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# Lysimeter Studies relevant to the Fate of Pesticides in the Soil

# CHARACTERISATION OF THE ENVIRONMENTAL FATE OF THE PYRIDINE DERIVATIVES CLOPYRALID AND FLUROXYPYR BASED ON LYSIMETER EXPERIMENTS

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## ABSTRACT

To obtain a more complete understanding of the fate of the herbicides clopyralid and fluroxypyr in soil under practical farming conditions, lysimeter experiments on two different soil types were conducted in 1988-1991. The molecules were applied as [2,6-$^{14}$C]clopyralid and [2,6-$^{14}$C]fluroxypyr at two rates to crops at typical application times.

Rapid metabolism in soil was observed for both compounds and only trace amounts of the herbicides were translocated deeper than 30 cm. After two years about 20 % and 40 % of the applied radiocarbon was recovered from soil of the clopyralid and fluroxypyr lysimeters, respectively. Radiolabelled clopyralid and fluroxypyr were generally found only in very low concentrations in the leachates (<< 0.1 µg a.e./l). With the exception of the mineralisation product $^{14}CO_2$, no other metabolites could be detected in soil and leachate samples from the lysimeters treated with [$^{14}$C]clopyralid. In the case of the fluroxypyr study the pyridinol and the methoxypyridine metabolite of fluroxypyr were extracted from soil. These metabolites were also detected in the percolates in negligible amounts. The results indicate that under practical farming conditions, contamination of ground water in excess of 0.1 µg a.e./l is highly unlikely for both herbicides.

## INTRODUCTION

Lysimeters with undisturbed soil monoliths linked with $^{14}$C-tracer techniques are very effective experimental systems to study in detail the distribution of pesticide residues in the environment under conditions closely resembling actual field conditions. However, for interpretation and assessment of lysi-

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meter leaching data some limitations have still to be taken into consideration (Bergström, 1990; Hance & Führ, 1992).

In Jülich, uptake by plants, degradation, transformation, sorption and bioavailability in soil of more than 40 $^{14}C$-labelled pesticides have been studied in lysimeters. A large number of these experiments covered a period of 2-3 growing seasons and were often combined with laboratory experiments. Based on the results of these extensive studies general conclusions about the long-term fate of pesticide residues in soil can be drawn (Führ *et al.*, 1991). To prove the transferability of lysimeter results to real field situations comparative studies with two herbicides were carried out in Jülich. It was shown that the residue situation in the lysimeters with respect to uptake, degradation, residue formation and translocation of active ingredient (AI) and metabolites in the topsoil of the lysimeters was in good agreement with the field data (Kubiak *et al.*, 1988a, 1988b). These results were supported by the soil temperature and moisture curves recorded in the two experimental units. More information about the importance of the measurement of climatic parameters in lysimeter studies are given by Pütz *et al.* (1992). To further illustrate the value of lysimeter experiments in environmental research, the following studies have been selected.

Clopyralid and fluroxypyr are two systemic herbicides belonging to the group of pyridine derivatives. Clopyralid is rapidly degraded by microbiological processes in soil (Pik *et al.*, 1977; Baloch & Grant, 1991), but can be relatively persistent under unfavourable moisture and temperature conditions (Pik *et al.*, 1977; Snel *et al.*, 1986; Smith & Aubin, 1989). The kinetics of degradation of fluroxypyr was found to be unaffected by diurnal variation of soil temperature or moisture, or by the presence of grass. The half-life was equal or less than three weeks (Lehmann *et al.*, 1990). Higher persistence of clopyralid in soil compared to fluroxypyr was reported by Nilsson & Arvidsson (1989) for Swedish conditions. In field experiments they detected phytotoxic residue levels of fluroxyypr in soil for 1-2 months whereas for clopyralid phytotoxic residues persisted as long as 3-4 months after application. Based on the physical and chemical properties of these chemicals (Worthing & Hance, 1991; DowElanco, unpublished data) and on laboratory tests (Lehmann *et al.*, 1990a, 1990b; Stork *et al.*, 1990), it can not be excluded that both AI can leach into deep soil layers under farming conditions. However most field studies with clopyralid and fluroxypyr show that herbicide residues could not be detected below 30 cm (Snel *et al.*, 1986; Nilsson & Arvidsson, 1989; Rexilius, 1990; Bergström *et al.*, 1990, 1991). Also Oliver *et al.* (1989) found that clopyralid was translocated not deeper than into the 15 to 30 cm horizon of a loamy sand soil although they applied 560 g a.e./ha (which is greater than four times the European recommended application rate).

The work reported here was initiated to investigate the behaviour of both compounds in lysimeter systems as described by Steffens *et al.* (1992) to get a more complete understanding of the fate of clopyralid and fluroxypyr under practical farming conditions.

## MATERIALS AND METHODS

The experimental section is described in detail elsewhere (Brumhard *et al.*, 1991, 1992a) and will be presented here only in outline.

### Chemicals

Technical grade and $^{14}$C-labelled active ingredients (Fig. 1) were supplied by DowElanco Europe as part of a cooperative research programme with the Institute od Radioagronomy, Jülich.

[2,6-$^{14}$C]clopyralid
(3,6-dichloropyridine-2-carboxylic acid)

[2,6-$^{14}$C]fluroxypyr
(4-amino-3,5-dichloro-6-fluoro-2-pyridyloxy-acetic acid)

FIGURE 1. The herbicidal active ingredients showing the position of $^{14}$C-labelling.

Clopyralid was formulated as LONTREL[R] 100 (100 g a.e./l as monoethanolamine salt) and fluroxypyr as STARANE[R] 180 (180 g a.e./l as 1-methylheptyl ester).

### Soils

The experiments were carried out with two soils, namely a clayey silt soil (degraded loess, orthic luvisol, 6.5 % sand, 83,0 % silt, 9,7 % clay, 1.3 % organic carbon, pH 6.6) and a silty sand soil (gleyic cambisol, 74.1 % sand, 21.7 % silt, 4.2 % clay, 0.9 % organic carbon, pH 6.9).

### Lysimeter experiments

Details of the lysimeter design and the collection of leachate samples are descibed by Führ & Steffens (1985) and Steffens *et al.* (1992). Clopyralid was applied post-emergence to sugar beet on two clayey silt monoliths in June 1988 and on one silty sand lysimeter in June 1989. Fluroxypyr was sprayed post-emergence to spring barley on two silty sand lysimeters in May

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emergence to spring barley on two silty sand lysimeters in May 1989. All lysimeter units were cultivated in accordance with agricultural practice with the addition that the lysimeters received additional irrigation to reach the equivalent of 800 mm total precipitation per annum. The crop rotation was as follows: sugar beet (treated crop), winter wheat and fallow for the clopyralid experiments and spring barley (treated crop), followed by sugar beet and fallow in the case of fluroxypyr.

## Analytical methods

Clopyralid: Soil samples were extracted 3x with 0.01 M $CaCl_2$-solution, and once each with acetone and dichloromethane. Soil bound residues were extracted with three portions of 0.1 M sodium pyrophosphate and fulvic and humic acids separated after acidification. Leachate was extracted 3x with dichloromethane or diethylether (water:organic solvent ratio 2:1 v/v). Samples were analysed by radio-thin-layer chromatography (radio-TLC) with cochromtography of non-labelled reference compounds.

Fluroxypyr: Soil samples were extracted 3x with 0,01 M $CaCl_2$-solution and 4x with acetone/water (9:1 v/v). Soil bound residues were extracted as described for clopyralid. Leachate samples were extracted 3x with hexane. Subsequently the water phase was acidified to pH 1 and extracted 3x with diethylether. Extracts were analysed by radio-TLC and radio-hplc/cochromatography.

## RESULTS

## Fate of clopyralid in soil

The distribution of $^{14}C$-labelled residues in the soil profile of the clayey silt (Lysimeters 1 and 2) and the silty sand (Lysimeter 3) is shown in Fig. 2. In the clayey silt lysimeters, 59 % and 37 % respectively of the applied radioactivity was recovered in soil at harvest of the treated sugar beet, four months after application (Tab. 1).

TABLE 1. Total $^{14}C$-residues recovered from soil monoliths at different sampling dates after application of $[^{14}C]$clopyralid. Applied radioactivity = 100 %.

| Time after application (months) | Lys. 1 clayey silt 120 g a.e./ha % | Lys. 2 clayey silt 240 g a.e./ha % | Lys. 3 silty sand 120 g a.e./ha % |
|---|---|---|---|
| 4 | 59.3 | 37.3 | 24.6 |
| 14 | 22.8 | 26.6 | 15.5 |
| 26 | 20.5 | 20.3 | 13.2 |

After the same time, 24.6 % was measured in the silty sand monolith (Lys. 3; Tab. 1). In this soil, most of the residual radiocarbon was located in the topsoil layer (0-30 cm) throughout the entire experiment whereas higher amounts of radioactivity were translocated to the 40-60 cm horizon during the first growing season in the silt soil (Fig. 2). At the termination of the experiment, the total residual radioactivity had decreased to about 20 % of the applied $^{14}$C-activity in Lys. 1 and 2 (clayey silt) and had reached 13 % in the sand soil (Lys. 3; Tab. 1). At this time, 26 months after treatment, no radiocarbon could be detected below 40 cm in either soil type (Fig. 2).

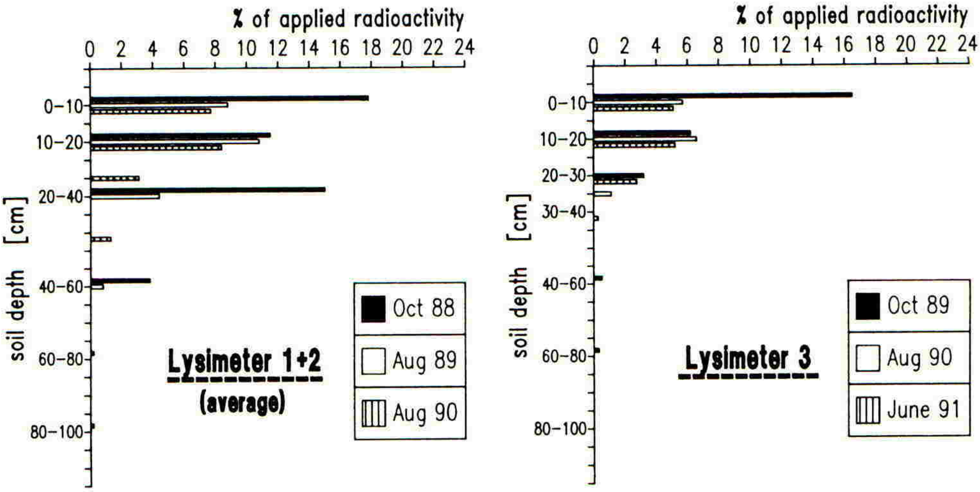

FIGURE 2. Distribution of $^{14}$C-residues in 110 cm deep soil monoliths of a clayey silt (Lys. 1 and 2) and a silty sand (Lys. 3) after application of [2,6-$^{14}$C]clopyralid in June 1988 (Lys. 1 and 2) and June 1989 (Lys. 3). Applied radioactivity = 100 %.

TABLE 2. Total precipitation, volume of leachate and $^{14}$C-activity in the leachate of the clayey silt (Lys. 1 and 2) and silty sand lysimeter (Lys. 3) in two years.
Applied radioactivity = 100 %.

| | Lys. 1 clayey silt 120 g a.e./ha | Lys. 2 clayey silt 240 g a.e./ha | Lys. 3 silty sand 120 g a.e./ha |
|---|---|---|---|
| precipitation [mm] | 1493 | 1493 | 1548 |
| leachate [mm] | 221 | 293 | 517 |
| $^{14}$C-activity [%] | 0.43 | 0.64 | 0.34 |

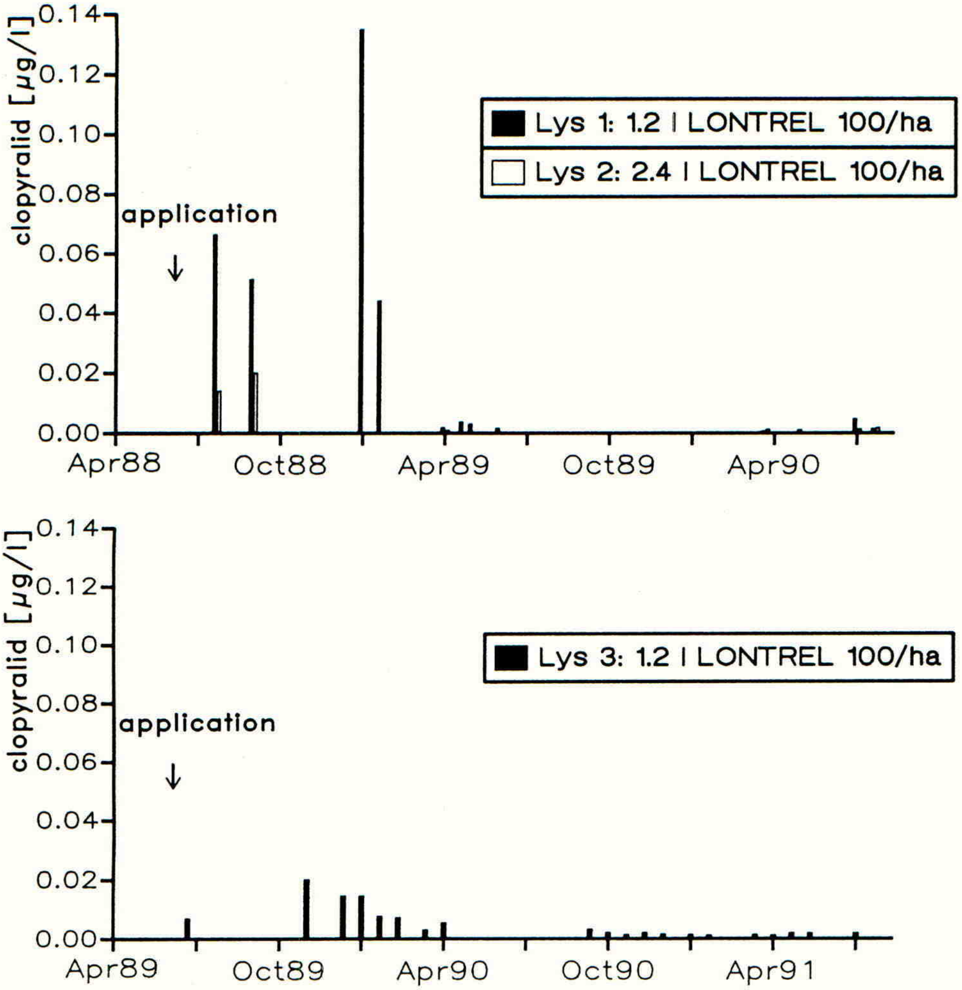

FIGURE 3. Concentration of [$^{14}$C]clopyralid in leachates of two 110 cm deep clayey silt lysimeters (Lys. 1 and 2) and a silty sand lysimeter (Lys. 3) after application of [2,6-$^{14}$C]clopyralid in June 1988 (Lys. 1 and 2) and June 1989 (Lys. 3). Applied radioactivity = 100 %.

At harvest of the sugar beet, 4 months after application, only 1.2-2.8 % of the applied AI was identified as unchanged parent compound in the aqueous extracts (0.1 M $CaCl_2$)of the 0-20 cm of the two clayey silt lysimeters. In addition a further 0.1-0.5 % respectively was extracted with organic solvents. In comparison: no clopyralid was detected in the extracts of the silty sand soil (Lys. 3). In soil samples taken 14 and 26 months after treatment, no unchanged clopyralid residues were detected. No metabolites were present in any of the soil extracts.

During the entire period of the experiment (26 months) the cumulative amount of radiocarbon leached from the clayey silt monoliths amounted to only 0.43 % and 0.64 % of the applied radiolabel, respectively (Tab. 2). Although the leachate volume collected from the silty sand soil was about twice as much as from the clayey silt soil, the portion of radiocarbon in the percolate was less (Tab. 2). Very low levels of labelled clopyralid could be detected in leachate samples of both soils ranging from 0.0005-0.135 µg a.e./l in case of the clayey silt soil and from 0.001-0.020 µg a.e./l in case of the silty sand soil (Fig. 3), the highest concentrations being measured in water samples collected during the first 8 months after treatment. The radio-TLC analyses (detection limit 0.0001-0.0003 µg a.e./l) were confirmed by gc-ms. From December 1988 onwards, approximately 85-98 % of the radioactivity measured in leachate samples of the clayey silt monoliths could be attributed to $^{14}CO_2$ and/or $^{14}C$-carbonates dissolved in the water.

Fate of fluroxypyr in soil

In the soil monoliths 73.5-75.0 % of the applied radiocarbon could be recovered 3 months after application, 41.1-48.9 % after 17 months, and 40.1-41.6 % at the end of the experiment after 24 months (Tab. 3). Vertical movement of $^{14}C$-labelled residues in the soil profile was very limited and as a result, no radiocarbon was detected deeper than 40 cm at any given time (Tab.4). Residue distribution in the topsoil was more affected by soil tillage (25-30 cm deep) than by translocation in the soil solution.

TABLE 3. Total $^{14}C$-residues recovered from soil monoliths at different sampling dates after application of [$^{14}C$]fluroxypyr. Applied radioactivity = 100 %.

| Time after application (months) | Lys. 4 silty sand 180 g a.e./ha % | Lys. 5 silty sand 360 g a.e./ha % |
|---|---|---|
| 3 | 75.0 | 73.5 |
| 17 | 48.9 | 41.1 |
| 24 | 41.6 | 40.1 |

At different dates after application of [2,6-$^{14}C$]fluroxypyr, the soil layers containing the largest portion of residual radiocarbon were extracted with aqueous and organic solvents.

The results, summarised in Tab. 5, indicate that the parent compound was rapidly degraded during the first growing season. On average, only 1 % of the applied AI was detected 3 months after treatment of the spring barley in the soil extracts. This portion further decreased below the detection limit until termination of the study. Using radio-TLC and radio-hplc, the methoxypyridine metabolite of fluroxypyr (4-amino-3,5-dichloro-6-fluoro-2-methoxypyridine), and the pyridinol metabolite (4-amino-3,5-dichloro-6-fluoro-pyridine-2-ol) could be characterised. Methoxypyridine represented about 10 % of the applied $^{14}$C-activity both 3 and 24 months after treatment, whereas pyridinol was present in soil at only low levels throughout the experiment (Tab. 5).

TABLE 4. Distribution of $^{14}$C-residues in 110 cm deep silty sand monoliths after application of [2,6-$^{14}$C]fluroxypyr in May 1989. Average of Lysimeters 4 and 5. Applied radioactivity = 100 %.

| depth | Time after application | | |
|---|---|---|---|
| | 3 months | 17 months | 24 months |
| [cm] | % | % | % |
| 0-10 | 64.0 | 11.7 | 16.1 |
| 10-20 | 9.3 | 19.1 | 15.6 |
| 20-30 | - | 14.3 | 9.0 |
| 30-40 | - | n.m. | 0.2 |
| 20-40 | 1.0 | n.m. | 9.2 |
| 40-110 | n.d. | n.m. | n.d. |

n.d.=not detected n.m.=not measured

TABLE 5. Fluroxypyr and metabolites characterised in aqueous and organic soil extracts by radio-TLC. Average of Lysimeters 4 and 5. Applied radioactivity = 100 %.

| Time after application/ sampling depth | **Fluroxypyr** % | **Methoxypyridine** % | **Pyridinol** % |
|---|---|---|---|
| 3 months/ 0-20 cm | 1.0 | 10.9 | 1.7 |
| 17 months/ 0-20 cm | 0.2 | n.d. | 0.5 |
| 24 months/ 0-30 cm | n.d. | 11.0 | 0.2 |

A total of 482-518 mm leachate was collected during the experimental period of 24 months containing 0.14 % of the applied radioactivity in both lysimeters. The parent compound was detected in the percolate samples in concentrations ranging from 0.001 to 0.034 µg a.e./l (detection limit 0.0001 µg a.e./l) without differences between application rates (Fig. 4). Methoxypyridine was the only metabolite characterised in the percolation water by cochromatography with reference standards (Fig. 4). With the exception of one sample, fluroxypyr and methoxypyridine concentrations did not exceed 0.005 µg a.e./l. For both compounds, the highest concentration was measured in the first leachate sample.

