	0	0

CONCLUSIONS

These six lysimeter studies show that considerable variability in the amount of analytes or total radioactivity can occur in replicate lysimeters, even when there is little variability in the amount of water being removed as leachate. Examination of soil cores from two of these studies indicate that holes produced by worms and moles may be a contributing factor to this variability.

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THE OCCURRENCE OF PESTICIDES IN DRINKING WATER

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ABSTRACT

Pesticides continue to account for the majority of the failures to meet drinking water standards. The types of pesticides found and the frequency of their detection can be related to the type of water sources in the area and the pattern of pesticide use.

Water companies are investing in new treatment plant to remove pesticides, but have also been encouraging better controls on pesticides at source. Concentrations of atrazine and simazine in drinking water have been significantly reduced over the past few years. The water industry's attention is now turning towards agricultural pesticides. Adverse weather conditions during the winter of 1993/4 resulted in very high concentrations of isoproturon in many water sources. Changes in the use of isoproturon are required to reduce the concentration in water sources.

INTRODUCTION

Since the privatisation of the water industry in 1989, objective information on drinking water quality has been published by individual water companies and summarised in an annual report by the Drinking Water Inspectorate (DWI). The report from DWI attracts widespread coverage in the press and on television. Unfortunately, these stories often reduce the quality of drinking water to the percentage of samples or tests that meet the required standards. The media seldom consider what underlies this simple statistic and the improvements in water quality which are being made.

This paper examines how pesticides in drinking water influence the compliance statistics, looks at the types and concentrations of pesticides found, and considers how the water industry is tackling pesticides in drinking water.

WATER QUALITY STATISTICS AND THE IMPORTANCE OF PESTICIDES

The Water Supply (Water Quality) Regulations 1989 fully incorporate, and go beyond, the requirements of the European Drinking Water Directive. There are two standards for pesticides in the Regulations, 0.1 μg/l for individual substances, and 0.5 μg/l for "total" pesticides. Although these standards are not based on health considerations water suppliers are legally obliged to meet them.

Since 1991, the Drinking Water Inspectorate has published summary reports on drinking water quality in England and Wales (DWI 1991;1992;1993;1994). There were more than 1 million analyses for individual and total pesticides in 1993 and 97.6% of these complied with

the relevant standards. However, this statistic gives little indication of the importance of pesticides as a cause of non-compliance. Table 1 shows the number of failures due to different water quality parameters in the period 1990-3.

TABLE 1. Contraventions of standards in water supply zones in England and Wales 1990-1993 (values in parentheses are % of total contraventions)

Parameter	1990	1991	1992	1993
Pesticides	13209 (51)	27585 (66)	35679 (75)	25531 (73)
Coliforms	3835 (15)	2709 (6)	2318 (5)	1575 (5)
Iron	2226 (9)	2515 (6)	2033 (4)	1593 (5)
Nitrite	1743 (7)	2228 (5)	2086 (4)	1876 (5)
Lead	1598 (6)	1736 (4)	1354 (3)	1263 (4)
Nitrate	1117 (4)	1170 (3)	852 (2)	364 (1)
Others	2204 (8)	3781 (9)	3317 (7)	2582 (7)
Total	25932	41724	47639	34784

The contraventions for pesticides (for both individual and total substances) dominate the compliance figures and, in numerical terms, are an order of magnitude more important than other high profile parameters such as lead and nitrate. It should be noted that the increase in the absolute number of contraventions from 1990 to 1992 is probably caused by increased sampling in areas where contraventions have been recorded. The data for 1994 is expected to continue the marked reduction in the absolute number of contraventions seen between 1992 and 1993 but pesticides will continue to dominate the figures.

TYPES OF PESTICIDES FOUND

The number and type of pesticides present in drinking water depends on several factors which include the type of water source, the nature of pesticide use in the catchment area and the nature of water treatment. The vast majority of pesticides found in drinking water are herbicides. This is almost certainly due to the large quantities used and their application in situations with a high risk of run-off or leaching. Table 2 shows the number of contraventions for different pesticides in five water company areas during 1993. The type of pesticides and number of contraventions found vary with the types of water resource in each area. For example, 65% of North West Water's resources are from upland catchments where pesticide use is limited.

For Thames Water, 75% of its raw water comes from lowland rivers draining large catchments with intensive pesticide use in both urban and arable situations. The remaining 25% comes from groundwater sources, many of which are in urban areas or close to railway lines or roads. The large number of contraventions in the Thames Water area can also be accounted for by the storage of water in large bank-side reservoirs prior to treatment. These reservoirs serve to blend out the peak levels of pesticides that are characteristic of lowland rivers. Unfortunately, the blending can result in prolonged periods when the concentrations of pesticides are above the 0.1 μg/l standard.

TABLE 2. Numbers of samples >0.1 μg/l for selected pesticides in drinking water reported by five water companies in 1993.