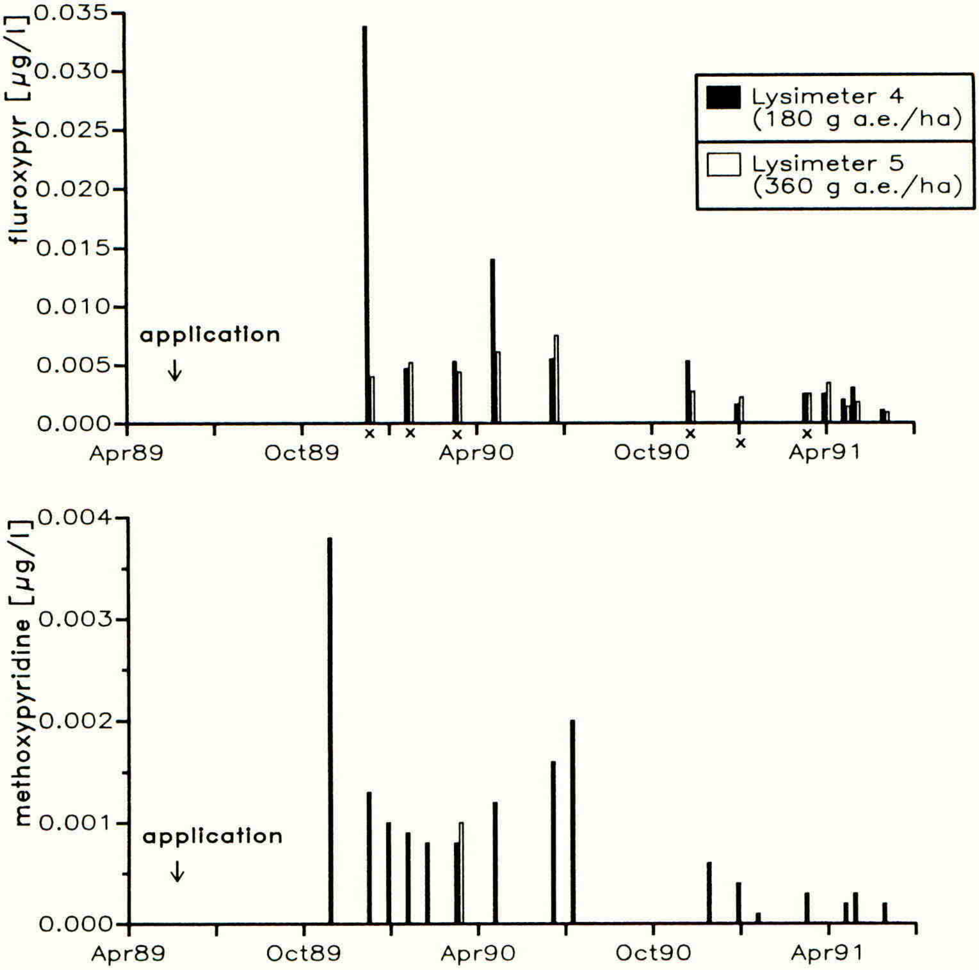

FIGURE 4. Concentration of [$^{14}$C]fluroxypyr and [$^{14}$C]methoxypyridine in leachates of two 110 cm deep silty sand lysimeters after application of [2,6-$^{14}$C]fluroxypyr in May 1989.
(*: leachate samples of two consecutive sampling dates were bulked)

## DISCUSSION

The early occurrence of traces of [$^{14}$C]clopyralid and [$^{14}$C]fluroxypyr in leachate samples supports the hypothesis that preferential flow mechanisms might be involved. However, this item will not be discussed here further since it has already been covered in detail by Brumhard *et al.* (1991, 1992a). Similar studies conducted in Sweden on different soil types by Bergström *et al.* (1990, 1991) clearly demonstrated that clopyralid and fluroxypyr have o low potential to reach a drainage depth of 110 cm. The experiments reported here confirmed the Swedish observations despite the fact that the lysimeters received considerably higher precipitation (Brumhard et al., 1992a, 1992b). In addition the rapid dissipation of clopyralid in soil under field conditions reported by Snel *et al.* (1986), Rexilius (1990) and Bergström *et al.* (1991) was further substantiated by this study. The use of $^{14}$C-label and chemical analysis in this type of lysimeter experiment allow the conclusion to be drawn that dissipation of clopyralid and fluroxypyr observed under field conditions is predominantly due to decomposition and only to a small extent to leaching or to binding to soil material.
Thus for both active ingredients, rapid decomposition in soil under practical farming conditions appear to be the dominating process for their behaviour in soil. This is the most important factor in limiting the potential translocation of clopyralid and fluroxypyr to very small amounts and to only a few months after application.

## ACKNOWLEDGEMENTS

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# EXPERIENCE WITH LYSIMETER STUDIES: SELECTED TOPICS FOR INTERPRETATION

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## ABSTRACT

Results of outdoor lysimeter studies on three active ingredients of herbicides, characterized by different soil sorption and biodegradation values, are discussed. The results show that in addition to soil sorption and biodegradation environmental variables considerably influence the fate and mobility of pesticides in soil. A general overview on results of 15 outdoor lysimeter studies demonstrates that pesticides can be clearly distinguished with regard to their leaching behaviour.

## INTRODUCTION

The relationship between soil sorption and biodegradability of a pesticide is important for its potential to leach into groundwater (Klein et al., 1990). The adsorption/desorption processes in soil can be described by the $K_{OC}$ value (adsorption coefficient normalized to organic carbon content of the soil) and the rate of biodegradation by the $DT_{50}$ value (disappearance or dissipation time for 50 % of the parent compound). These two parameters are themselves influenced by environmental conditions such as climate and vegetation, hydrogeological parameters and the chemical, physical and microbial soil properties.

Large scale outdoor lysimeter studies with undisturbed soil monoliths (Kördel et al.; Traub-Eberhard et al., chapter III) are integrative and partly standardized systems. They allow for considerably more precise predictions of the fate of pesticides in soil and their potential to contaminate the groundwater than laboratory or field experiments. Lysimeter studies are designed to simulate a field situation. In contrast to field studies, the use of radiolabelled compounds for lysimeter experiments makes it possible to detect non-extractable residues, to establish mass balances and to achieve low detection limits.

## RESULTS OF EXPERIMENTS

All experiments reported in this chapter were performed using large scale outdoor lysimeters (1.2 m depth and 1 $m^2$ surface area) installed at the grounds of the Fraunhofer-Institute in Schmallenberg (FRG) with undisturbed soil cores of sandy soil (for the soil characteristics see Table 1). Active ingredients of pesticides were applied in their $^{14}C$-labelled form.

TABLE 1. Characteristics of the sandy soil (location: Borstel near Hannover, FRG)

| Horizon (cm) | 0-30 | 30-57 | 57-73 | 73-90 | 90-110 |
|---|---|---|---|---|---|
| % sand | 68.3 | 67.0 | 96.2 | 99.8 | 100 |
| % silt | 24.5 | 26.3 | 2.0 | 0.2 | 0 |
| % clay | 7.2 | 6.7 | 0.9 | 0 | 0 |
| % organic carbon | 1.5 | 1.0 | 0.2 | 0 | 0 |
| pH | 5.7 | 4.9 | 4.9 | 5.0 | 4.8 |

Results of outdoor lysimeter studies with three active ingredients of herbicides are reported in detail in the following. For confidential reasons the test substances are referred to as herbicides "A", "B" and "C". The test substances are characterized by different soil sorption and biodegradation values. Further results are presented as a general overview.

## Lysimeter study of "herbicide A"

### Characteristics of "herbicide A"

Laboratory data on soil sorption and biodegradability for "herbicide A" show $K_{OC}$ values < 100 and $DT_{50}$ values in the range of 10 to 30 days.

### Experimental procedure

The parent compound was applied in spring on two lysimeters grown with summer wheat at dosages corresponding to the normal and double field application rate of 100 resp. 200 g active ingredient per hectare. After an experimental period of two years the soil monoliths were analysed in detail.

### Results of the study

After the application in spring "herbicide A" was rapidly degraded. During the experimental period of two years neither "herbicide A" nor its metabolites occurred in the leachate. After two years the active ingredient had been completely dissipated and most of the remaining radioactive residues, 24 to 33 % of the applied radioactivity, were recovered in the tillage layer (see Figure 1). Less than 1 % of the applied radioactivity had been translocated into the 60-120 cm deep subsoil. Approx. 60 to 74 % of the herbicide had been degraded during the study and had left the soil as $^{14}CO_2$ or other volatile compounds. Approx. 48 to 58 % of the remaining radioactivity were found to be extractable radioactive residues. For the summarized results refer to Table 2.

Similar findings were obtained from lysimeter experiments with spring applications of several compounds with $K_{OC}$ and $DT_{50}$ values similar to "herbicide A".

The results can be explained as follows:
Due to increased evapotranspiration in summer very low leachate volumes were obtained in the first months after the application (June to September), whereas high leachate volumes were obtained from October to March. This situation is characteristic of German conditions (Henning & Liebscher, 1978; Keller, 1978). Rapid degradation of the compounds in summer meant that translocation did not occur. Thus for a spring application, the probability that a pesticide with low sorption tendency and a relatively fast biodegradation rate will leach into groundwater is estimated to be low. However, groundwater contamination by this type of pesticide cannot be excluded following an autumn application.

## Lysimeter study of "herbicide B"

### Characteristics of "herbicide B"

"Herbicide B" is characterized by a moderate sorption tendency ($K_{OC}$ 235). Laboratory data on biodegradability show $DT_{50}$ values in the range of 70 to 90 days.

### Experimental procedure

The herbicide was applied to three fallow lysimeters (single application in spring) at dose rates corresponding to 2.7, 4.0 and 8.1 kg/ha.

### Results obtained from the first year of the study

In the leachates of all three lysimeters the parent compound did not occur in concentrations above the determination limit. Two metabolites were found in the leachate at concentrations exceeding the permissible EEC level for drinking water. The average concentrations of the main metabolite in the leachate were determined to be 7 / 55 / 94 µg per litre for the low / medium / high application rates.

The following important aspects should be pointed out:

a) The negligible variation in the annual leachate volumes indicates the similarity of the water regime of the lysimeters. However, a linear relationship between the application rate of "herbicide B" and the total amount of metabolites does not exist for all concentrations (see Figure 2). This may be explained by complex dissipation kinetics. Thus for risk assessment it is not generally possible to extrapolate from the results obtained from a lysimeter experiment of a pesticide with a certain application rate to the extent of leaching at lower dosage and vice versa.

b) The results described demonstrate that metabolites may have a higher potential to reach groundwater than the parent compound. Therefore the potential toxicity of main metabolites has to be considered.

TABLE 2. Data related to the fate of **"herbicide A"** in the lysimeter study

| | Application rate | |
|---|---|---|
| | normal | double |
| Precipitation over two years (mm) | 1781 | 1781 |
| Leachate over two years (litre) | 960 | 956 |
| Average concentration of radioactivity in leachate over 2 years (µg* litre $^{-1}$) | 0.03 | 0.15 |
| Total amount of radioactivity in leachate over 2 years (% ITR) | 0.3 | 0.7 |
| Concentration of herbicide A and its metabolites in the leachate over 2 years (µg/l) | <0.05 | <0.05 |
| Total amount of radioactive material in soil after 2 years (% ITR) | 26 | 40 |
| Herbicide A in soil after 2 years | n.d. | n.d. |
| Metabolites in soil after 2 years (% ITR) | 0.1 | 1.4 |
| Mineralization (% ITR, estimated) | c. 74 | c. 60 |

* expressed in equivalents of the test substance
ITR = initially applied total amount of radioactive material
n.d. = not detectable
the detection limit of "herbicide A" was determined to be <0.09 µg kg$^{-1}$ soil

FIGURE 1. Total radioactivity in 10 cm horizontal soil segments of lysimeters two years after treatment with "herbicide A"

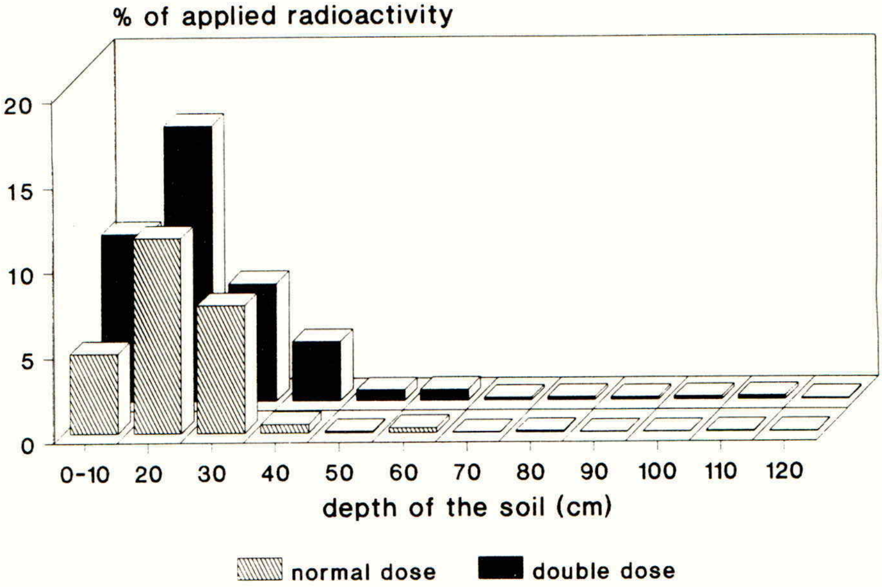
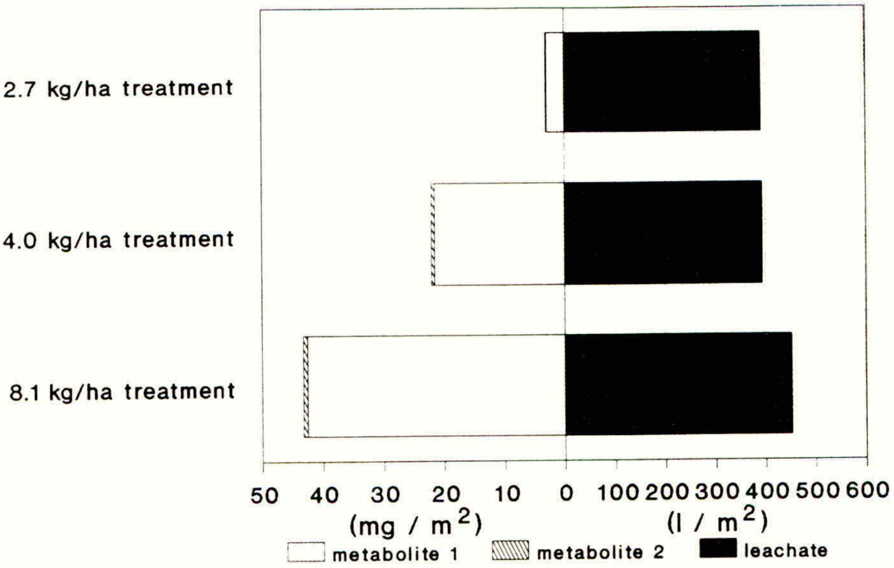


FIGURE 2. Total amount of metabolites in the leachate of the first year after the treatment with "herbicide B"



## Lysimeter study of "herbicide C"

The main objective of this study was to determine the extent of accumulation of "herbicide C".

### Characteristics of "herbicide C"

"Herbicide C" is characterized by a very high soil sorption tendency ($K_{OC} > 10000$). In laboratory experiments its half-life in soil was determined to be in the range of 60 to 90 days at 20 °C.

### Experimental procedure

Annual autumn applications on two lysimeters at dosages corresponding to the normal field application rate are performed over 4 years. To obtain information about the mobility, the degradation kinetics and the metabolism of "herbicide C" in the 0-20 cm topsoil layer, core samples (diameter 2.2 cm) are taken twice a year (every spring and autumn before the retreatment) and analysed in detail.

### Results obtained for the first year of the study

Neither the test substance nor metabolites occurred in the leachate.

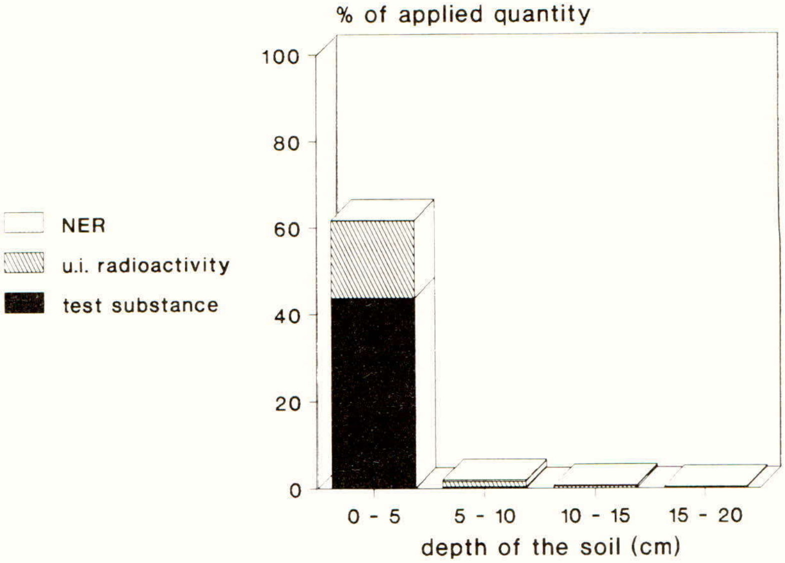
The amounts of test substance, bound residues (NER) and unidentified radioactive material in the 5 cm horizontal segments of the 0-20 cm topsoil layer taken 6 and 11 months after the first application are presented in Figure 3. The extreme immobility of "herbicide C" and its metabolites becomes obvious since even 11 months after the application less than 0.5 % of the applied herbicide was recovered below a depth of 5 cm and only minor amounts of the applied radioactivity had leached into the 5-20 cm zones of the topsoil layer.

The slow disappearance of "herbicide C" during the winter period was obviously caused by low average temperatures. Generally, in laboratory experiments an increase in half-lives by a factor of 2 to 3 was observed when lowering the temperatures by 10 °C (between 10 °C and 30 °C) (Helweg, 1987; Walker, 1978; Walker et al. 1983; Walker 1987). The unexpectedly slow degradation of the herbicide during the following dry summer (from 44 % in spring to 34 % of the initially applied dose in autumn) may be explained by a decreased microbial activity in a period of low soil humidity. Further results of several research groups demonstrate, that below a certain soil moisture content no degradation is observed (Helweg, 1987; Patil et al., 1988). Since under field conditions the soil surface is usually drier than the bulk of the soil, material left on the surface may be more persistent than incorporated.

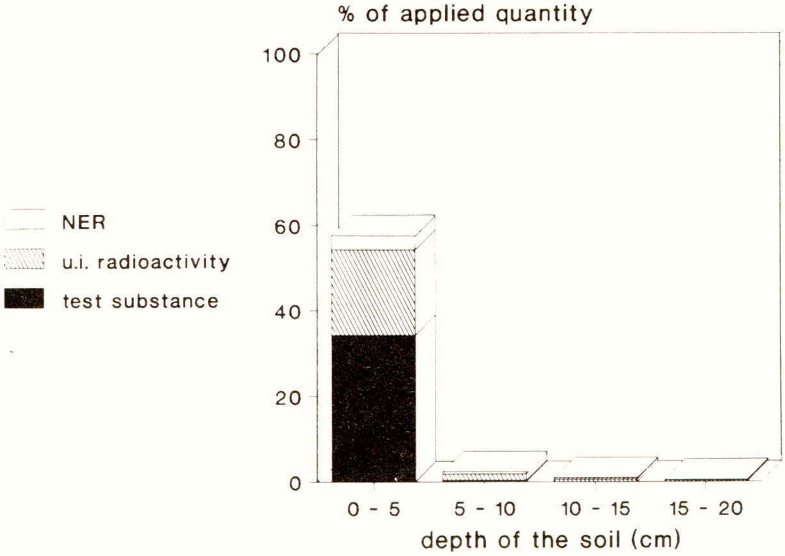
In comparison with the $DT_{50}$ values determined in laboratory experiments at 20 °C and a water content of 75 % of the field capacity, the degradation of "herbicide C" was slower under outdoor conditions in the lysimeter study. Considering the fact that before the retreatment in autumn approx. one third of the applied herbicide was still present, an accumulation of the active ingredient in the topsoil layer cannot be excluded.

FIGURE 3. Quantity of "herbicide C", non extractable radioactive residues (NER) and unidentified radioactive material in the topsoil layer (the values are mean values obtained from two replicate lysimeters)

a) 6 months after the 1. application in autumn



b) 11 months after the 1. application in autumn



## Grouping of pesticide results for mobility in soil

Results obtained on outdoor lysimeter experiments with 15 different active ingredients of herbicides, conducted at the Fraunhofer Institute in Schmallenberg, are summarized in Table 3. The results reveal that different pesticides can be clearly distinguished with regard to their leaching behaviour.

TABLE 3. Grouping of results of outdoor lysimeter experiments with 15 different active ingredients of herbicides

| Group | Herbicide | Metabolites |
|---|---|---|
| | average concentrations in leachate<br>(µg/l) | (µg/l) |
| 1 | < 0.05 | < 0.1 |
| 2 | c. 0.1<br>decreasing in 2nd year | < 0.1 |
| 3 | 0.1 - 0.5<br>in 2nd year < 0.1 µg/l | 0.1 - 0.5 |
| 4 | 0.1 - 1.0<br>decreasing in 2nd year | 0.1 - 1.0<br>in 2nd year |
| 5 | < 0.5 | 1 - 10<br>decreasing in 2nd year |
| 6 | < 0.1 | 10 - 100 |

## DISCUSSION AND CONCLUSIONS

In addition to soil sorption and biodegradability environmental variables considerably influence the fate and the mobility of pesticides in soil. Therefore results from outdoor lysimeter studies are to be regarded as singel values obtained under the specific experimental conditions of climate, vegetation, mode, rate, time of application and soil type. Although some of these parameters can be standardized, lysimeter studies are close to field conditions. Accordingly interpretations of the results from lysimeter studies have to be more complex compared to standardized laboratory tests.

Performing lysimeter experiments under various conditions to obtain average data would be an expensive and time consuming procedure. Therefore for further risk assessment of a pesticide`s leaching behaviour under various conditions, the results from one set of experiments have to be extrapolated to others, e.g. from an autumn to a spring or from a single to a multiple application. This can be realized by using mathematical simulation models such as SESOIL (Bonazountas & Wagner, 1984) and PRZM (Carsel et al., 1984). For a critical estimation and extrapolation to other scenaria, processes and experimental conditions of the respective lysimeter experiment must be known. Therefore at least the following parameters have to be taken into account:

**a) Climatic and hydrogeological conditions:**
Daily monitoring of precipitation, soil moisture and temperature of soil and air is necessary. Especially for compounds with short half-life values, the experimental conditions in the first months after the application can strongly influence their fate. Therefore the climatic conditions during this period have to be especially considered.

**b) Metabolism and degradation kinetics in soil:**
It can be concluded from the results obtained (see lysimeter experiment of "herbicide C") that a determination of the metabolism and the degradation kinetics in the topsoil is possible. Within one year several core samples can be taken from the topsoil without impairing the study.

For compounds with fast biodegradation rates an investigation of metabolism and degradation kinetics especially during the first months after the application is of interest, whereas the degradation behaviour of a more persistent pesticide should be observed over a longer experimental period. Regular soil analyses of annually treated lysimeters give useful information on the long-term fate and the potential of accumulation.

Refilled soil cores represent a unnatural inhomogeneity and influence leaching (Kördel et al., 1991). Thus soil sampling during the study should be restricted to the tillage layer.

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# FATE OF $^{14}$C-TERBUTHYLAZINE IN OUTDOOR LYSIMETERS

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## ABSTRACT

Ring-labelled $^{14}$C-terbuthylazine-$^{14}$C was applied to lysimeters repacked with natural horizons of a sandy agricultural and a sandy forest soil. Leachate was collected for 262 days from a depth of 1 m and contained 0.612 and 0.059 %, respectively, of $^{14}$C applied. Less than 5 % of $^{14}$C in leachate was present as unchanged terbuthylazine. The major portion was highly polar, high-molecular weight compounds, probably residues bound to soluble humic substances. In spite of the uniform packing of the lysimeters, triplicates showed variations in hydraulic properties.

In addition to leaching, volatilization of the unchanged pesticide and its organic metabolites, as well as $^{14}CO_2$ resulting from mineralization, were measured. During the first 67 days, volatilization accounted for 0.5 % and mineralization for 5 % of the applied $^{14}$C. The volatilization and mineralization data are relevant to practical conditions because of the realistic simulation of wind velocity in the volatilization chamber.

## INTRODUCTION

For light-textured soils, differences between undisturbed soil monoliths and natural soil horizons repacked into lysimeters are minor compared to those in clay soils (Bergström, 1990). In this study, repacked lysimeters were used with soil horizons in natural sequence, whose natural bulk densities were restored, in order to avoid the large variations between replicates, that may occur if undisturbed soil cores are used.

## MATERIALS AND METHODS

Three lysimeters were filled with a sandy agricultural soil (brown soil with colluvium cover, 1.03 % organic carbon), and three lysimeters were filled with a sandy forest soil (podsol, 4.93 % organic carbon). Details are given in Schroll *et al.* in Chapter 3 of this volume. The test substance terbuthylazine - a member of the triazine class with a vapour pressure of $1.5 \times 10^{-4}$ Pa at 20°C - was applied at a rate of 890 g/ha. The $^{14}$C-ring-labelled pesticide (1 mCi per lysimeter) was dissolved in acetone, then mixed with the formulation "Gardoprim" (Ciba-Geigy AG) and applied in water at a volume rate of 1300 l/ha on the test surfaces.

Equipment to measure gaseous $^{14}C$ losses from $^{14}C$ terbuthylazine was installed to compare volatilization and mineralization losses with those in percolate water, as described in Schroll et al. in Chapter 3.

In the lysimeters containing the agricultural soil, maize (Zea mais) plants (10 plants per lysimeter) were sown on the 10th. of May 1990. In the lysimeters containing the forest soil, grass was grown.

## RESULTS AND DISCUSSION

### Leaching

The amounts of leachate collected over 262 days are shown in Fig. 1 (sandy agricultural soil) and Fig. 2 (sandy forest soil). In spite of the uniform repacking of the lysimeters, variations in the amounts of percolate water are evident. This shows that the hydraulic properties of the three lysimeters are not identical.

Figs. 3 and 4 present the concentration of $^{14}C$, equivalent to terbuthylazine, in leachate. They show that the concentration of $^{14}C$ in the leachate from the agricultural soil is about 10 fold higher compared to the forest soil. This probably is due to the higher organic carbon content of the forest soil. The total amount leached from the agricultural soil after 262 days was 0.612 % of $^{14}C$ applied and from the forest soil, 0.059 %. The analysis of $^{14}C$ leached from agricultural soil showed that less than 5 % of the radioactivity was present as unchanged terbuthylazine; the major part consisted of highly polar, high-molecular compounds, probably residues bound to soluble humic substances, as shown by gel chromatography (for details of analytical procedure, see Huber et al. 1992). On the basis of the ATP contents in different soil layers and in leachate, conversion probably occurred largely in the upper soil horizon.

## VOLATILIZATION AND MINERALIZATION

Volatilization from the agricultural soil into the atmosphere is shown in Fig. 5. It amounted to 0.49 % of the applied $^{14}C$ during the first 67 days (mean value of three lysimeters). After this time, volatilization discontinued and started again only one year later when the soil was tilled. Mineralization of $^{14}C$-terbuthylazine in the agricultural soil is presented in Fig. 6. It was 5.12 % of the applied $^{14}C$ during the same time (mean value of three lysimeters) and then stopped

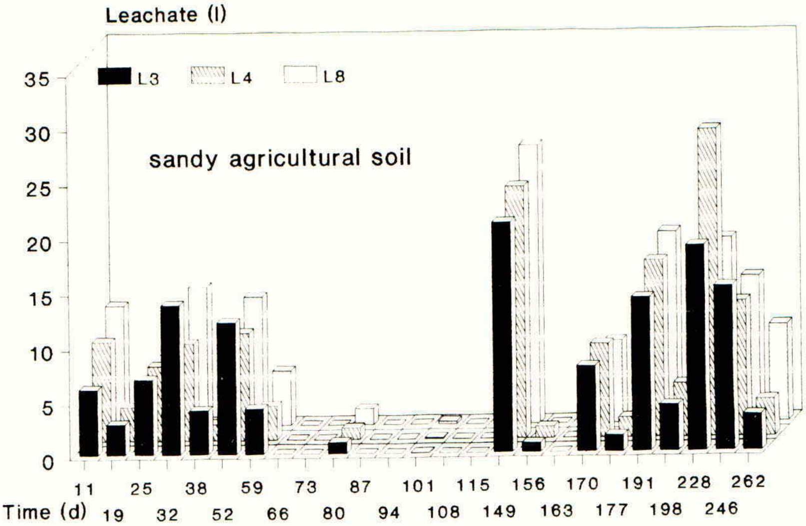

Fig. 1. Amounts of leachate from three lysimeters containing a sandy agricultural soil

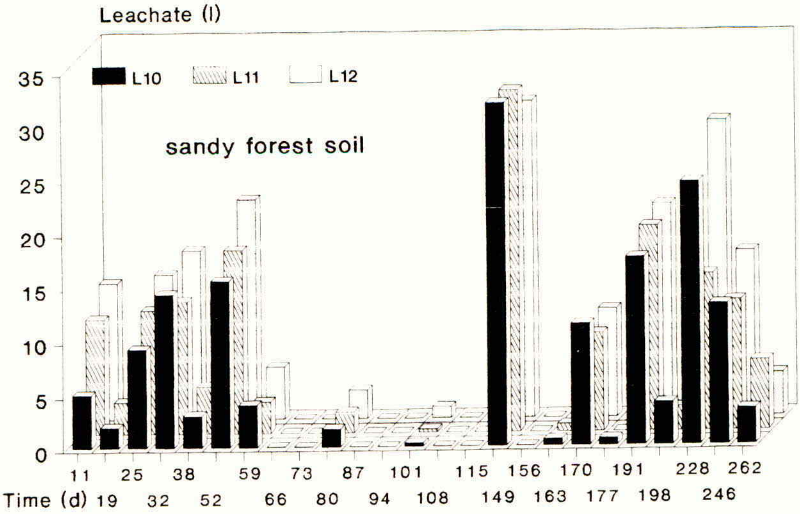

Fig. 2. Amounts of leachate from three lysimeters containing a sandy forest soil

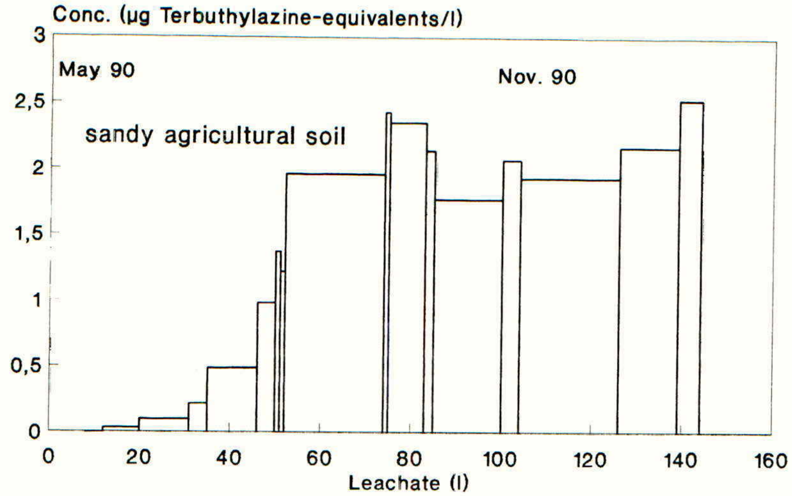

Fig. 3. $^{14}$C-Concentration (µg equivalent to terbuthylazine) in leachate from three lysimeters containing a sandy agricultural soil, following application of $^{14}$C-terbuthylazine to soil

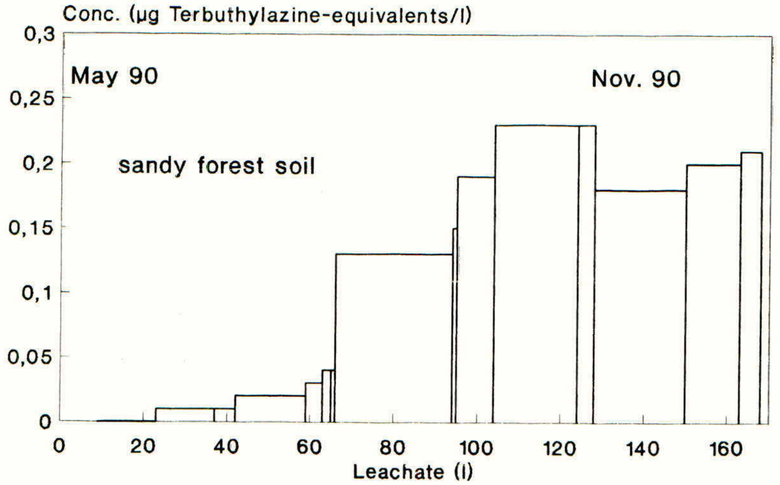

Fig. 4. $^{14}$C-Concentration (µg equivalent to terbuthylazine) in leachate from three lysimeters containing a sandy forest soil, following application of $^{14}$C-terbuthylazine to soil

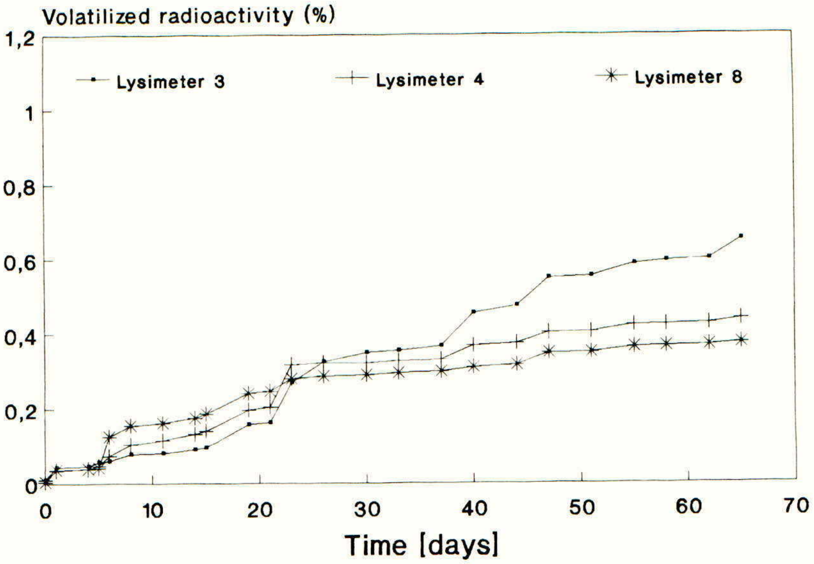

Fig. 5. $^{14}C$ volatilized from three lysimeters containing a sandy agricultural soil, following application of $^{14}C$-terbuthylazine to soil (in cumulative % of $^{14}C$ applied)

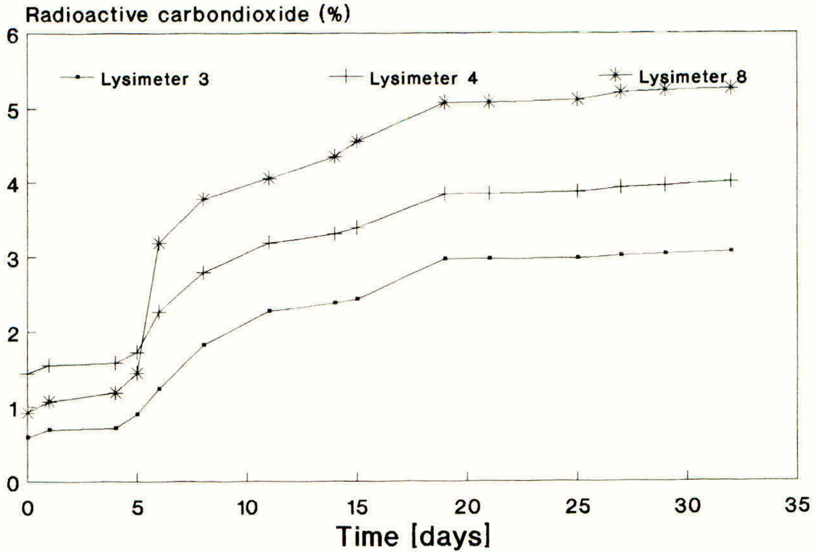

Fig. 6. $^{14}CO_2$ evolved from three lysimeters containing a sandy agricultural soil, following application of $^{14}C$-terbuthylazine to soil (in cumulative % of $^{14}C$ applied)

until tilling in the next year (Schroll et al., 1992). Since in the volatilization chamber a wind velocity similar to that measured on normal soil surfaces was produced, these data are relevant to the field situation.

## MASS BALANCE

The mass balance of $^{14}C$ after 67 days in the agricultural soil is presented in Table 1. The table shows that in this initial period after application mineralization is the most important process of dissipation of the residues in soil. However, since this process discontinues after 67 days and leaching (Figs. 1-4) continues, the latter process is more important for the long-term evaluation of the fate of terbuthylazine in soil. The removal of pesticide residues by plants cropping was not a major component of the mass balance.

The quantification of residues in soil in relation to the $^{14}C$ applied is extremely difficult due to the spatial variability of soil parameters and, thus, also of $^{14}C$-residues. Moreover, lysimeters were too small to allow destructive soil sampling during the experiment. Therefore, the figure for $^{14}C$ remaining in the soil in Table 1, was calculated only as the difference between $^{14}C$ applied and $^{14}C$ recovered in the other compartments.

TABLE 1. $^{14}C$-Mass balance 67 days after application of terbuthylazine-$^{14}C$ to a sandy agricultural soil (mean values of three replicates)

| | |
|---|---|
| Volatilization into the atmosphere: | 0.49 % |
| Mineralization to $^{14}CO_2$: | 5.12 % |
| Uptake by 10 maize plants: | 0.22 % |
| Leaching into percolate water (1 m depth): | 0.04 % |
| Parent compound + conversion products in soil: | ≈ 94 % |

## CONCLUSION

The described lysimeters show promise for the determination of pesticide losses from soil by leaching, volatilization, biomineralization and cropping.

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# FATE OF TWO SELECTED $^{14}$C-LABELLED COMPOUNDS IN PLANT AND SOIL AFTER REPEATED APPLICATION

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## ABSTRACT

The fate of glufosinate and dichlofluanid in a sandy loam and a silt loam planted with vine were investigated after repeated application during a three year period in lysimeters. In both experiments $^{14}$C losses occured due to the mineralisation of the labelling position. Most of the remaining radioactivity was detected in the 0-10 cm soil layers of both soils. Repeated application of the compounds did not lead to accumulation of residues. Investigation of wine prepared with grapes treated with dichlofluanid showed that no residues of the A.I. appeared in the wine.

## INTRODUCTION

In typical agricultural practice, a pesticide is applied to soils not only once, but often several times every year for a number of years (i.e. monocultures) or several times during the same vegetation period (i.e. viticulture). Repeated application may affect the long term behavior of the applied substances with regard to degradation, plant uptake, soil residues and leaching. In most experiments to study the fate of pesticides, the behavior of the compound in question after only a single application is examined. They often are carried out under standardized laboratory conditions. The results from these studies cannot be transferred to the field situation since it is known that the changing climatic conditions, the soil structure and the influence of plant roots may have a decisive effect on the fate of a compound under field conditions (Führ 1987, Kubiak et al. 1988) and especially investigation concerning the effect of repeated applications is not possible.

Field studies take this problem into account but provide only limited information since only unlabeled substances can normally be applied. Lysimeter studies with undisturbed soil cores as used in the Neustadt Research Center combine the advantages of the tracer technique with transferability to the field situation. Using this type of experiment, long term studies can be carried out to investigate pesticide behavior after repeated applications.

Considering that, especially in viticulture, most compounds are applied to the plant, contamination of soil during application and wash off from plants caused by precipitation also influence the total amount and fate of the compound in soil.
Depending on the physical and chemical properties of the active ingredient and the climatic conditions, the type of soil, its structure and microbial biomass may also affect the fate of a compound.

In the following, the fate of [3,4-$^{14}C$] glufosinate in two soils during a 1108 day period with five applications and the fate of [benzolring-U-$^{14}C$] dichlofluanid during a 1046 day period with 15 applications (5 per year) to vine is reported. For both experiments two soils were used, a sandy loam and a silt loam (Table 1), each planted with one grape vine (Vitis vinifera, var. Müller Thurgau).

Table 1: Chemical and physical data of the test soils (0-30 cm)

| | Sandy loam | Silt loam |
|---|---|---|
| $C_{org}$ [%] | 1.4 | 1.5 |
| Cat. exch. cap. [meq/100g] | 8.8 | 15.0 |
| pH [$CaCl_2$] | 6.8 | 7.4 |
| Clay (%) | 7.6 | 20.2 |
| Silt (%) | 23.7 | 59.2 |
| Sand (%) | 68.7 | 20.6 |

## FATE OF $^{14}C$-GLUFOSINATE (Kubiak 1990, 1991)

The ammonium salt of glufosinate (200 g A.I./l as "Basta", Hoechst AG) is a herbicide for weed control in vines and cereals. The amounts applied in the experiment corresponded to the maximum quantity allowed for field application in Germany (Table 2). They were used for two lysimeters, one filled with an undisturbed soil profile of a sandy loam and the other filled with an undisturbed soil profile of a silt loam. The radioactive solutions were sprayed on the soil surface of the lysimeters.

Table 2: Amounts of glufosinate applied during the experimental period

| Application No. | Date | Day | Amount used for application A.I./lys. mg | spec. radioact. kBq/mg | amount/ha l Basta |
|---|---|---|---|---|---|
| 1. | May 25, 87 | 0 | 112 | 805 | 7.5 |
| 2. | July 15, 87 | 51 | 73 | 805 | 5.0 |
| 3. | May 24, 88 | 364 | 110 | 833 | 7.5 |
| 4. | July 14, 88 | 415 | 73 | 833 | 5.0 |
| 5. | Sep. 09, 88 | 472 | 71 | 776 | 5.0 |

The application losses and the resulting amounts actually applied to the lysimeters are given in table 3. Soil sampling was carried out 130, 361, 471, 522, 742, 856, and 1108 days after the first application.

During the whole experimental period most $^{14}C$ residues remained in the 0-10 cm soil layer of both lysimeters.

Table 3: Application losses and amounts applied

| Application no. | Lysimeter 1 |  |  | Lysimeter 2 |  |  |
|---|---|---|---|---|---|---|
|  | loss | applied |  | loss | applied |  |
|  | % | MBq | mg A.I. | % | MBq | mg A.I. |
| 1 and 2 | 6.4 | 139 | 173 | 6.8 | 135 | 168 |
| 3 and 4 | 4.8 | 145 | 174 | 3.6 | 147 | 177 |
| 5 | 6.9 | 52 | 66 | 6.1 | 52 | 67 |

Radioactivity in the 10-20 and 20-30 cm soil layers was less and in the 30-40 cm soil layers of both soils accounted for less than 1% of the total radioactivity applied. Investigation of the whole soil profiles at the end of the study confirmed the low degree of translocation of $^{14}C$ compounds to the deeper soil layers. Figure 1 gives an overview of the experimental results on the base of the total radioactivity applied during five applications.