Pesticide	Anglian	North West	Severn-Trent	South West	Thames
Atrazine	80	33	45	2	5263
Simazine	32	1	7	0	3652
Diuron	0	1	32	0	3242
Isoproturon	33	1	12	0	2860
Mecoprop	13	5	157	0	44

WATER TREATMENT FOR PESTICIDES

Where standards for pesticides have been contravened, water companies are required to take steps to meet the regulatory requirements. For Thames Water this has involved the installation of new treatment processes at more than 25 treatment works which supply more than 80% of the volume of water supplied.

Treatment plant to remove pesticides is expensive, with initial capital costs of approximately £400 million in the Thames Water area alone. Both the capital and operating cost of this treatment plant is heavily dependent upon the concentration of pesticides. The treatment processes must be designed to deal with the highest concentration of a pesticide that might be present in the raw water, even if only present as infrequent peaks.

PROTECTING WATER FROM PESTICIDES

Although water companies have been obliged to install new treatment processes to remove pesticides, it has been recognised that lower concentrations of pesticides are easier to treat. With this in mind, several water companies have been working to reduce the amounts of pesticides reaching water sources and shifting, in a small way, the burden of the 0.1 μg/l standard towards the users of pesticides.

Up until 1993, atrazine and simazine have been the most commonly detected pesticides in drinking water. Therefore, water industry interest was initially directed at their widespread use on roads and railways. Extensive contact has been made with users of these compounds to explain their potential impact on water quality (White & Pinkstone, 1993).

Many amenity and industrial users initially switched to diuron as the next cheapest residual acting herbicide. This resulted in an increase in diuron concentrations in many surface water sources (see below). This demonstrated that protecting water sources required more than simply banning active ingredients. Further discussions with amenity/industrial users, as well as pesticide manufacturers, have emphasised the need for a more sophisticated and targeted approach to protecting water. Where there is a high risk of contaminating water resources (e.g. along railway lines close to boreholes), local agreements have been reached to restrict the use of residual acting herbicides in certain areas.

More general activities to protect water involve tighter specification on when, and how, a pesticide is used. The changes in the label recommendations for diuron are a good illustration of what can be done. Avoiding diuron use in rapidly draining areas (such as road gulleys) and reducing application rates have obvious benefits for water protection. Restricting applications to the early part of the year has more subtle advantages. It allows lower dose rates to be used and, because the flow in rivers is generally greater earlier in the year, it means that there will be greater dilution if run-off does occur.

PATTERNS IN HERBICIDE CONCENTRATIONS

Amenity and industrial herbicides

Over the past few years, changes in the use of industrial and amenity herbicides have had a marked effect on the concentrations of these substances in water resources and hence water supplies. Figures 1a and 1b show the concentrations of atrazine and diuron in drinking water from a large treatment works serving London. This works, which does not yet have any treatment plant to remove pesticides, is fed by large storage reservoirs filled with water from the river Thames. Despite the buffering afforded by the reservoirs, both atrazine and diuron concentrations show marked seasonal variation with the highest concentrations following the major application periods.

Since 1990, there has been a dramatic fall in the concentration of atrazine, mirroring changes, both voluntary and now compulsory, in the use of this herbicide. Diuron concentrations have increased slightly over the same period but the data, particularly those for 1994, suggest that the user community has recognised the risks to water posed by this substance and worked to avoid replacing one problem with another.

Agricultural herbicides

As measures to reduce contamination by industrial and amenity herbicides have taken effect, the relative importance of agricultural pesticides such as isoproturon has increased (see Table 3). It is anticipated that data for 1994 will show isoproturon accounting for the majority of pesticide contraventions in England and Wales.

TABLE 3. Percentage of pesticide contraventions in drinking water in the Thames Water area due to individual pesticides (1994 data are provisional).

Pesticide	1990	1992	1994
Atrazine	52	46	8
Simazine	27	23	2
Diuron	5	20	13
Isoproturon	10	10	68

FIGURE 1. Concentrations of atrazine, diuron and isoproturon in drinking water supplies from a water treatment works serving London.