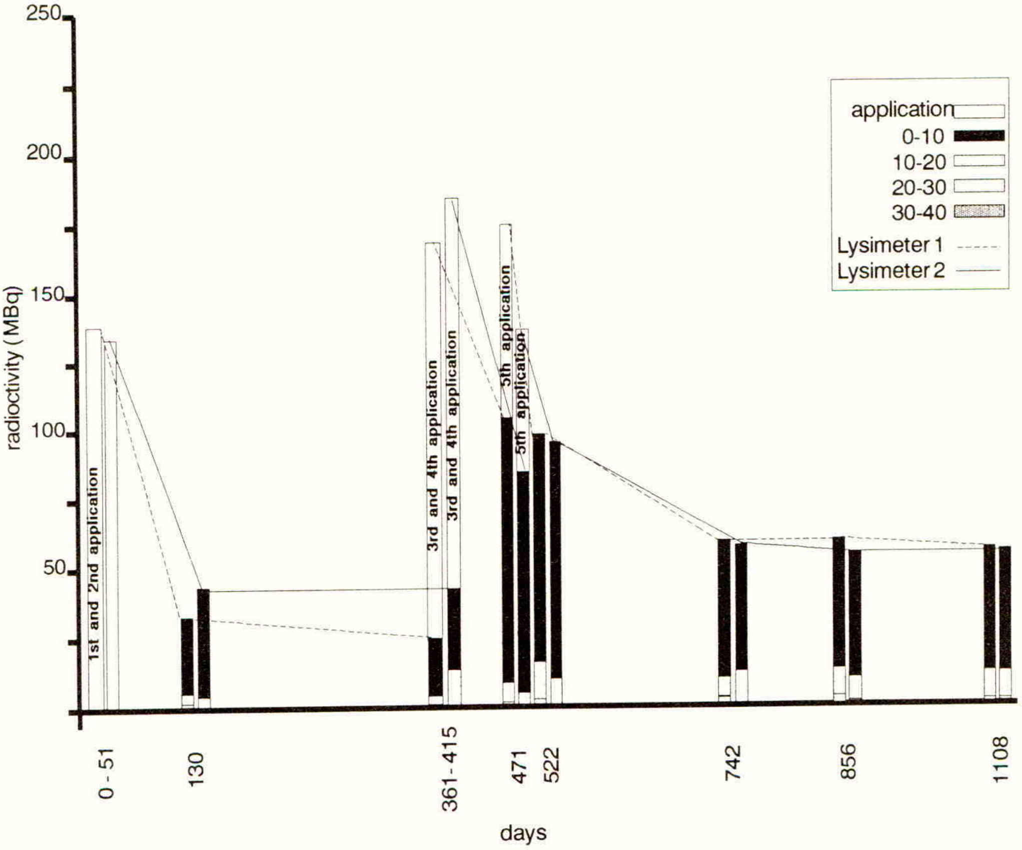

**Figure 1:** Experiments with glufosinate
$^{14}C$-residues in soil of lysimeter 1 and 2

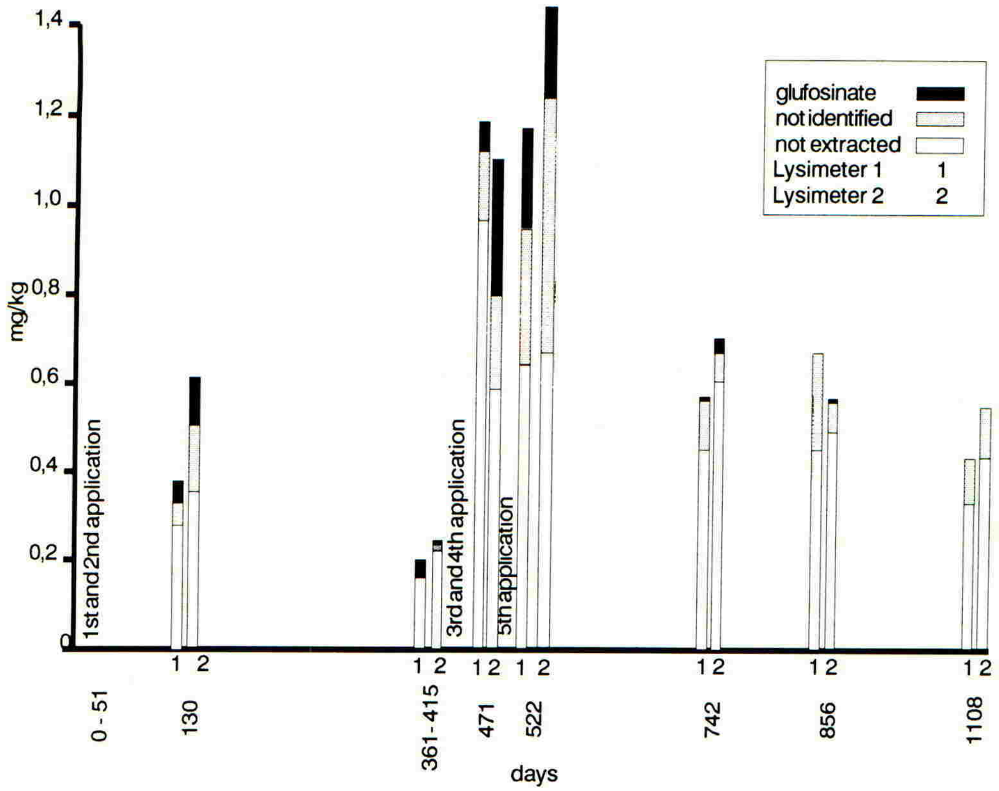

**Figure 2:** Experiments with glufosinate
Extraction results of the 0-10 cm soil layer of lysimeter 1 and 2

Since most of the remaining radioactivity was localized in the 0-10 cm soil layers, samples were extracted and determined by TLC. The results are given in Figure 2. The data indicated that the glufosinate residues were low during the whole experimental period. After 1108 days no further residues were detected in either lysimeter. At this last sampling date additional extractions of all soil layers down to a depth of 1.2 m showed the same result. Most $^{14}C$-residues could not be extracted, they were responsible for the slight increase in total residues from 0.4 mg/kg A.I. equivalents after 130 days to 0.6 mg/kg A.I. equivalents at the end of the study in the sandy loam. In the silt loam, no increase in the total residue concentration was observed with time.

$^{14}C$-losses due to uptake by vines and weeds were less than 1% of the total $^{14}C$ applied. Experiments from Goetz et al. (1992) indicated that the compound is degraded very fast in the soil so that most of the losses were due to mineralization of the labelling position.

In both soils, the greatest loss of radioactivity occurred during the first weeks after application because the bioavailability and biodegradability of the applied compound is high immidiately after spraying and temperature and moisture conditions are favourable for microorganisms in spring and autumn. During winter the $^{14}C$-losses were smaller. As found with other compounds (Kubiak et al. 1988), the largest amount of radioactivity was always localized in the 0-10 cm soil layers, regardless of the type of soil used (Figure 1). Analysis of samples taken from these soil layers showed that only a small amount of the total $^{14}C$-residues was still present as glufosinate in both soils (Figure 2). No active ingredient was determined 856 and 1108 days after the 1st application in the sandy loam, or after 1108 days in the silt loam (Figure 2). Some of the radioactivity consisted of unidentified compounds which were degraded to $^{14}CO_2$ with time (Figure 2). Another part of the radioactivity which was not extractable became mineralized with time in both soils indicating that some of the non-extractable $^{14}C$-compounds became bioavailable again.

Thus, no increase in the active ingredient and other extracted radioactive compounds was observed in either soil after five applications of glufosinate. Also there was no significant increase in the non-extracted $^{14}C$-residues in either soil because part of the bound residues was degradable with time.

The results show that repeated application of large amounts of glufosinate to soils do not lead to an accumulation of residues in the top soil layer. The transfer of $^{14}C$-compounds to deeper soil layers was also limited under field conditions.

## FATE OF $^{14}C$-DICHLOFLUANID (Kubiak & Eichhorn 1990)

To investigate the residues of dichlofluanid the active ingredient formulated as "Euparen" (50% WP, Bayer AG) was sprayed on four vines, growing in four different lysimeters five times a year during a three year period. The dates of application and the amounts applied were in line with viticultural practice. Five applications per year represent a maximum which is only applied when infestation of *Botrytis cinerea*, *Plasmopara viticola* or *Phomopsis viticola* is significant (Table 4). Radioactivity in different soil layers and the remainig $^{14}C$-compounds in plants were investigated and wine was prepared in the second and third experimental year to investigate $^{14}C$-residues in wine. The results showed that only 0.9 to 2.6% of the radioactivity applied was present on the plants 35 days after the last

Table 4: Amounts of $^{14}C$ and dichlofluanid applied

| Lysimeter | 1st test year | | 2nd test year | | 3rd test year | |
|---|---|---|---|---|---|---|
| | MBq | mg A.I. | MBq | mg A.I. | MBq | mg A.I. |
| 1 | 94 | 1124 | 137 | 1513 | 129 | 1549 |
| 2 | 101 | 1116 | 127 | 1388 | 132 | 1590 |
| 3 | 99 | 1207 | 137 | 1499 | 125 | 1498 |
| 4 | 111 | 1250 | 127 | 1380 | 133 | 1597 |

application, mainly present on the leaves. Radioactivity on grapes was 0.1 to 0.7% (Table 5).

<u>Table 5:</u> Distribution of radioactivity in grape vines
(Radioactivity applied = 100%)
(Average value of four lysimeters)

| Test year | Leaves | Tips and wood | Grapes |
|---|---|---|---|
| | % | % | % |
| 1 | 0.6 | 0.2 | 0.1 |
| 2 | 1.6 | 0.0 | 0.7 |
| 3 | 2.2 | 0.1 | 0.5 |

After making wine about 70% of the radioactivity of the grapes remained in husks and dregs (Table 6)

<u>Table 6:</u> Balance sheet of wine preparation
(Radioactivity in grapes = 100%)
(Average value of four lysimeters)

| | 2nd test year | 3rd test year |
|---|---|---|
| | % | % |
| Husks, dregs | 71.1 | 69.3 |
| $^{14}CO_2$ | 0.0 | 0.1 |
| Wine | 28.9 | 30.6 |

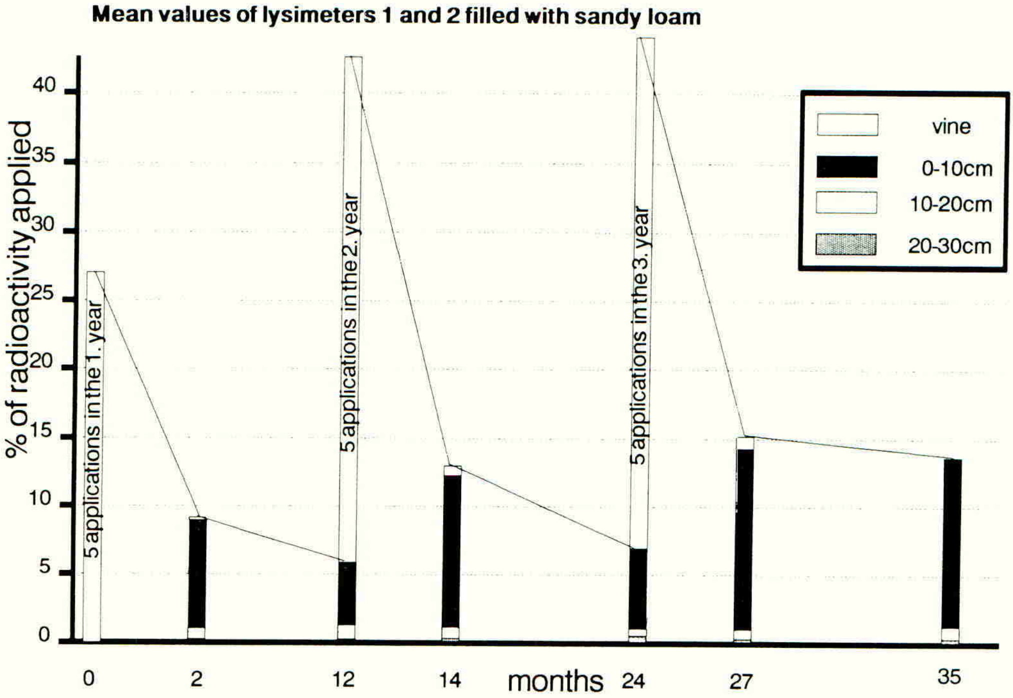
**Mean values of lysimeters 1 and 2 filled with sandy loam**

**Figure 3:** Experiment with dichlofluanid
$^{14}C$-residues in vine and sandy loam

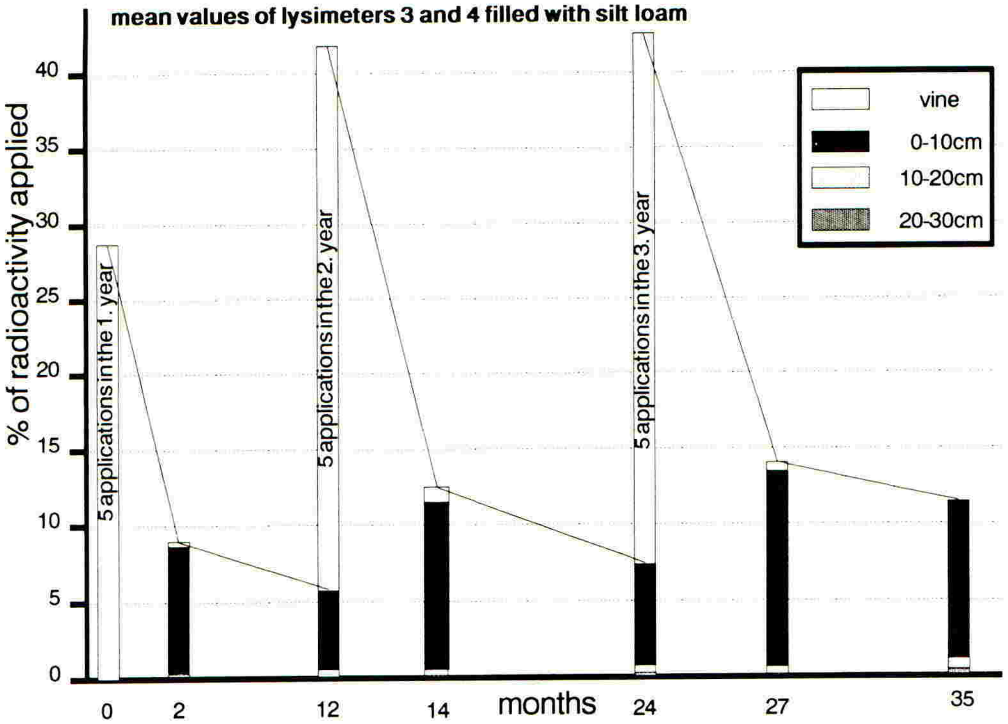

Figure 4: Experiment with dichlofluanid
$^{14}C$-residues in vine and silt loam

Further investigation of the wine prepared showed that no dichlofluanid was present. Only the main metabolite dimethylaminosulfanilide was determined in concentrations of 0.5 and 0.8 mg/l representing 0.05 and 0.07% of the total radioactivity applied. Total balance sheets for soils and plants during the whole experimental period showed that most of the radioactivity still available had reached the soil and was present in the 0 to 10 cm soil layers of both test soils (Fig. 3, 4). This radioactivity no longer represented the active ingredient. The losses of $^{14}C$ amounted to about 85% of the total radioactivity applied and were mainly due to mineralisation of the compound which has a short half life of 6 to 9 days.

The results show that after application of dichlofluanid only small $^{14}C$-residues remained on the plants. $^{14}C$ residues on grapes were further reduced during wine preparation and no dichlofluanid was present in the wine, 35 days after the last application. Most of the remaining $^{14}C$ in the lysimeter was detected in the 0 to 10 cm soil layer but was not present as the active ingredient any more.

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# LYSIMETER STUDIES RELEVANT TO THE FATE OF PESTICIDES IN THE SOIL

## EXPERIMENTAL LIMITATIONS/CONCLUSIONS

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## ABSTRACT

Although lysimeter studies with $^{14}C$-radio-labelled pesticides can produce valuable results for the assessment of their mobility in soil the following factors should be taken into consideration:
- moisture content of the soil in lysimeters tends to be lower then in natural field plots -only vertical flow in the lysimeter - significant radioactive back ground levels of 0.05 µg/l - soil heterogeneity - inhomogenous application at 1m² - difficulties in seperation and characterisation of trace level residues due to relatively high concentration of TOC.

Therefore the final step in evaluating mobility should be a groundwater monitoring.

## INTRODUCTION

For the assessment of the mobility and the long-term behaviour of pesticides and their metabolites in soil, a step-wise testing and evaluation scheme is commonly used. Physical-chemical data (solubility in water, $k_d$ and $k_{oc}$-values in soil) parent and aged leaching experiments on artificially filled columns are taken into account together with estimations by computer modelling, which also include application rate, half-life in soil and a lot of climatic and soil data. These considerations may indicate the need for a lysimeter study. Lysimeter studies with $^{14}C$-labelled active ingredient produce a large amount of information about the behaviour of the pesticide in the soil/plant system under field conditions. Nevertheless, some experimental limitations and conclusions have to be considered when evaluating their results.

## SIMULATION OF THE WATER BALANCE OF FIELD CROPS

The small area of lysimeters (0.5 to 1.0 $m^2$) requires expert care and attention including protection against pests and diseases to ensure good growth of the crops. Only in this way is it possible to obtain the same net amount of leachate which occurse in the field. This has to be considered when comparing lysimeter leaching results with the situation in the field.

However, even if the cultivation of crops in a lysimeter is comparable to a field situation the resulting net amount of leachate in lysimeters is a worst case situation. In contrast to the field, where the crops are able to use some of the water which has reached a depth of more than 1 m, the leachate from the lysimeter is constantly removed from the soil core.

Furthermore, in the type of lysimeter used today the leaching behaviour of substances can only be evaluated in the vertical direction. The water balance and the movement of dissolved matter coused by different slopes in a field can not be determined.

## EVALUATION OF THE RADIOCTIVITY IN THE LEACHATE

Using $^{14}C$-tracer techniques the exact determination of residues of a pesticide in the leachate requires that the natural radioactivity always present in the sample is known. This so-called "back-ground" results particularly from the natural radioactivity content of rainwater which leaches through the soil core together with contributions from the mineral constituents of the soil.

Our measurements over several years have shown that the back-ground values are by no means constant and can vary in the range from 5 Bq/l to more than 35 Bq/l. It is true that in absolute terms this radioactivity content is quite low. However, when considering the EC drinking water limit value of 0.1µg/l , and a specific radioactivity of 1 MBq per mg test substance (which is a relatively high value), the back-ground alone would be equivalent to 5 to 35 % of the EC limit value as the total residue of a pesticide. The use of material with a lower specific activity is not recommended as it would cause greater uncertainty.

## BALANCE OF THE RESIDUES IN THE SOIL CORE

The inhomogeneous distribution of residues in the top soil layers causes great problems in the evaluation of the total residues of a pesticide in the lysimeter during as well as after the end of the test period.

Some differences in homogeneity result from the spray application at the start of the experiment. In the case of a seed dressing this inhomogeneous distribution is inevitable and extremely high. Additionally, crop cultivation, preparation of the seed bed and harvesting may lead to further inhomogeneity. Depending on the cultivated crops (e.g. sugar beet) and the selected crop rotation, these influences can be important down to a depth of 30 cm. Earthworm activity, water and wind movement on the surface, more intensive uptake by plants or metabolism in the vicinity of their roots can increase inhomogeneous distribution over a long test period.

For these reasons, the results obtained from a few small soil samples may cause great errors when extrapolated to estimate the total residues of the soil core. For the first three top layers of the lysimeter (0-30 cm) we would like to recommend that the total balance of residues should be calculated by the results of aliquots from the thoroughly mixed total soil layers.

The amounts of radio-labelled substances which are emitted into the air by mineralisation, volatility or wind erosion, can not be recorded at all. Therefore, calculation of the total balance of a lysimeter experiment is not possible.

## UNKNOWN POLAR RADIOACTIVITY IN THE LEACHATE

Using $^{14}C$-tracer techniques the identification of unknown, mostly very polar radioactivity in the leachate makes great demands on analytical and spectroscopic techniques. The results from lysimeter studies have shown that, depending on the properties of the applied pesticide, the radioactivity measured in the leachate is in most cases not identical with the applied parent compound or any of its known metabolites. The dimensions of naturally occuring ingredients in the leachate taken from a loamy sand  a depth of meters are summarized in the following table.

Table 1: Concentration of selected compounds in leachate
(total from one year)

| Item | Concentration (µg/l) |
|---|---|
| Chloride | 60.000 |
| Nitrite-N | < 100 |
| Nitrate-N | 144.900 |
| Ammonium-N | < 500 |
| Sulfate | 144.000 |
| TOC | 7.000 |
| Total residue expressed as Al equivalents | 0,070 |
| **Ratio TOC/radioact. residue** | **100.000 : 1** |
| pH-value: 6.3 | |

Besides the measured values of the anions listed in Table 1 the leachate contains corresponding amounts of cations.

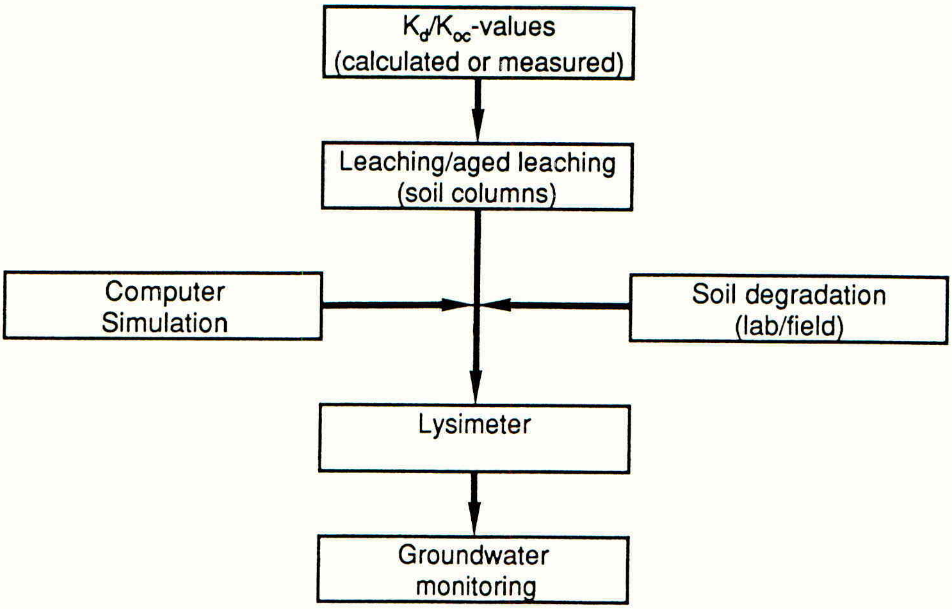
It should be a primary task of basic sientific research to elaborate, in which form and chemical structure the occurring TOC-content (surplus factor 100.000 here; about 40.000 in ground-water) is present in the leachates of lysimeters. Only then will we be able to assess whether

- a radioactively labelled compound, which behaves like the natural TOC, originates  from the metabolism of the applied pesticide
  or
- whether the radioactive carbon has already been included into the natural cycle of  carbon in the soil.

Based on the present state of scientific knowledge, proof can only be obtained by methods of exclusion, i.e. by showing that known metabolites are not present.

## CONCLUSIONS

Lysimeter studies with $^{14}C$-radio-labelled active ingredient can produce excellent results for the assessment of the mobility of pesticides in soil. Nevertheless, the afore-mentioned experimental limitations and conclusions have to be considered when evaluating their results. If there are still some questions left open, the last steps in the evaluation procedure of a pesticide should be field trials under practical conditions and long-range and long-term groundwater monitoring programs. Therefore, the following procedure is reasonable:



# THE USE OF LYSIMETERS TO STUDY THE FATE OF AN EXPERIMENTAL PESTICIDE FOLLOWING AUTUMN AND SPRING APPLICATION TO WINTER CEREALS.

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## ABSTRACT

The results of a lysimeter experiment with an experimental compound for both autumn and spring use in cereals are described in this paper. Undisturbed soil monoliths of a sand and medium loam over clay were used and treatments were made in December 1989 and March/April 1990. The distribution of parent and metabolite in the leaching water samples collected throughout the first year of the experiment and in soil collected at the end of the first year are presented. The results show differences in the behaviour of the compound in the 2 soil types and also show significantly more leaching following an autumn application.

## INTRODUCTION

Undisturbed soil monolith lysimeters at the DowElanco Research and Development laboratory have been used to study the fate and behaviour of an experimental pesticide under proposed agricultural use practices. The system has been described in chapter 3. The experiment was conducted broadly in accordance with the BBA guideline for lysimeter studies (Fuhr **et al.**, 1990). Laboratory testing had shown the pesticide to be moderately persistent and to have moderate mobility. The experiment was designed to study both the spring (major market) and autumn useage of the pesticide in 2 soil types (sand as specified in the BBA guideline and medium loam over clay [mloc] of a type that is more typical of UK cereal soils). 8 lysimeters were treated in total (4 of each soil type) with 1 of each soil type treated in autumn and the remainder treated in the following spring. All lysimeters had a winter barley crop during the first year. Only data from the first years work will be presented here and for reasons of confidentiality, no structures, application rates, absolute concentrations etc. can be given.

## EXPERIMENTAL

### Preparation and maintainance of lysimeters

The lysimeters were cultivated, fertilised (NPK, 9/24/24 at 250 kg/ha) and drilled with winter barley (variety Panda at 200 kg/ha) on 13 October 1989. Additional fertiliser was added the following spring (split dressing of Nitram, 100 kg/ha in March and 200 kg/ha in April) and the crop was harvested on 17 July 1990.

### Treatment

The radiolabelled pesticide (2.23 - 3.26 MBq) was formulated as a suspension concentrate and was dispersed in tapwater to give a spray volume equivalent to 400 l/ha. An extra 10-15% of spray solution was prepared to allow for losses during application and resulted in 23 ml of spray solution per lysimeter. Treatments were made using hand pumped garden sprayers in autumn and spring. The early spring treatments were duplicated for the first year. Treatment details are summarised in Table 1.

TABLE 1. Lysimeter soil types and treatment dates.

| Lysimeter | Soil type | Treatment date |
|---|---|---|
| A | sand | 6/12/89 |
| B | mloc | 6/12/89 |
| C | sand | 21/03/90 |
| D | sand | 21/03/90 |
| E | sand | 3/04/90 |
| F | mloc | 21/03/90 |
| G | mloc | 21/03/90 |
| H | mloc | 3/04/90 |

## Water samples

Water samples were collected in 25 l reservoirs connected to each lysimeter. These were emptied at least weekly when leachate was available and more frequently in response to heavy rains. The volume and pH of the samples was measured immediately upon collection and the gross radioactivity was determined by direct Liquid Scintillation counting (lsc). Bulk samples were also prepared which were representative of the total leachate collected over the first year and these were also analysed. The samples were stored at ca. -20°C prior to further analysis. The distribution of radioactivity in the bulk samples and in selected samples was determined by passing aliquots of leachates through pre-washed $C_{18}$ Sep-Pak cartridges, eluting with methanol/acetic acid reagent (50:1 v/v), concentrating the eluate on a nitrogen line and submitting the samples for thin layer chromatography analysis (tlc) against reference standards of known structure.

## Soil samples

Soil cores were taken from selected lysimeters after the first harvest. The cores (50 mm diam. x 50 cm depth) were subdivided into 10 cm horizons for analysis. Samples were stored at ca. -20°C prior to analysis. The gross radioactivity in these samples was determined by combustion of aliquots of soil (ca. 300 mg) in a Harvey Biological Materials Oxidiser (Harvey Instument Corp.,Hillsdale, New Jersey, USA.), trapping the resulting $^{14}CO_2$ and quantifying this by lsc. The nature of the radioactivity was determined by extracting aliquots of the soil with acetonitrile/water/1M HCl (3 x 100 ml portions, shake, centrifuge , then combine extracts). Portions of the extract were concentrated and submitted for tlc analysis.

### Crop samples

The cereal crops were harvested and separated into grain, straw and root fractions. These were processed into a fine powder using a hammer mill prior to analysis by combustion to determine the gross distribution of radioactivity. To date no further analysis has been conducted on these samples.

### Irrigation

During the summer of 1990, the measured rainfall at Letcombe fell significantly below the monthly averages for Hamburg so it was necessary to irrigate the lysimeters with an equivalent of 230 mm of rain (115 l per lysimeter). Where possible this was done during a rain event.

## RESULTS AND DISCUSSION

The monthly air temperature, rainfall and irrigation data for the period December 1989 to March 1991 are summarised in Table 2. Rainfall between December and March was 763.1 mm and, with irrigation was brought up to 993.1 mm. The average monthly air temperature ranged between 2°C in February 91 and 21°C in July 90.

TABLE 2. Average monthly air temperature, rainfall and irrigation (dec 89 - mar 91).

| Month | Temperature (°C) | Rainfall (mm) | Irrigation (mm) |
|---|---|---|---|
| Dec. | 6.0 | 134.7 | 0.0 |
| Jan. | 7.7 | 89.8 | 0.0 |
| Feb. | 8.2 | 113.8 | 0.0 |
| Mar. | 9.1 | 21.9 | 0.0 |
| Apr. | 8.6 | 32.1 | 0.0 |
| May. | 13.7 | 10.5 | 0.0 |
| Jun. | 17.4 | 27.8 | 32.0 |
| Jul. | 20.2 | 24.7 | 70.0 |
| Aug. | 21.4 | 24.5 | 70.0 |
| Sep. | 16.5 | 30.2 | 44.0 |
| Oct. | 13.2 | 53.3 | 14.0 |
| Nov. | 6.1 | 21.6 | 0.0 |
| Dec. | 3.8 | 58.6* | 0.0 |
| Jan. | 3.6 | 38.1 | 0.0 |
| Feb. | 1.9 | 21.3 | 0.0 |
| Mar. | 6.7 | 60.2 | 0.0 |

* Fault with rain gauge, value low.

The application rates to the lysimeters were within 91-108% of the theoretical field rate for the test compound. Of the applied chemical an estimated average of 16% of the dose was intercepted by the crop treated in autumn and an estimated 49-93% for plants treated in spring.

The leachate volumes collected during the first year and % of applied radioactivity present as parent or metabolite in the leachates from the various treated lysimeters are summarised in Table 3. The residues in leaching water from lysimeters A and B,

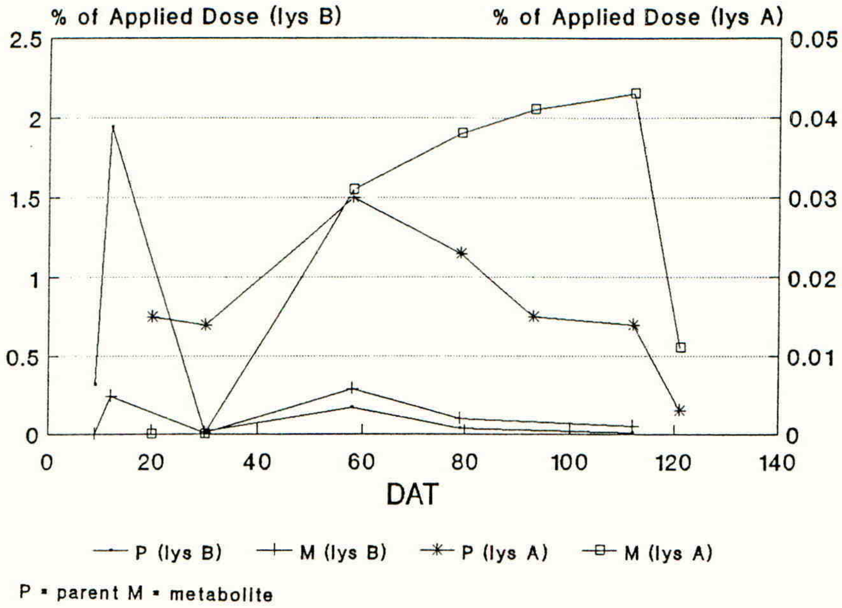

Figure 1. The distribution of Parent and Metabolite with time in selected leachate samples from Lysimeters A and B.

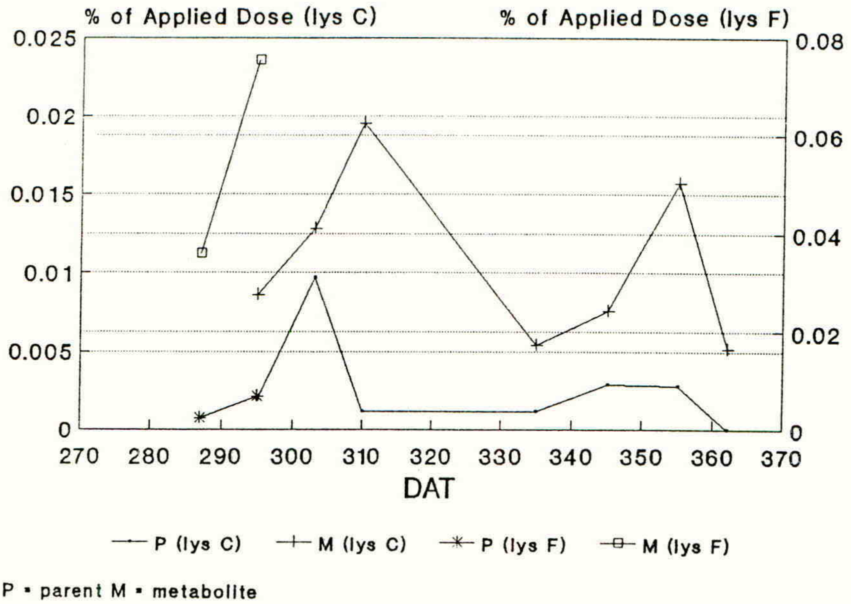

Figure 2. The distribution of Parent and Metabolite with time in selected leachate samples from Lysimeters C and F.

following an autumn application, are significantly greater than those observed for C and F and represent the movement of chemicals downwards through the soil profile during the winter months with recharge water. The leaching profiles (Figure 1) show that the sum of the various inhomogeneities (eg. pore flow versus macropore flow and microbial degradation rates) is different in the 2 lysimeters. The sand shows a steady increase in the amount of parent leached until a maximum is reached ca. 110 DAT. The metabolite appears to be more mobile, reaching a maximum after 60 days. The mloc shows a maximum for the parent within 20 days (the first major rainstorm and leaching water collection was 8-9 DAT) followed by a steady decline. By contrast, the metabolite maximises after ca. 60 days. These patterns are consistent with "pore flow" in the sand where water moves slowly through the pore structure of the soil and "by-pass" flow in the mloc where water movement is preferentially through channels in the soil profile, in this instance through earthworm and root channels. Lysimeters C and F (Figure 2) both show greater amounts of metabolite than parent which is consistent with long residence times in the soil (with associated metabolism) before being dissolved in soil solution and moved to the leachate. The profile for the sand shows a steady "bleed" of chemical through the profile and is also consistent with pore flow.

TABLE 3. Leachate volumes and % parent and metabolite measured during the first year.

| Lysimeter | Leachate vol. (l) | % Parent | % Metab. |
|---|---|---|---|
| A | 173.3 | 0.52 | 0.68 |
| B | 156.9 | 8.42 | 3.81 |
| C | 127.2 | 0.04 | 0.15 |
| D | 155.7 | 0.12 | 0.39 |
| E | 151.8 | 0.10 | 0.46 |
| F | 101.7 | 0.07 | 0.17 |
| G | 147.6 | 0.25 | 0.28 |
| H | 119.9 | 0.06 | 0.08 |

The distribution of parent and metabolite in the soil profiles (to 50 cm depth) taken from selected lysimeters after the harvest of the first crop are shown in Table 4. These residues also show trends that can be related to application timing and to soil type. The autumn treated sandy lysimeter (A) showed relatively low residues of parent in the top 50 cm but the metabolite was present in greater amounts and had moved to 50 cm and probably further. The autumn treated mloc lysimeter (B) on the other hand had greater residues of parent which together with the metabolite were tied up in the top 20 cm of the soil profile. These observations are also consistent with the mechanisms for water movement postulated above because mobile residues in the sand would have to pass steadily through the soil profile whereas, in the mloc, residues are well dispersed in the top 20 cm (plough layer) and then travel through discrete channels to the bottom of the profile. The spring applied lysimeters (C and F) both have higher residues of parent and comparable levels of metabolite to those observed following autumn application, both of which are associated with the top 10 cm of the profile. This lack of movement of residues is entirely consistent with the net water movement being upwards during the summer months due to evapotranspiration exceeding precipitation.

TABLE 4. Distribution of parent and metabolite in the soil profile of selected lysimeters after the first harvest.

| Lysimeter | DAT | Horizon | % Parent | % Metab. |
|---|---|---|---|---|
| A | 240 | 0-10 | 0.40 | 0.15 |
| | | 10-20 | 0.28 | 0.93 |
| | | 20-30 | 0.00 | 1.75 |
| | | 30-40 | 0.00 | 4.31 |
| | | 40-50 | 0.71 | 7.22 |
| B | 240 | 0-10 | 1.57 | 1.09 |
| | | 10-20 | 1.06 | 1.61 |
| | | 20-30 | 0.20 | 0.28 |
| | | 30-40 | 0.04 | 0.19 |
| | | 40-50 | 0.00 | 0.15 |
| C | 135 | 0-10 | 3.83 | 3.35 |
| | | 10-20 | 0.47 | 0.56 |
| | | 20-30 | 0.20 | 0.31 |
| | | 30-40 | 0.76 | 0.62 |
| | | 40-50 | 0.27 | 0.36 |
| F | 135 | 0-10 | 7.32 | 6.40 |
| | | 10-20 | 0.48 | 0.93 |
| | | 20-30 | 0.34 | 0.84 |
| | | 30-40 | 0.24 | 1.01 |
| | | 40-50 | 0.20 | 0.57 |

Parent and metabolite expressed as % of applied radioactivity.

The gross radioactivity distribution in the crop samples taken at harvest are presented in Table 5. The crop results show a strong correlation with application timing with lower residues in straw and roots following the autumn application (average 0.02 and 0.38% resp.) compared with spring (0.09 and 5.71%). Residues in grain were approximately the same for all treatments. Slightly higher residues were observed for the sandy soils.

TABLE 5. Distribution of radioactivity in plant fractions taken at harvest.

| Lysimeter | % in Grain | % in Straw | % in Roots |
|---|---|---|---|
| A | 0.01 | 0.02 | 0.45 |
| B | 0.02 | 0.02 | 0.30 |
| C | 0.02 | 0.06 | 5.33 |
| D | 0.02 | 0.08 | 11.05 |
| E | 0.02 | 0.16 | 3.65 |
| F | 0.02 | 0.06 | 5.80 |
| G | 0.02 | 0.06 | 5.73 |
| H | 0.01 | 0.08 | 2.70 |

Data expressed as % of applied radioactivity.

## CONCLUSION

The data show the distribution of radiotracer between the crop, soil and water fractions after one growing season and marked trends are observed that relate to the timing of the application. Generally, there are lower crop and soil residues but higher water residues following an autumn application with the reverse pattern obtained for the spring application. In the autumn applications trends are also observed that relate to soil type and the mechanism of water movement through the soils. The sandy soil showed a leaching profile that was consistent with pore flow for water movement while the mloc leaching profile was consistent with by-pass or macro-pore flow. The mechanism for water movement was less important for the movement of chemicals through the soil profile after the spring application.

When assessing the significance of results of this type there are a number of important considerations; 1) Concentrations of pesticides measured in the leaching water are not the same as concentrations in groundwater because there are additional dilution effects due to water from untreated parts of a catchment and also limited market shares for individual pesticides. 2) Certain scenarios studied in lysimeters may not occur very frequently in nature. For example, the mloc lysimeters will only be a significant model for aquifer contamination where the clay layer at the bottom of the profile is not thick enough to form an impermeable layer and the underlying soil is porous (eg. sandstone, limestone or fractured chalk). In these limited cases rapid by-pass flow through the loam and clay and into the porous material could lead to contamination of groundwater.

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# LEACHING STUDIES OF PESTICIDES IN SWEDISH SOILS MEASURED IN FIELD LYSIMETERS

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## ABSTRACT

A selection of Swedish pesticide leaching studies carried out in monolith field lysimeters are described. The pesticides (bentazon, chlorsulfuron, clopyralid, dichlorprop, fluroxypyr and metsulfuron) are all considered to be fairly mobile based on information obtained in laboratory experiments. It was shown that soil properties generally had a larger influence on amounts of pesticides leached than the physico/chemical properties of the compounds. Leaching was commonly larger in clay monoliths than in sand monoliths, due to macropore flow in the former. A more pronounced macropore flow was also thought to be the main reason why pesticide leaching could be larger in clay monoliths treated with a small compared to a large water input. To get a more complete picture of pesticide leaching, the use of a nonadsorbed, nondegrading tracer is recommended, as are investigations of soil chemical/biological properties critical for pesticide fate and mobility in deeper soil layers. Attention was also focused on the importance of correctly evaluating the significance of measured concentrations and loads of pesticides in lysimeter leachate in terms of actual field conditions.

## INTRODUCTION

To characterize the mobility of pesticides in soils, it is still common practice to conduct well controlled, short-term laboratory tests, often simulating a "worst-case" scenario. It is even more common simply to determine physico/chemical properties of pesticides (e.g. adsorption constants and water solubilities) and degradation rates in soil, and based on such information predict leachability (Tooby & Marsden, 1991). However, the environmental conditions in such tests are quite different from natural field conditions so that mobility of a compound estimated in such laboratory tests may not reflect its behaviour in the field. Results obtained in properly established lysimeter experiments have demonstrated that they can simulate actual field conditions with respect to leaching of pesticides in soil (Kubiak *et al.*, 1988). However, results obtained in field lysimeters also have to be interpreted correctly in order to represent field situations and to be valid as a basis for carrying out proper risk assessments.

In the presentation below, a selection of Swedish pesticide dissipation experiments carried out in monolith lysimeters are

TABLE 1. Soils, amounts of precipitation + irrigation, leachate volumes and experimental treatments of some Swedish lysimeter studies.

| Herbicide | Dose $(g\ ha^{-1})$ | Soil | Irrig. treat. | Prec.+Irr. (mm) | Leach. vol. (mm) |
|---|---|---|---|---|---|
| **Chlorsulfuron** | 4/8 | Sand (Kjet.)[a] | A[b] | 447 | 89 |
| **Metsulfuron** | 4/8 | Sand (Kjet.)[a] | A[b] | 447 | 86 |
| **Dichlorprop** | 1600 | Sand (Mellby) | A[b]/WC[c] | 518/603 | 79/142 |
|  | 1600 | Clay (Lanna) | A[b]/WC[c] | 518/603 | 158/196 |
| **Bentazon** | 600 | Sand (Mellby) | A[b]/WC[c] | 583/619 | 124/250 |
|  | 600 | Clay (Lanna) | A[b]/WC[c] | 583/619 | 268/280 |
| **Clopyralid** | 120/240 | Sand (Kjet.)[a] | NW[d]/A[b] | 414/609 | 34/228 |
| **Fluroxypyr** | 188/375 | Sand (Kjet.)[a] | NW[d]/A[b] | 414/609 | 60/229 |

[a] The Kjettslinge soil is described in detail by Steen *et al.* (1984); the Mellby and Lanna soils are described in chapter 3 (this volume). [b] A = "Average" precipitation. [c] WC = "Worst-case" precipitation. [d] NW = Not watered.

summarized. Attention has been focused on illustrating the advantages and limitations with regard to mobility in soil and trying to interpret the results in terms of actual field conditions.

## LEACHING OF PESTICIDES IN SOIL MONOLITHS

All the results presented here are based on measurements performed in 0.3-m diam. and 1-m high soil monoliths, in accordance with a standard Swedish protocol (see chapter 3, this volume). Treatments have included three soils (two sandy soils and one clay soil), "average" and "worst-case" precipitation, and normal and double the normal application rates of applied pesticides (see Table 1). The compounds included are the herbicides bentazon, chlorsulfuron, clopyralid, dichlorprop, fluroxypyr and metsulfuron.

### Influence of physico/chemical properties and degradation on pesticide leaching

All the herbicides included here are considered to be fairly mobile based on information obtained in laboratory tests, such as estimates of adsorption constants ($K_{oc}$), half-lives ($t_{1/2}$) and water solubilities (Table 2). However, when considering the amounts of the herbicides that actually leached out during periods between

TABLE 2. Physico/chemical properties, degradation and leaching of some herbicides.

| Herbicide | $K_{oc}$ (ml $g^{-1}$) | $t_{1/2}$ (d) | Water solubility (g $l^{-1}$) | Leached of appl. (%) |
|---|---|---|---|---|
| **Chlorsulfuron** | 40[a] | 50[a] | 27.9 (pH 7)[b] | 0.02 - 0.16[c] |
| **Metsulfuron** | 35[a] | 40[a] | 9.5 (pH 6.11)[b] | 0 - 0.06[c] |
| **Dichlorprop** | 20 - 25[d] | 1 - 4[e] | 0.35[b] | 0.03 - 0.20[f] |
| **Bentazon** | 13[g] | 12 - 20[e] | 0.5[b] | 0 - 0.07[f] |
| **Clopyralid** | 4.6[a] | 15 - 87[a] | 1.0[b] | 0[h] |
| **Fluroxypyr** | 51 - 81[a] | 7 - 55[a] | 0.9[b] 8.0[a] | 0 - 0.04[i] |

[a]Data from the manufacturer; [b]Worthing & Hance (1991); [c]Bergström (1990a); [d]Ghorayshi & Bergström (1991); [e]John Stenström (pers. comm.); [f]Bergström & Jarvis (1992); [g]Kersti Gustafsson (1989); [h]Bergström *et al.* (1991); [i]Bergström *et al.* (1990).