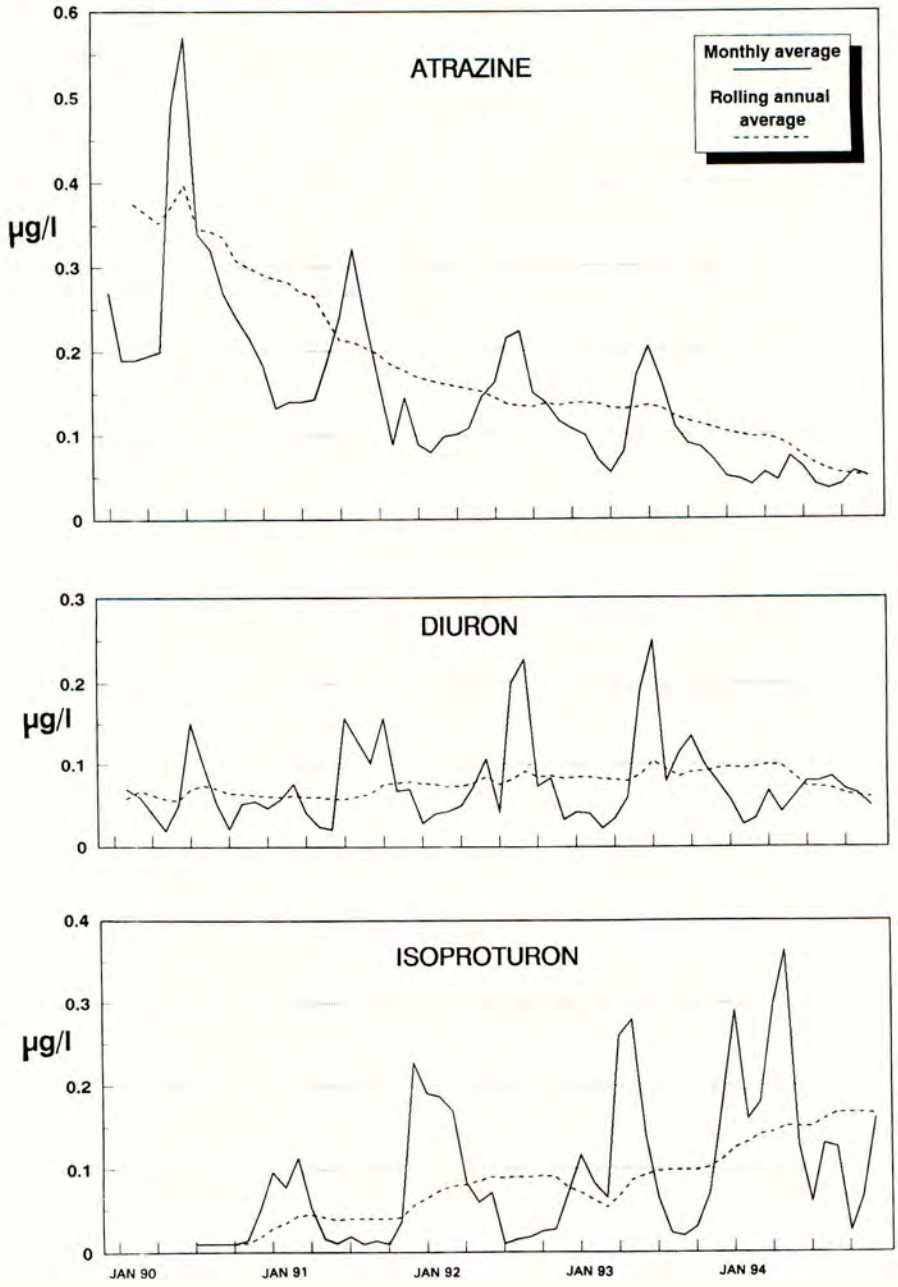

Figure 1c shows the concentrations of isoproturon in drinking water from the same works as Figures 1a and 1b. Isoproturon concentrations in surface water supplies typically show seasonal peaks in the late autumn and winter following application patterns. The data also suggest an upward trend in isoproturon concentrations. This is probably the result of wetter autumn and winters in the past few years. In both 1992/3 and 1993/4 wet autumns restricted the opportunities for spraying while the subsequent heavy rain encouraged extensive run-off into rivers.

THE FUTURE

The European Drinking Water Directive is currently being revised. Although there have been calls for the introduction of scientifically-based standards for pesticides, there has also been strong resistance to change. If the standard of 0.1 μg/l for individual pesticides is retained, further steps to protect water sources will be necessary. In the non-agricultural sector, areas for improvement include better specification and monitoring of weed control programmes and a better understanding of how pesticides move once applied to hard surfaces. In the agricultural sector, new controls on isoproturon use are required. The water industry is looking to the review by the Advisory Committee on Pesticides to make recommendations that will minimise the impact upon water quality. It is hoped that these recommendations can be made even though definitive information on their effectiveness is not yet available.

CONCLUSIONS

Water quality data for England and Wales in 1994 will not be available until later in 1995. It is anticipated that catchment control and the introduction of new treatment methods will reduce markedly the number of pesticide contraventions in drinking water. Despite these measures, it must be recognised that pesticides in raw water continue to be a problem for water suppliers and further action is required to minimise concentrations in water supplies.

ACKNOWLEDGEMENTS

The authors would like to thank Thames Water's Director of Environment and Science, Mr J Sexton for his permission to publish this paper. The authors also wish to acknowledge the invaluable support of Mr A Nield. The views expressed are those of the authors.

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