7 and 11 months in our lysimeter studies, all seemed relatively non-leachable, i.e. <0.2 % leached out in percent of applied (Table 2). For example, Bergström *et al.* (1991) found no detectable concentrations of clopyralid in leachate, despite a $K_{oc}$-value of 4.6 ml $g^{-1}$ (Woodburn & French, 1987) and a half-life of 15-87 d (Swann *et al.* 1976). Moreover, when comparing adsorption and degradation of bentazon and dichlorprop (Table 2), both tested in the same soils, one would expect the former to leach at larger amounts. However, this was shown not to be the case (Bergström & Jarvis, 1992; Table 2). This gives further evidence for the problems involved in classifying pesticide leaching based only on physico/chemical properties and degradation. One explanation is that field studies usually take several forms of dissipation into account (e.g. leaching, volatilization), whereas in many laboratory studies, losses only occur through degradation and thus overestimate the residence time of a compound in soil. It is notable that even sophisticated mathematical simulation models of pesticide mobility rely heavily on parameters, such as the sorption coefficient and half-life, for which the model results show great sensitivity (Boesten & van der Linden, 1991).

## Influence of soil properties on leaching

Traditionally, there is a tendency to emphasize the influence of chemical properties of the pesticide molecule rather than soil properties, when classifying leachability of a compound (see above). However, there are several studies which show that soil physical conditions may have a major impact on pesticide leaching and may overshadow compound related properties. In all the studies referred to in this summary, preferential flow processes related to soil structural features, hydraulic properties and profile heterogeneities considerably influenced pesticide leaching. For example, rapid breakthrough of fluroxypyr in the middle of summer (the only time when this herbicide appeared in leachate) when the soils were dried out, was taken as clear evidence of preferential flow (Bergström *et al.*, 1990). This suggests that structured clay soils may be even more susceptible to pesticide leaching than sandy soils, which are normally considered to be more leachable (Gustafson, 1983). In a study with bentazon, this was also shown to be the case: a maximum average amount of 0.1 and 0.4 g a.i. $ha^{-1}$ leached from Mellby sand and Lanna clay respectively (Bergström & Jarvis, 1992).

Another process that could partly explain these results could be sorption of the pesticides to clay mineral surfaces or dissolved organic carbon (DOC) and subsequent displacement and migration by water during heavy rainfall (cf. Chiou *et al.*, 1986). Preferential flow processes would still be involved, however.

A more complete picture of the inpact of water flow paths on the leaching pattern of pesticides would require the use of a nonadsorbed, nondegrading tracer, which was attempted in the study with bentazon (Bergström & Jarvis, 1992). $^{36}Cl$ was applied on both the sand and clay soils together with the herbicide. In the clay soil, an approximate straight-line relationship between accumulated $^{36}Cl$ transport and drainage discharge (i.e. constant concentration in leachate) was found, whereas in the sandy soil, a more "normal" miscible displacement behaviour, or piston flow, occurred (Fig. 1). This is further evidence to support the suggestion that solute transport in a clay soil mostly occurs in macropores.

A general problem with lysimeters, which has the same effect on solute transport as macropore flow, is the water flow that may occur along the lysimeter wall, often referred to as "side-wall flow". This problem is extremely important to pesticide leaching studies, since the compound is often concentrated within the few top centimeters of soil and may thus be transported rapidly along the wall. Side-wall flows are usually limited to soils susceptible to shrinkage (i.e. clay soils and soils with a high organic matter content). Moreover, side-wall flow effects typically become more accentuated with decreasing lysimeter surface area. As mentioned previously (see chapter 3, this volume), the structured soils in our studies are collected when they are as dry as possible to avoid this problem. Indeed, preliminary results from tests in which $^{36}Cl$ and tritiated water were applied to equally large annular and central disc zones of our 0.07 $m^2$ monoliths suggest that the lysimeter type does not suffer from side-wall flow to any significant extent.

An unexpected and consistent effect of irrigation treatment on dichlorprop concentrations in lysimeter leachate occurred in the structured clay soil studied by Bergström & Jarvis (1992). In the clay monoliths with the "average" irrigation treatment, concentrations varied between 1 and 5 $\mu g\ l^{-1}$ throughout the 8 month period. However, only two samples containing concentrations above

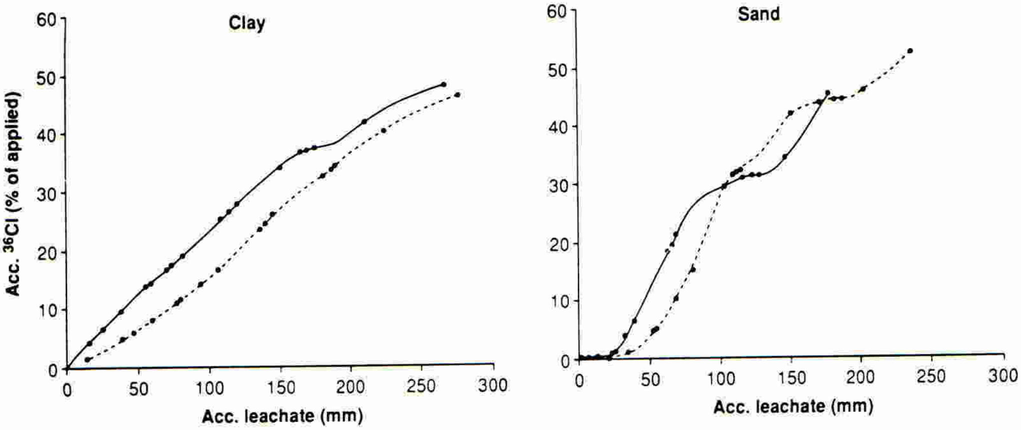

Fig. 1. $^{36}$Cl breakthrough curves; solid lines represent the "average" watering treatment and broken lines the "worst-case" watering treatment. Each point represents the mean value of 2 to 4 replicates.

the detection limit (>0.5 μg $l^{-1}$) were found in the "worst-case" irrigation treatment. Again, preferential or bypass flow is the most likely explanation, since the dried-out topsoil of "average" treatment monoliths may have allowed water flow in cracks to a much greater extent than in "worst-case" treatment monoliths, thus moving some of the pesticide rapidly through the topsoil to the subsoil. Once the compound reached the subsoil, it would be largely protected against degradation and thus stored for later leaching. In laboratory incubation tests in the Lanna clay subsoil, no degradation of dichlorprop was detected during the course of a 43-d experiment, whereas the dichlorprop half-life in the topsoil was only 4 days (Stenström, pers.comm.). The fact that $^{36}$Cl leached out at much higher rates in the "average" than in the "worst-case" watered clay (Fig. 1), provides further support for this preferential flow hypothesis, even though the tracer was applied one year later than dichlorprop.

## EVALUATION OF RESULTS

### Interpretation of lysimeter results in terms of field conditions

The pesticide concentrations obtained in lysimeter leachate represent levels which, under natural field conditions, are typical for water in the unsaturated zone, below the root depth. If we wish to convert concentrations to loads, the fact that this leachate in a field situation is split up into tile-drainage and deep groundwater may have to be considered. In other words, nondegraded, nonadsorbed pesticide residues leaving the root zone will ultimately either reach a river or lake or a groundwater reservoir. The geohydrological conditions which determine whether we have a discharge area, i.e. a net upward-directed gradient of the groundwater flow, or a recharge area, i.e. infiltration to deep groundwater, vary considerably in the landscape (Gustafson, 1987). It is, therefore, difficult to specify a standard value for the ratio between tile-drainage or shallow subsurface flow (forming surface water) and groundwater percolation. Water reaching the soil as rain or irrigation may at times also form surface runoff, which is normally not considered in lysimeter studies. Very few lysimeters allow separation between surface runoff and percolation (Jones & Hinsley, 1986). However, soon after spraying a spring applied pesticide, when the pesticide concentrations are likely to be high in the few top centimeters of soil and the infiltration capacity is high, the risk for surface runoff is minimal. Another factor requiring consideration in pesticide risk assessments for rivers and lakes or groundwaters is land use. How much of a watershed or intake area of a groundwater reservoir can be treated with a specific pesticide? Moreover, degradation of the pesticide in water and possible carry over from one season to another of the compound should preferably be taken into account.

In a risk assessment for potential surface water pollution by sulfonylurea herbicides, which considered the factors mentioned above (Bergström, 1990a), it was estimated that the measured peak concentrations in lysimeter leachate of ca. 0.02 $\mu g\ l^{-1}$ could be lowered one order of magnitude if converted to reflect stream water concentrations (Bergström, 1990a). This rough estimate represents a concentration with no known biological activity. In a similar calculation for dichlorprop, a 20-fold decrease in herbicide concentration in river water was expected (Bergström, 1990b). We have to keep in mind, however, that neither the initial herbicide level and degradation in stream water, nor possible seasonal carry over of the herbicides were taken into account in these calculations. However, we should also keep in mind that the estimates were based on peak concentrations whereas not all the lysimeter leachate contained herbicide concentrations above the minimum detectable.

## The significance of analytical detection limits

Analytical detection limits may have significance for the estimation of leaching loads based on concentrations measured in lysimeter leachate. For example, in the study with bentazon and dichlorprop discussed above, the difference in amounts leached of the herbicides was much larger than given in Table 2, if the five times higher detection limit of dichlorprop was considered (i.e. 0.1 and 0.5 $\mu g\ l^{-1}$ for bentazon and dichlorprop, respectively). If the same analytical detection limit was true for bentazon as for dichlorprop, only two samples would have had detectable concentrations, giving measurable losses only in the clay soil when the "worst-case" irrigation was applied. In contrast, if we had taken into account that the analytical detection limit in fact was lowered from 0.1 to 0.05 $\mu g\ l^{-1}$ for most of the water samples collected later in the season (which was not considered in the estimate listed in Table 2), considerably larger losses would have been estimated for this compound. For example, a mean value of 0.14 g a.i. $ha^{-1}$ of bentazon (0.02 % of applied) would then be calculated to leach out of the "average" watered clay soil compared to 0.06 g a.i. $ha^{-1}$ (0.01 % of applied) based on a detection limit of 0.1 µg $l^{-1}$. This emphasizes that it is extremely critical to evaluate correctly the significance of measured concentrations and loads of pesticides in leachate. Indeed, much of the increased concern over pesticides in water can, to a great extent, be attributed to significant improvements in analytical methods enabling detection limits to be lowered several orders of magnitude during the past 20 yr (Pionke *et al.* 1988). We must take into account such considerations when regulatory officials introduce arbitrary criteria for acceptable leaching losses.

There is also another problem related to the very low levels of detection, which has impact on evaluation of pesticide dissipation results. Coextracted interfering material may cause simultaneous peaks on gc-chromatograms with the studied pesticide. Soil samples taken to 1-m depth in tile-drained plots, during a 112-d period after spraying with clopyralid, also had detectable clopyralid concentrations in preapplication samples (Bergström *et al.*, 1991). These concentrations were similar to those detected in the subsoil during the rest of the experimental period. However, the use of a mass spectrometer confirmed that the observed peaks on preapplication samples were not in fact clopyralid. This stresses the importance of viewing results like this with great caution and that the unverified clopyralid peaks in the study referred to here could be considered only as potential maximum levels. Use of radiolabeled pesticides in lysimeter experiments would certainly substantially reduce problems with interfering material.

## CONCLUSIONS

From the studies discussed above, the following conclusions can be made:

It is important to carry out environmental risk assessments for pesticides mainly based on results from field studies rather than laboratory tests. The latter are appropriate only as preliminary studies to indicate when further field tests are needed.

Lysimeters offer an excellent experimental framework for studies of pesticide leaching, with very few exceptions (e.g. if unacceptable side-wall flows occur). The value of lysimeters is that they not only allow the investigator to control all water movements through the soil but also allow manipulation of environmental factors as well.

Leaching of pesticides in clay soils may be as large or even larger than in sandy soils, due to the occurrence of macropore flow in the former.

Use of a nonadsorbed, nondegrading tracer in pesticide leaching studies can give some important addtional information about the pathways and mechanisms of soil water movement.

Investigation of soil chemical/biological properties of significance for pesticide fate and mobility is important not only in the topsoil but also in deeper layers of the profile.

A correct evaluation of the significance of measured concentrations of pesticides in leachate is extremely critical. When interpreting lysimeter results of pesticide leaching in terms of actual field conditions, considerations of landscape hydrology, land use pattern and pesticide persistence in water have to be taken into account.

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# COMPARISON OF THE TIME COURSE OF TEMPERATURE, WATER CONTENT AND ORGANIC CARBON IN TOPSOIL AND SUBSOIL IN LYSIMETERS WITH THE FIELD[1]

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## ABSTRACT

Soil temperatures measured in lysimeters and the field were in good agreement. The water contents in the lysimeters were always below those in the field indicating that water movement in lysimeters was influenced by the lack of continuity with deeper soil layers. Fertilization with [$^{14}$C]oat straw brought about a rapid charging of the soil solutions with $^{14}$C-labelled conversion products. The maximum straw carbon concentrations of 21 mg C $l^{-1}$ were measured in soil solutions taken from a depth of 10 cm, although concentrations of between 0.1 - 1 mg C $l^{-1}$ were observed even in the leachate.

## INTRODUCTION

In order to assess the potential for intrusion of pesticides into ground water, it is mandatory in Germany to carry out a large number of detailed studies plus a lysimeter experiment with an undisturbed soil monolith (BBA - Federal German Biological Agency, 1990). Various projects have already attempted to assess the relationships between results from lysimeter experiments and the field situation (Hansper, 1986; Kubiak, 1986; Brumhard, 1991; etc.). In this connection, the water content and temperature are of paramount significance for the mass transport, adsorption, degradation and thus the residue formation of organic substances in the soil (Haider, 1985; Wolfe et al., 1990; Malkomes, 1991). Moreover, a natural reference material is necessary for the evaluation of any possible translocation events involving pesti-cides in the soil.

The aim of this experiment was to compare changes in water content and soil temperature at various depths in the field and lysimeter and to study the translocation processes of natural organic substances at an intensively cultivated site using $^{14}$C-labelled oat straw in order to obtain a reference value to assess the translocation behaviour of organic substances input by human activities.

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[1] Part of a cooperative project with the Pesticide Research Center Monheim, BAYER AG Leverkusen and partly supported by the Deutsche Forschungsgemeinschaft.

MATERIALS AND METHOD

Five round lysimeters, surface area 1 $m^2$ and 110 cm deep were filled with undisturbed orthic luvisol monoliths taken from a commercial farm. An access tube with a neutron probe LB6654 A-2 (Berthold) was installed centrally in order to measure the water content in each. As a supplement to this instrumentation, Pt-100 temperature sensors were installed in two lysimeters at depths of 5 cm, 10 cm, 30 cm and 60 cm, and two suction candles each at depths of 10 cm, 20 cm, 40 cm and 60 cm in one lysimeter (**Figure 1**). The soil solutions were withdrawn with the suction candles at periods of high water soil content. In parallel to this, a comparable measuring installation was set up in the field in Merzenhausen, at a distance of about 12 km from the lysimeter station, from which the soil monoliths had been removed. There were three measuring points to determine the water content. A detailed description of the physico-chemical parameters, the profile description of the orthic luvisol used and the technical set-up to record the soil temperature, soil moisture and soil solutions is given in Pütz (1993).

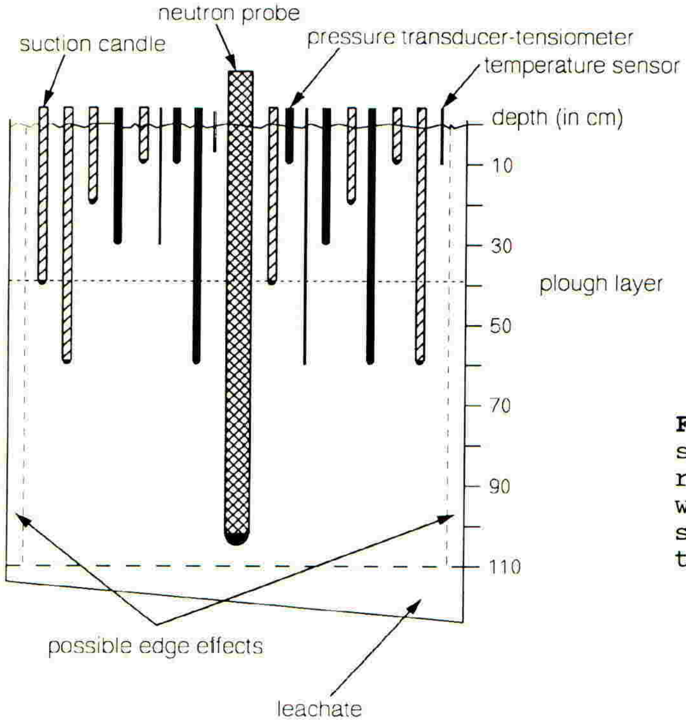

**Fig. 1:** Cross section through a round 1 $m^2$ lysimeter with access tube, suction candles and temperature sensors.

On 4th October 1988, 631 g of uniformly $^{14}C$-labelled oat straw with a specific radioactivity of 146.1 kBq $g^{-1}$ and a specific radiocarbon activity of 373.3 kBq $g^{-1}$ C (carbon content 39.1 % ± 0.5) was worked into the upper 5 cm of the soil of a round 1 $m^2$ lysimeter equipped with measuring instruments and suction candles, corresponding to a quantity of 6 t $ha^{-1}$

according to good agricultural practice. The total quantity of applied radioactivity amounted to 92.17 MBq.

## RESULTS

### Soil temperature

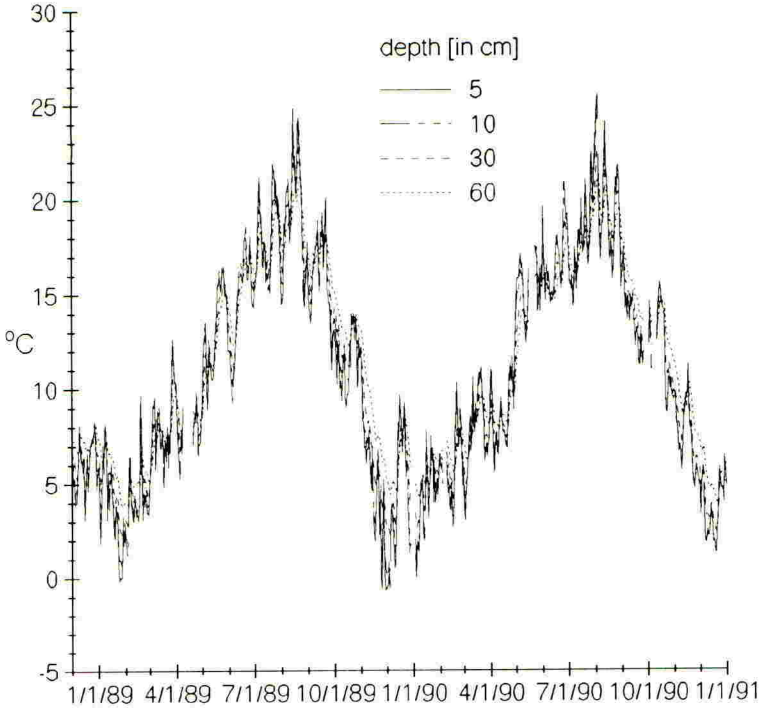

**Fig. 2:** Curve of average daily values for the soil temperature in a 1 $m^2$ lysimeter at various depths.

After the measuring stations at the Merzenhausen field and the lysimeter station had been put into operation (Pütz, 1993), the soil temperature was recorded from 1.12.1988 to 31.12.1990. The soil temperature curves from the field and lysimeter display a distinct annual variation with minimum values in the winter months and maxima in the summer months (**Figures 2 and 3**). Soil temperatures in the two lysimeters were in very good agreement at the four depths studied. In contrast, the lysimeter and field soil temperatures showed some differences. During the first vegetation period 1988/89, the temperature curves for the field deviated perceptibly from those of the lysimeters. It should, however, be noted that due to a change of crop rotation sugar beet was planted in the field and winter wheat on the lysimeter. During the second vegetation period, good agreement of the temperature curves was observed both in the lysimeter and in the Merzenhausen field. An important requirement for this good agreement was that both the field and the lysimeter were planted with cereals (winter wheat and winter barley). The lowest soil temperatures observed in the lysimeters and field were between - 1°C at a soil depth of 5 cm and + 4°C at 60 cm. The range of the temperature maxima was + 27°C at a soil depth of 5 cm and + 19°C at 60 cm. It is not possible to observe a continuous curve in the course of the annual variations, on the contrary a number of relatively warm phases follow periods with cooler soil temperatures. The temperature changes at soil depths of 5 cm and 10 cm were considerably more rapid and larger than at 30 and 60 cm. This effect led to the observation that during a phase with rising temperatures the measurements in deeper soil layers were always + 3°C - + 4°C lower and on the other hand during a phase with decreasing temperatures + 3°C - + 4°C higher, than those at 5 and 10 cm.

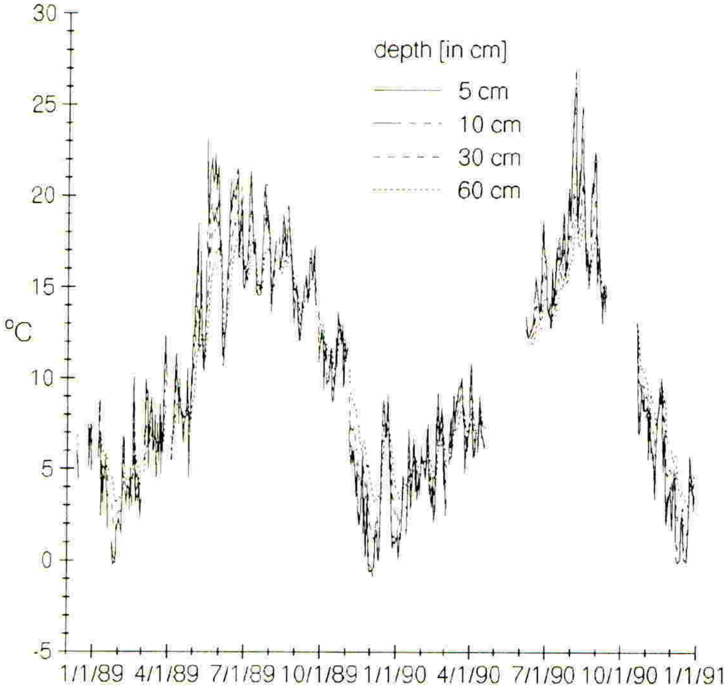

**Fig. 3:** Curve of the average daily values for the soil temperature in the Merzenhausen field at various depths.

Water content at different soil depths

During the observation period from August 1988 to December 1990, the water content was determined in five lysimeters and three different measuring points in the Merzenhausen field at three different depths with the neutron probe. In order to achieve the highest possible time resolution, measurements were intitially made twice a week at each depth. However, since it was only possible to record changes in water content in the soil after considerable quantities of precipitation only one measurement per week was made from December 1989 onwards.

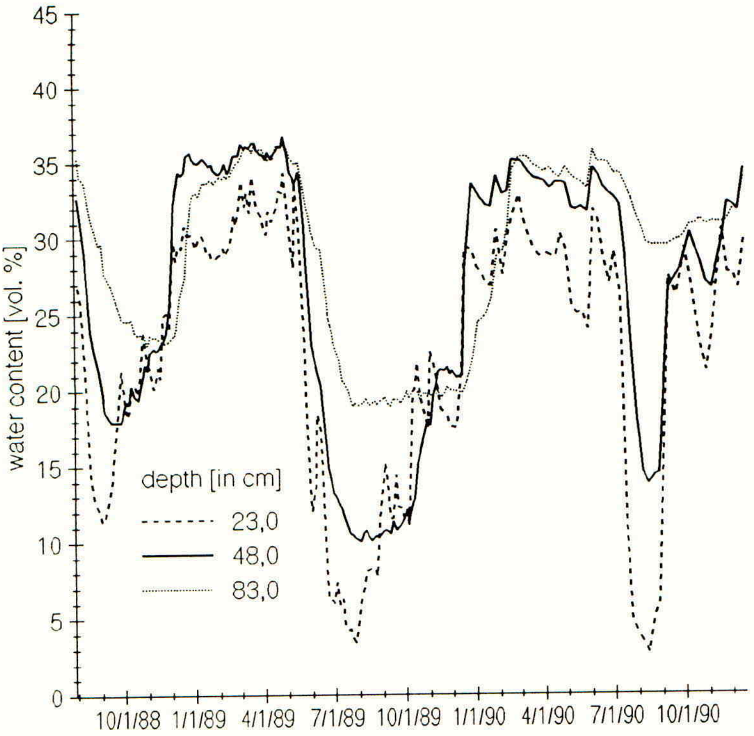

**Fig. 4:** Curve of the water content in the 1 $m^2$ lysimeter at various depths (average from five lysimeters).

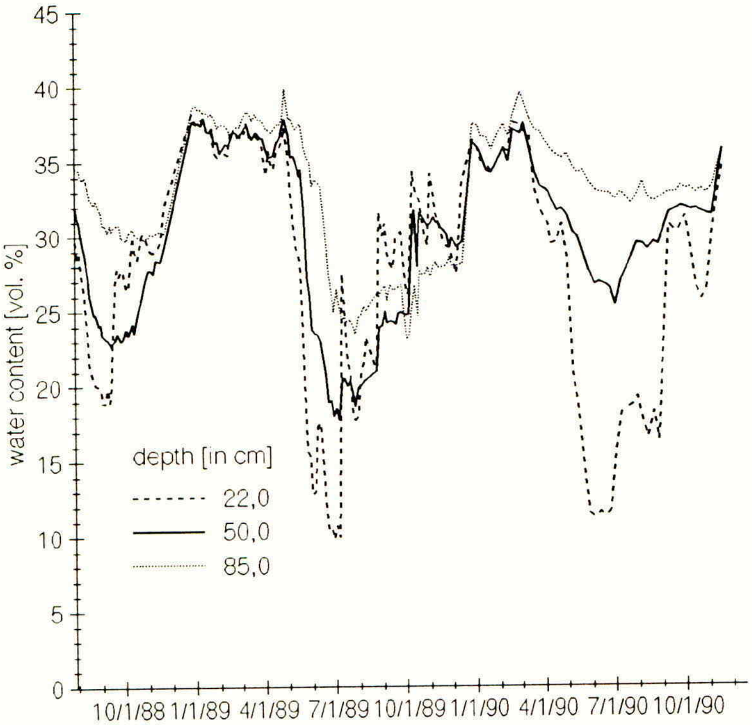

**Fig. 5:** Curve of the water content in the Merzenhausen field at various depths (average from three measuring points).

The curve of the water contents in the lysimeters and the Merzenhausen field displayed typical annual fluctuations. During periods with intensive plant growth the water contents in the lysimeters dropped to values between 4 - 12 vol.% in the upper soil region whereas in the field the minimum values were in the range of 10 - 19 vol.% (**Figures 4 and 5**). In the deeper soil regions at about 80 cm the lowest water contents in the lysimeter were 19 - 32 vol.% while in the field they amounted to between 24 - 32 vol.%. In the summer months, two precipitation events had a decisive effect on the course of the water contents. Firstly, 70 mm of precipitation fell in the Merzenhausen field in July 1989 during a thunderstorm, but only 14 mm on the lysimeters. Secondly, in May 1990 the lysimeters had to be irrigated with 27 mm of water in order to save the crop so that discrepancies in the topsoil occurred during the summer months. In phases with high water contents in the lysimeter values between 29 - 34 vol.% were observed in the upper soil region and about 35 vol.% in deeper soil layers. In comparison, water contents between 35 - 38 vol.% were measured in the upper soil layers of the Merzenhausen field and 36 - 40 vol.% in the deeper soil layers. Whereas at of high water contents, the individual soil layers in the field contained similar amounts, in the lysimeter clear differences in water content were observed between the individual soil layers.

<u>Oat straw fertilization</u>

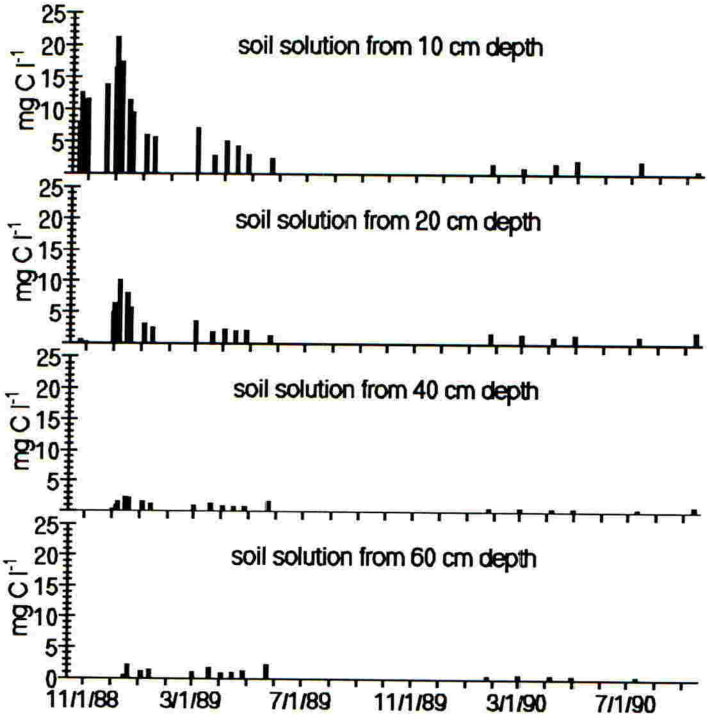

**Fig. 6:** Straw carbon concentrations, calculated on the basis of the specific $^{14}C$ activity of the oat straw carbon, in the soil solution after $^{14}C$-oat straw fertilization (averages from two suction candle samples per depth).

## Organic carbon in the soil solution

It was possible to quantify the carbon in the soil solution and percolate originating from oat straw fertilization with the aid of $^{14}C$-labelling. A very rapid conversion process began after the $^{14}C$-labelled oat straw had been worked into the soil as was expected from the literature (Jenkinson, 1965; Führ & Sauerbeck, 1968; Oberländer & Roth, 1974; etc.). After the addition of the oat straw, the straw-derived carbon concentrations in the soil solution taken from a depth of 10 cm increased to a maximum of 21.2 mg C $l^{-1}$ and then subsequently dropped continuously to contents below 5 mg C $l^{-1}$ (**Figure 6**). In the course of 1990 the straw-derived carbon concentrations rose slightly. A similar curve of the straw-derived carbon concentration was measured in the soil solution taken from a depth of 20 cm. However, at 11.5 mg C $l^{-1}$ the maximum was clearly below the contents measured at 10 cm, as was the level of the other samples. Due to the low water contents in the soil layers below 40 cm, it was only possible to withdraw soil solutions from early December 1988 onwards. The soil solution from 40 cm already contained the highest straw carbon concentration in December at 2.6 mg C $l^{-1}$, which then dropped continuously in the remainder of the experiment (**Figure 6**). No clear trend could be observed for the soil solution from a depth of 60 cm with fluctuating concentrations of about 1 - 2 mg C $l^{-1}$. In the percolate that emerged from the bottom of the lysimeter, straw-derived carbon concentrations were 0.1 - 1 mg C $l^{-1}$.

**Table 1:** Distribution of the radioactive residue in various soil layers after $^{14}C$-oat straw fertilization on a round 1 $m^2$ lysimeter on 4th October 1988. Applied radioactivity = 100 %.

| soil layer | 1989[1] | 1990 |
|---|---|---|
| 0-10 cm | 27.4 % | 15.6 % |
| 10-20 cm | 0.4 % | 8.6 % |
| 20-30 cm | 0.1 % | 0.5 % |
| 30-40 cm | 0.4 % | 0.7 % |
| 40-90 cm | <0.1 % | 1.9 % |
| **Σ** | **28.4 %** | **27.3 %** |

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[1] After sampling the lysimeter soil was turned over to a depth of 25 cm.

The clear decrease of straw-derived carbon concentrations in the soil solutions indicates the rapid conversion and exhaustion of the pool of readily degradable oat straw constituents. This was underlined by the residue situation at the end of the first vegetation period in 1989 (**Table 1**). 333 days after [$^{14}C$]oat straw fertilization a total of 28.4 % of the applied radioactivity was recovered in the soil monoliths, of which 27.4 % occurred in the 0 - 10 cm layer. The fact that 27.3 % of the applied radioactivity was still detectable at the end of the second vegetation period, 685 days after oat straw fertilization, indicates that the straw-derived carbon had already been tied down in relatively stable humic substance fractions at the end of the first vegetation period.

## DISCUSSION

In a two-year comparison of measurements at four different depths in two lysimeters and in the field, very good agreement was usually observed in the temperature curves. No differences were seen in either winter or summer. However, such a good agreement between the field and lysimeter soil temperatures is dependent on comparable crops since both the period and intensity of shade, which vary as a function of physiological development, seem to be important factors influencing the soil temperature. The typical picture (Scheffer & Schachtschabel, 1984) of fluctuating soil temperatures in the field also occurred in the lysimeters, where the fluctuations were similarly reduced with increasing depths. With respect to the effect of temperature on the rate of degradation of organic substances (Führ & Mittelstaedt, 1979; Haider, 1985), it is noteworthy that the one $m^2$ lysimeter sunk into the ground showed comparable conditions corresponding with the field. Kubiak (1986) also obtained similar results.

The water contents in the lysimeters and the field site were not in very good agreement. The discrepancy was caused by two locally limited precipitation and irrigation events which had a lasting effect on the water contents. However, although in phases with similar precipitation the curves of the water contents displayed similarities, in absolute terms higher water contents were always measured in the field. The lack of continuity with deeper soil layers in the lysimeter had two different effects. Firstly, in seasons with a positive water balance there is a lack of water storage capacity and with resistance to counteract rapid leaching. As a consequence, in the lysimeters between 10 - 30 % of the annual precipitation is released as leachate at the bottom of the soil monolith (Brumhard, 1991). Secondly, during phases with a negative water balance (quantity of rain < evapotranspiration) perceptibly lower water contents were always measured in the lysimeter than in the field because there is no replenishment of water from deeper soil layers. Moreover, in contrast to the field, the lysimeters show a greater range between maxima and minima. With respect to the significance of the lysimeter as an instrument for estimating the leaching tendency of pesticides endangering the ground water, it must be noted that more than 95 % of the leachate is collected in the lysimeter during seasons with excess water balance (Pütz, 1993). In comparison with the field, with its greater storage capacity, the lysimeter had an intrinsically higher leaching potential. This difference was reinforced by the restricted upward movement of water in a lysimeter during periods with a negative water balance.

Within a few days of oat straw fertilization small carbon concentrations were observed in the soil solutions. As a function of a rapid conversion of the $^{14}$C-labelled oat straw, $^{14}$C-concentrations rose with a clearly observable maximum in the top 20 cm with a corresponding, though considerably attenuated peak down to 40 cm. The fact that straw-derived carbon was found in the first soil solution samples, points to a rapid translocation of these conversion products, which were detected down to a depth of 110 cm. The translocatability of the degradation products of the oat straw meets an essential prerequisite for the possible cotransport of pesticide and dissolved organic compounds. However, the rapid translocation down to 110 cm contrasts with Sørensen's (1987) results in which no residues were found below 50 cm following $^{14}$C-labelled barley straw fertilization. In this case, however, the first sampling first carried out eight years after the application of the $^{14}$C-labelled straw so that the mobile carbon compounds occurring initially had already been leached into deeper soil regions.

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# AUTORADIOGRAPHY

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## ABSTRACT

The use of specialized radiotracer techniques in well structured lysimeter experiments have been demonstrated to improve the application of pesticides in practical agriculture. In addition, the results achieved by the combination of autoradiography of whole plants or plant segments and conventional analytical methods assists the pesticide producer, applicator and consumer by providing more information about residues in feed and food.

Close cooperation between pesticide chemists, phytopathologists, entomologists and plant physiologists is a prerequisite for the full exploitation of the potential of the tracer technique to provide information on routes of uptake, barriers, translocation and systemic behaviour.

## INTRODUCTION

During the last 20 years new fungicides and insecticides with considerable long-term effectiveness, achieved with small amounts, have been developed and brought onto the market. Especially in cereal cultivation, treatments with these new compounds are still worthwhile in the last phase of grain development in order to attain and exploit yield potentials. The uptake of these compounds and their transport behaviour govern whether a curative, eradicative or even protective effect is achieved, either at the site of application, in other parts of the plant not covered with spray solution, or later in new growth. In general, however, only a few percent of the applied pesticide quantity reaches the target pest. Currently, we do not know enough about the route of uptake and the internal distribution as a basis to establish the optimal concentration of a compound which is needed to ensure the required activity. These studies can easily be combined with lysimeter studies as described elsewhere or special lysimeter experiments can be conducted for specific questions. Especially for time sequence studies enough plant material is required for macro-, semimicro- and microautoradiography and this can be assured with appropriate lysimeter experiments (Führ and Wieneke, 1973; Wieneke and Führ, 1983; Führ, 1984).

## AUTORADIOGRAPHY

Systematic studies making use of $^{14}C$-labelled compounds provide detailed information on uptake and translocation. Especially, macroautoradiography of whole plants, fruit or seed slices, and plant tissue sections can provide information on uptake sites, translocation routes and accumulation compartments. Microautoradiography is established by the combination of autoradioagraphy with histological and microscopic techniques using fine grained photoemulsions to present a visual record of radioactivity within the tissue of a biological specimen and to yield additional information on absorption and penetration sites, barriers, internal distribution, and accumulation. However, rarely can conventional histological methods be applied because it is difficult to be sure that the labelled pesticides stay at the original position in the tissue during treatments involving aqueous and other solvents. In plants, cryostat sectioning combined with stripping film techniques appears under many circumstances the method of choice. The major steps of the procedure are described in detail by Wieneke and Führ (1983). During the last 10 years this method has been systematically adapted and partially developed for use of a routine technique. The bases of autoradiographic techniques can be studied in Roger's (1969) and Lüttge's (1972) comprehensive descriptions. Excellent examples of the possibilities provided by the quantitative evaluation of microautoradiography can be taken from the related field of plant physiology (Clarkson & Sanderson, 1978; Itai *et al.*, 1978).

Macroautoradiography is a relatively simple and easy method of detecting radioactivity in plant tissue. Microautoradiography of plant objects, however, is extremely difficult and can only be applied on a routine basis by operators with considerable experience.

## PLANT STUDIES

As has been outlined in chapter two, the lysimeter system is an ideal basis to combine soil studies with those on uptake and distribution of pesticides in relation to the developmental stages of the treated plant and the vegetation period. Some results from investigations with fungicides and insecticides will demonstrate the value of this radiodetection technique in pesticide studies.

## LEAF UPTAKE

The fungicide [benzene-ring-U-$^{14}C$]triadimefon, was applied in a lysimeter study in bands to defined leaf sections of the second, almost completely developed barley leaf using a spraying technique tested by Steffens and Wieneke (1974). The amounts of active substances applied were between 6 and 14 $\mu g$ per leaf section (approx. 18-25 kBq $^{14}C$ activity), corresponding to spraying a hectar with 225 g of active substance in 500 l of water.

The macroautoradiographs (Kodak Regulix BB14X-ray film) of the leaves at various times after triadimefon application clearly showed translocation into the leaf tip region (Fig. 1). Under field conditions this amounts to 28 % of the radioactivity applied within 12 days (Führ *et al.*, 1978).

The leaf sections treated and those upper leaf sections which were not treated were completely protected against infestation with mildew. This was tested by selectively treating the leaves with the appropriate fungus spores (*Erysiphe graminis var. hordei)*. In the same way, a protective effect against mildew in the lower leaf regions was observed, also a basipetal re-translocation amounted to a maximum of 0.3 % of the radioactivity used. However, the protective effect or reduction in infestation in the untreated basal region was considerably weaker.

Fig. 1:
Translocation of radioactivity (macroautoradiograph) in summer barley after treating the upper side of the lower half of the leaf with [$^{14}$C]triadimefon (Führ *et al.,* 1978).

The microautoradiographs (Fig. 2) clearly indicate that triadimefon and its daughter compounds are rapidly taken up within one day, and radioactivity is found in all areas of the treated leaf sections. Further transport takes place exclusively in the transpiration stream in the xylem. This transport system was, however, rapidly abandoned again so that radioactivity was found in all areas, even in the untreated acropetal leaf regions, and thus explains the protective function of triadimefon (Führ et al., 1978; Buchenauer, 1979).

## SEED DRESSING

The uptake and distribution of [benzene ring-U-$^{14}$C]triadimenol applied as a seed dressing to spring barley and spring wheat as well as winter barley was also investigated in lysimeter experiments, (Steffens et al., 1982; Thielert, 1984; Thielert et al., 1986, Thielert et al., 1988; Schneider, 1988; Schneider et al., 1988; Schneider et al., 1990). The test soil was a loess loam (alfisol) which is among the most fertile soils in Germany (Mückenhausen, 1977).

A calculation using the specific activity of the labelled fungicide indicated that a seed dressing application of 12-16 $\mu$g active substance/grain corresponded to 160 or 177 g Baytan$^R$/100 kg of seed. During the early development up to shoot elongation, a maximum of 7.5 % of the radioactivity applied was taken up and translocated into the wheat stalks and leaves, with the majority of the translocation occuring between the 10th and 28th day after sowing. Macroautoradiographs (Fig. 3) of wheat plants show that the radioactive substance or metabolites were translocated into the leaf tips with the transpiration stream.

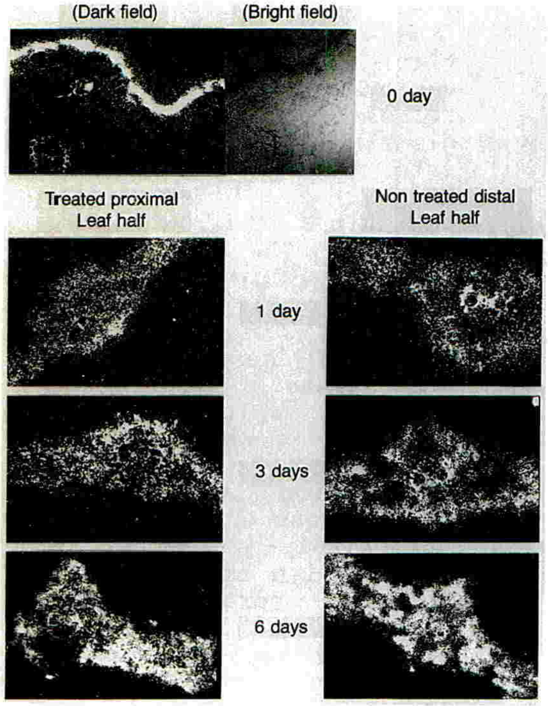

Fig. 2:
Radioactivity in barley leaf tissue after treating the upper side of the lower half of the leaf with [$^{14}$C]triadimefon. Dark field microautoradiograph (Führ *et al.*, 1978).

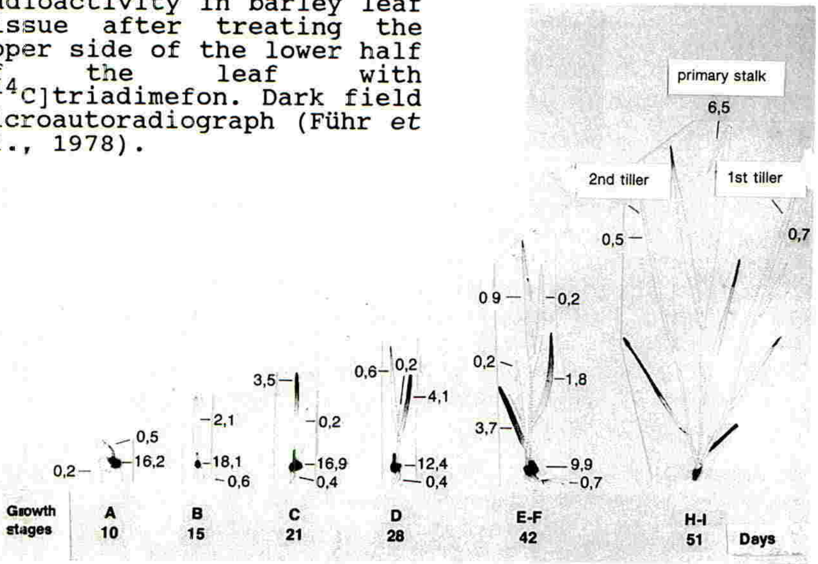

Fig. 3:
Macroautoradiograph of spring wheat plants in various stages of development after seed dressing with [$^{14}$C]triadimenol (Steffens et al., 1982).

Guttation droplets excreted from barley seedlings were collected and analyzed for parent material (Schneider, 1988; Schneider et al., 1990). Single guttation droplets from seedlings at the first leaf stage carried between 4-6 % of the total $^{14}$C in the shoots at that time. About 80 % of this $^{14}$C-activity still represented triadimenol with a stereoisomer ratio of 11 (A): 1 (B). In additional experiments with winter wheat and winter barley (Steffens et al., 1986) it was demonstrated that even the fourth, fifth and sixth leaf of the plants as well as the tillers had taken up radioactivity. Up to 50 % of the $^{14}$C was still present as the unchanged original compound but the ratio of the stereoisomers was different.

The uptake of radioactivity into the treated barley seeds was followed using a semi-microautoradiographical technique (Schneider et al., 1990). At growth stages 10-11 and 11-12 (Zadoks et al., 1974), the remaining endosperms of germinated caryopses were analyzed for [$^{14}$C]triadimenol. The uptake of the radiolabel into the embryo and the scutellum occurred within 24 hours of imbibition (Fig. 4), but the testa apparently prevented a rapid penetration into the interior of the grain so that the uptake of the triadimenol into the starchy endosperm lagged behind the uptake of water. At the first- and second-leaf-stage $^{14}$C-activity was found in all of the remainder of the starchy endosperm (Fig. 4). However, in related experiments, only about 2/3 of the $^{14}$C-activity could be attributed to the parent material.

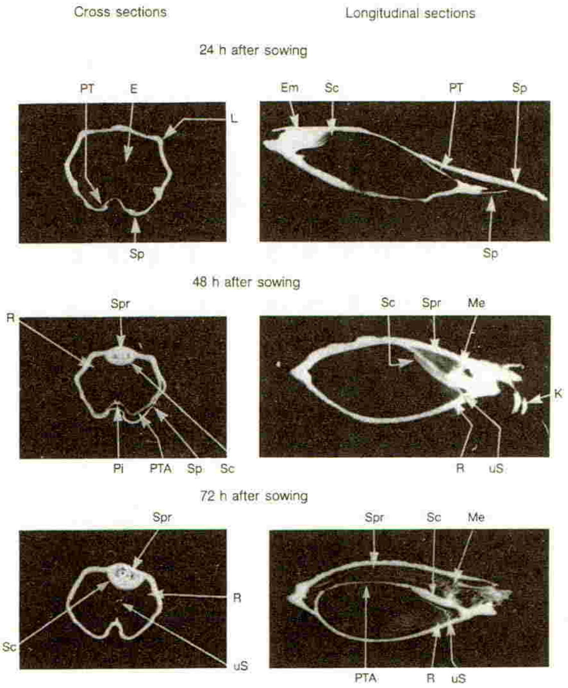

Fig. 4:
$^{14}$C-uptake into the seed of [$^{14}$C]triadimenol treated winter barley grown in soil (Schneider et al., 1990).

E = endosperm (intact);
Em = embryo; K = radicle;
Me = provascular bundle;
PTA = pericarp/testa/aleuron;
PT = pericarp/testa;
R = $^{14}$C inside endosperm;
Sc = scutellum; Sp = husk;
Spr = shoot;
uS = undidentified structures

Apparently, the triadimenol entered the endosperm preferentially at the interface of scutellum and crease and it also accumulated in the tissue of pericarp/testa and aleurone (Fig. 4).

Presently extensive lysimeter experiments are conducted to study the uptake of the seed dressing insecticide [pyridinyl-$^{14}$C-methylen]imidacloprid in relation to soil moisture (Stein-Dönecke, 1992), its translocation, internal distribution as well as its movement from the treated seed (winter wheat) or pellet (sugar beet) into the surrounding soil, demonstrating again the special advantages of lysimeter experiments to explore the potential of seed dressed pesticides.

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# 7. THE PRESENT SITUATION

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## ABSTRACT

On the basis of the limited number of comparisons currently available, it seems that lysimeters produce results that are compatible with field observations but those from laboratory experiments often are not. More information is needed to confirm this and also to assess how far lysimeter studies will be restricted by soil characteristics and how much replications is needed to take account of field variability. The interpretation of lysimeter data in the context of water pollution remains a subject of debate. However, the lysimeter experiment is now an established technique in studies of the environmental fate of pesticides.

Only a few laboratories have so far reported results from lysimeter experiments so it is possible to make only a preliminary assessment of the validity of the system in relation to both laboratory and field observations.

## COMPARISON OF LYSIMETER AND LABORATORY RESULTS

### Pesticide transformations

As discussed in chapter 2, a number of differences between outdoor and laboratory environments can be identified that are likely to produce corresponding differences in transformation rates and pathways. It is also possible that the differences could counteract each other to some extent so that the outcome of laboratory and outdoor experiments would be similar.

Studies with isocarbamid in lysimeters (Mittelstaedt and Führ, 1875a) and in a closed micro-ecosystem (Mittelstaedt and Führ, 1975b) showed a good correlation in that the loss of $^{14}C$ from the lysimeter was consistent with what would have been predicted from mineralisation rates in the micro-ecosystem. Similarly, losses of $^{14}C$-metamitron in a lysimeter experiment (Mittelstaedt and Führ, 1981) corresponded well with mineralization rates under standard laboratory incubation conditions (Führ and Mittelstaedt, 1979). However, Kubiak (1986) and Kubiak *et al.* (1990) found there were differences in the extent of loss or mineralization of the labelled radiocarbon of the trazine ring of metamitron and also in the extent of bound residue formation from $^{14}C$-metamitron and $^{14}C$-methabenzthiazuron. One hundred and sixty days after [3-$^{14}C$]metamitron pre-emergence spray application to sugar beet the losses of radiocarbon from 5 lysimeters were of the order of approx. 50 % of that applied. In parallel to this, a degradation experiment, following the guidelines of the Biologische Bundesanstalt (BBA) was implemented with the same soil (orthic luvisol) at constant moisture of 40 % of the maximum water-holding capacity and a constant temperature of 22°C. There was 25 % mineralization of the radiocarbon within 100 days. In a further experiment the same soil moisture was maintained but fluctuating soil temperatures as occur in the field topsoil at a depth of 10 cm in the months of May, June and July. The daily average temperatures varied between 10 and 25°C. However, the sum temperature did not reach the value of the constant 22°C treatment.

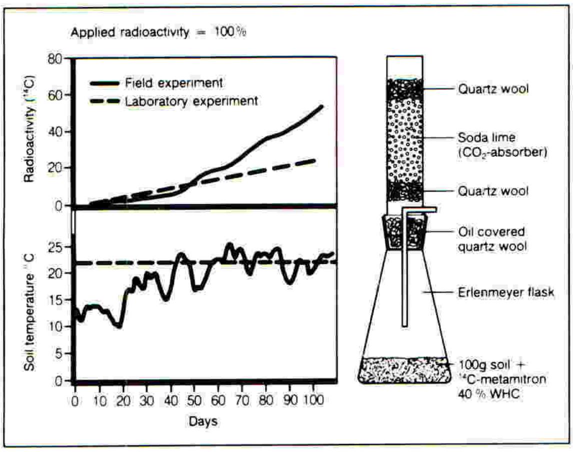

Figure 1

Nevertheless, the total mineralization of the carbon atom from the $C_3$-position of the triazine ring of metamitron was higher by factor a of 2.5 compared with the constant temperature treatment after 100 days (Fig. 1) The temperature changes apparently led to an altered spectrum of microorganisms and/or increased microbial activity in the soil, and thus to more rapid degradation and mineralization of the active ingredient. In the lysimeter system after 13 weeks 20 % of the $C_3$-position of the triazine ring of metamitron was unextractable compared with 50 % in soil incubated in the laboratory at 22°C and 50 % of water holding capacity. Corresponding figures for [carbonyl-$^{14}C$]methabenzthiazuron were 25 % and 30-40 %. Results from soil in a pot experiment with plants were intermediate. Figures for mineralisation losses and for unchanged, extractable parent compounds were not reported.

Kubiak and Eichhorn (1990) also found some differences in the fate of glufosinate. In a lysimeter study 2-5 kg AI/ha applied in April left a glufosinate residue of 0.05 mg/kg soil after 130 days with 33.8 % of the applied $^{14}C$ still detected in the soil. In a pot experiment, 1-5 kg AI/ha produced a glufosinate residue of only 0.01 mg/kg soil after 130 days with 8.9 % of the applied $^{14}C$ left in the soil. At least part of the difference will have been caused by different root to soil ratios as both the lysimeters (0.8 $m^2$ and 1.3 m deep) and the pots (containing 8 kg soil) contained one vine *(Vitis vinifera L.)* plant.

Studies with clopyralid also produced differences between field and laboratory results. In a laboratory incubation system, Stork *et al.* (1990) estimated a $DT_{50}$ value of 99 days while in a lysimeter experiment with the same soil, Brumhard *et al.* (1991) found only 1.2-2.8 % was extracted unchanged after 131 days. Assuming first order kinetics applied, these figures are equivalent to a half-life of about 25 days or less.

Thus, as is to be expected, there do seem to be differences in the fate of pesticides in lysimeters compared with laboratory and greenhouse systems.

## Mobility of pesticides in the soil

There is little published data with which to compare pesticide movement in laboratory columns with that in lysimeters, possibly because it is already well established that laboratory columns do not reproduce field conditions (see chapter 2). The work of Stork *et al.* (1990) and Brumhard (1991) with $^{14}C$-clopyralid does, however, provide a direct comparison. Stork et al. (1990) placed 4 cm layers of soil containing clopyralid that had been aged for 0.42 and 121 days on top of 26 cm soil columns and applied irrigation for 48 h, equivalent to 200 mm water. With columns treated with soil aged for 121 days about 48 % of the radioactivity appeared in the leachate, 85 % of which was unchanged clopyralid (about 40 % of that applied). With the unaged treatment, 100 % of the $^{14}C$ was found in the leachate, all as unchanged clopyralid. In the lysimeter study of Brumhard *et al.* (1991), in which sugar beet was grown, after 131 days and about 255 mm of precipitation up to 60 % of the $^{14}C$ remained in the soil with only a small proportion below 60 cm. After 429 days, 25 % of the $^{14}C$ was recovered, 80 % of which was in the top 20 cm with almost none below 40 cm. Only 0.3 % of the $^{14}C$ in the first year and 0.6 % in the second year appeared in the leachate of the 110 cm soil profiles. The average concentration of clopyralid was less that 0.05 µg/l (range 0.002 - 0.14 µg/l); the intial applications being 120 and 240 g AI/ha. Thus a compound that would be classified as unacceptably mobile in a laboratory column gave no cause for concern on the basis of the lysimeter experiment.

Earlier work with $^{14}C$-metamitron and methabenzthiazuron (Brumhard *et al.*, 1987) also produced differences between laboratory and lysimeter. The laboratory columns were treated in the same way as in the clopyralid work of Stork *et al.* (1990) except the ageing periods were 0.30 and 105 days. With metamitron 6.5 % of the $^{14}C$ appeared in the leachate of a sandy soil (BBA standard soil 2.2) treated with unaged residues compared with 4.3 % and 1.3 % for the treatments with residues aged for 30 and 105 days. With a loess soil (orthic luvisol) the corresponding figures were 1.6 %, <1 % and <1 % respectively. Methabenzthiazuron was less mobile with up to 0.3 % of the applied $^{14}C$ leaching through the column of sandy soil and 0.1 % or less through the loess soil. In related lysimeter experiments Brumhard (1991) found that over a 5 year period a total of 0.62 % of the applied $^{14}C$ from $[3-^{14}]$ metamitron appeared in the leachate with a corresponding figure for methabenzthiazuron of 0.46 %. The nature of the $^{14}C$ compounds was not identified but in the laboratory, metamitron is much less persistent than methabenzthiazuron so it was thought to be unlikely that the leachates contained unchanged metamitron but some methabenzthiazuron could have been present. The conclusion is that the laboratory column suggested metamitron might be sufficiently mobile to pose a hazard to groundwater but methabenzthiazuron would not, whereas in the lysimeter study, because transformation processes could occur the leaching behaviour of $^{14}C$ was similar and, in terms of unchanged parent compound, methabenzthiazuron was probably present to a greater extent in the leachate than metamitron.

### Plant uptake of pesticides

Führ and Mittelstaedt (1983) compared the uptake of $^{14}C$-isocarbamid by sugar beet in a lysimeter with that in a closed micro-ecosystem in the greenhouse. Each was treated with 4 kg/ha of "Merpelan AZ" but the herbicide was incorporated into the 1 kg of the micro-ecosystem soil while it was applied to the surface of the lysimeter soil. In the pot experiment 64 % of the applied $^{14}C$ was found in the sugar beet leaves after 64 days but in the lysimeter the figure was only 1.23 % after 75 days. Part of the differences were that the root/soil ratio was higher in the pot than in the lysimeter and the pot soil was watered daily so that transformation and growth rates were higher. Thus by conducting an experiment under artificial conditions an erroneously high uptake of $^{14}C$ was produced. A further consideration is that in the greenhouse ecosystem the shoot and root atmospheres were kept separate so that any $CO_2$ produced by mineralisation of the isocarbamid was available only to the roots. In the lysimeter, evolved $^{14}CO_2$ could also have been taken up by the aerial parts of the plants. Indeed, some was apparantly absorbed by plants in adjacent untreated lysimeters. Therefore radioacitivity taken up by plants in lysimeters is not confined to the root uptake of residues.

## COMPARISON OF LYSIMETER AND FIELD EXPERIMENTS

### Soil conditions

In chapter 5 detailed information is presented on soil moisture and temperature in lysimeters and the field from which the lysimeters were filled. Over a two year period the soil temperatures were almost completely in agreement (see Figures 2 and 3). Soil moisture differed slightly, the lysimeters being drier due to lack of water supplied from the underlying layers except when irrigation had been applied to them (Figures 4 and 5).

## Pesticide fate and behaviour

Hansper (1986) and Kubiak *et al.* (1988) also compared the distributions of [3-$^{14}$C]metamitron and [carbonyl-$^{14}$C]methabenzthiazuron in lysimeters with those in the field after application of formulated unlabelled active ingredients. Fortyone to 53 days after pre-emergence application to sugar beet about 4 % of the applied $^{14}$C was present in the top 20 cm of the field soil, either as metamitron or desamino-metamitron, compared with 8 % in the lysimeter. None was detected below 20 cm in either case. Corresponding figures for methabenzthiazuron applied to winter wheat in April after 127-133 days were about 38 % in the field and 34 % in the lysimeters but all was found in the top 10 cm (Table 1).

TABLE 1. Methabenzthiazuron and metabolites in the lysimeter soil compared to the field experiment 127 and 133 days respectively after spraying onto winter wheat. Active ingredient application corresponding to 2 or 4 kg respectively of Tribunil ha$^{-1}$.

Quantity of active ingredient applied = 100 %

| Experiment | Quantity of active ingredient applied | Soil layer | Methabenzthiazuron and metabolites | |
|---|---|---|---|---|
| | mg m$^{-2}$ | cm | mg kg$^{-1}$ soil | % |
| Field experiment | 140 | 0 - 5 | 0.90 | 38.7 |
| | | 5 - 10 | 0.03 | 1.3 |
| | 280 | 0 - 5 | 1.70 | 35.9 |
| | | 5 - 10 | 0.03 | 0.6 |
| Lysimeter | 140 | 0 - 5 | 0.71 | 31.3 |
| | | 5 - 10 | 0.03 | 1.5 |
| | 280 | 0 - 5 | 1.60 | 35.1 |
| | | 5 - 10 | 0.04 | 0.9 |

These results are encouraging but require confirmation over a longer time. This is particularly important with regard to pesticide concentrations in the lysimeter leachates and soil water in the field at an equivalent depth, which were not compared in this study. Further experiments with $^{14}$C-labelled compounds repeating partly the experiments of Kubiak (1986) and Hansper (1986) will be initiated in autumn 1992 and spring 1993 with two agricultural soils an ortic luvisol and gleyic cambisol.

## INTERPRETATION OF LYSIMETER DATA WITH REGARD TO WATER POLLUTION

As Bergström (1990) has pointed out, concentrations of pollutants in lysimeter leachates indicate levels in water leaving the root zone. In the field, some of this goes through tile or mole drainage to surface water and some goes into deep ground water. In either case dilution will ultimately occur. The relative proportions taking each path and the ultimate dilution factors vary with topography and hydrogeology. Concentrations in both surface and groundwater also depend on what, if anything, is already present from previous applications. Thus it is difficult to decide on the significance of a lysimeter leachate concentration of a pollutant in relation to drinking water quality. Probably some semi-arbitrary level will be established for registration purposes for pesticides. A limit of 0.1 μg/l averaged over one year's harvest of leachate seems to be the criterion currently favoured by the BBA (1991). Given that subsequent dilution in surface or groundwater is likely in most cases, this is perhaps rather harsh in relation to the EC (1980) Drinking Water Directive. However, from the administrative viewpoint it has, for this reason, the merit of including an inherent safety margin. On the other hand, lysimeter designs currently available do not make provision for estimating losses by surface run-off and erosion which can lead to concentrations in the μg, sometimes mg/litre range (Leonard 1990). Therefore pesticide concentrations in lysimeter leachates should not be evaluated in isolation.

## UNANSWERED QUESTIONS CONCERNING THE USEFULLNESS OF LYSIMETER STUDIES

### <u>Validation</u>

As discussed in sections A) and B), the results available so far indicate that the behaviour of pesticides and the physical conditions in lysimeters are reasonably similar to those in the field and that divergences from related laboratory results are consistent with the acknowledged differences between field and laboratory conditions. However, the number of such comparisons is very small and, except for the work of Kubiak and Eichhorn (1990) they have nearly all been made with one soil type, the orthic luvisol (Parabraunerde) from Merzenhausen near Jülich. Whilst this soil is representative of a large agricultural area in Germany, it is by no means typical of agricultural soils in Europe, far less the world. It is important to know how well other soils will perform, particularly those with a higher clay content (which will crack) and those with a high proportion of gravel or larger stones. The latter are likely not only to show anomolous hydrological properties but also, for mechanical reasons, may be difficult to collect as undisturbed profiles by the standard methods of pressing the lysimeter casings into the field soil. It seems possible that a cracking soil will produce leachates with a higher pesticide concentration than a low organic sandy soil because of the higher possibilities for "by-pass" flow of water, although whether pesticides should be evaluated on the evidence of the "worst case" situation is debatable.

## Statistical considerations

Lysimeter experimentation is expensive so the tendency has been to use only 2 or 3 replicates. This raises the question of how much of the variability that occurs in the field is reproduced in a lysimeter study. A large number of studies of soil variability in the context of pesticides has been reviewed by Rao & Wagenet (1985) and Smith *et al.* (1987). Estimates of coefficients of variation calculated by Smith *et al.* (1987) were 48-320 % for saturated hydraulic conductivity, 40-97 % for infiltration rate, 7-202 % for pesticide transformation rate, 34-56 % for sorption coefficients and 40-450 % for pesticide concentration profiles (increasing with time after application). Some of these calculations must be treated with caution as they seem to have been based on the assumption that the variations followed normal (Gaussian) distributions whereas it is known that some properties do not vary in this way, so that the geostatistical regionalized variable theory is more appropriate (Rao & Wagenet, 1985). In the context of lysimeters, the relevence of these calculations is uncertain because they are derived from measurements made in individual core samples which are likely to have been of the order of 2.5-5 cm in diameter. Nothing is known of the variability of "cores" the size of lysimeters (0.5-1 $m^2$) except that it is likely to be smaller. Beckett & Webster (1971), reviewing data for basic soil properties such as organic matter and nutrient contents, concluded that up to half the variance within a field may be present within an area of 1 $m^2$. It is important to resolve this statistical uncertainty if lysimeter experiments are to play a major role in studies of pesticide behaviour in soil.

## CONCLUSIONS

Lysimeter experiments using $^{14}C$ labelled pesticides can be conducted in a manner which closely reproduces agricultural practice and allow close monitoring of soil temperature and moisture relations together with mass balance estimations of the fate of pesticides in the soil-plant-water-air complex. They can provide a more realistic appraisal than is possible in laboratory studies. In particular they allow long-term studies, including the influence of, and effects on, crops grown in seasons subsequent to a pesticide application as well as studies involving repeated applications over several seasons.

At the moment, although field and lysimeter experiments have given similar results, the data base is too small to give complete assurance that lysimeters reproduce field conditions with total accuracy. Also little is known of how far they reflect field variability, so it is not possible to calculate appropriate numbers of replicates. In addition, the range of soil types that has been used in lysimeter studies is very narrow so there is uncertainty as to how far lysimeters are generally applicable.

If these problems can be resolved satisfactorily it should be possible to incorporate most of the work now done in separate laboratory and field experiments into one set of lysimeter experiments. Already it can be seen that the comprehensive information gained on a compound applied in accordance with good agricultural practice means that new compounds will be studied in lysimeter experiments at a relatively early stage of development.

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