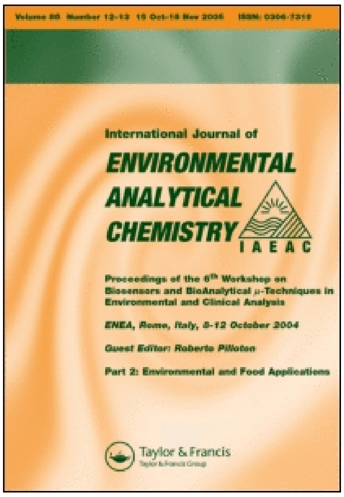

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VOLATILIZATION OF PESTICIDES FROM PLANT AND SOIL SURFACES – FIELD VERSUS LABORATORY EXPERIMENTS

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Comparative volatilization experiments were carried out using isoproturon and parathion-methyl sprayed on French beans in field experiments and on plant stands (0.5 m^2) in the volatilization chamber developed by the SLFA Neustadt using both compounds ^{14}C-labelled. The experimental conditions in the field experiments concerning wind speed, temperature and humidity fluctuations were simulated in the volatilization chamber. The laboratory experiment reflected the actual outdoor situation, showing only a negligible amount of volatile isoproturon directly measured in air samples, and providing no reduction of the A.I. residues in plants compared with the initial value in the corresponding field experiment. 77.2% of the parathion-methyl applied to the plants were volatilized and measured directly in air samples in the volatilization chamber while a reduction by 74.7% was found for the corresponding field experiment by residue analysis of the plants after 24 h. No details could be given concerning the nature of the evaporated portions in the field experiment.

KEY WORDS: Volatilization, field studies, laboratory studies, tracer technique.

INTRODUCTION

Volatilization from plant and soil surfaces is vaporization followed by movement into the atmosphere[1]. Actual vaporization rates depend on the physico-chemical behaviour of the compounds and their formulation, the application technique, climatic conditions such as temperature, relative humidity, wind speed, the soil properties and the structure of plant surfaces. The pesticide concentration may also affect the volatilization rate[2].

Looking at the field situation, all these factors and their interactions determine not only volatilization from plant and soil surfaces, but also other processes like adsorption, soil leaching, uptake via the leaves, and chemical and microbial degradation[3,4]. As a consequence, the results obtained can only give information on the dissipation behaviour of the compounds if the other influences mentioned, are known to play an important role concerning the fate of the compound in the environment. Other disadvantages, however, are the lack of reproducibility and the provision of only limited information because no ^{14}C-labelled compounds can be used. To overcome these disadvantages, laboratory experiments can be helpful tools.

For this reason, an application apparatus was designed, which permits spraying of compounds using nozzles, droplet sizes, water amounts and driving speeds similar to those common in agricultural practice, and an experimental chamber was built in which a wide range of outdoor conditions can be simulated[5].

The characteristics of this experimental tool are:

- — a fully enclosed chamber which allows the use of ^{14}C-labelled compounds
- — the use of bare soil or any kind of plants up to a height of 80 cm
- — direct absorption of volatile A.I. metabolites and $^{14}CO_2$ by isokinetic air sampling and investigation by TLC/HPLC
- — a balance of the total amount applied after additional investigation of plant or soil at the end of the experiment
- — the realization of either standardized temperature, humidity and wind speed conditions in plant stands and above bare soil or plant stands or simulation of realistic outdoor scenarios
- — a fully computer-controlled performance of the experiments allowing also data protocols according to GLP regulations

The reproducibility of this kind of experiment was tested with ^{14}C-labelled isoproturon and parathion-methyl sprayed on French beans grown under greenhouse conditions in two experiments each carried out under the same standardized experimental conditions (20 °C, 50% air humidity, 1 m/s windspeed). The results obtained from the isoproturon experiments after a 24 h experimental period showed that both experiments were in good accordance: 0.6 and 0.8% of the radioactivity applied were volatile isoproturon, 0.5 and 2.6% were no longer extractable from the plants and 98.4 and 95.3% were extractable from the plants and could be determined as unchanged isoproturon. The total recovery of both experiments was 99.5 and 98.7% of the amounts applied proving the reproducibility and sufficient recovery of this type of experiment[6]. Concerning the both parathion-methyl experiments, the results obtained showed the reproducibility of the experimental system also for a high volatilization rate. 68.2% and 64.1% of the compound applied to the French beans were directly measured in the air samples after 24 hours[7].

To investigate whether the results from these studies reflect the volatilization processes under real outdoor conditions, comparative experiments were carried out using isoproturon and parathion-methyl.

MATERIAL AND METHODS

Important physical-chemical data and application details of both compounds used are given in Table 1. Radiochemical purity of both ^{14}C-labelled compounds used in the laboratory experiments was > 99%. ^{14}C-isoproturon was mixed using not labelled isoproturon and blind formulation. In the corresponding field experiment not labelled isoproturon was mixed with

Table 1 Physical-chemical data and application details of isoproturon and parathion-methyl

	isoproturon[8]	*parathion-methyl*[8]
IUPAC-name	N-(4-isopropyl-phenyl) -N,N-dimethylurea	O,O-dimethyl-O-(4-nitrophenyl)-monothio-phosphate
Sum-formula	$C_{12}H_{18}N_2O$	$C_8H_{10}NO_5PS$
Mol. weight	206.3	263.21
Water solub.	65 mg/l at 20°C	55 mg/l at 20°C
Vap. press. (at 20 °C)	< 1 mPa	1.3×10^{-5} hPa
kg A.I./ha	1.5	0.2
Formulation	SC	WP
Amount of water/ha	400 L	400 L
Nozzle-type	Tee Jet E-8001	Tee Jet E-8001
Spray pressure	1.5 bar	1.5 bar
Field plot	25 m^2	62 m^2
Exp. platform of lab exp.	0.5 m^2	0.5 m^2
French beans	"Canadian Wonder"	"Canadian Wonder"
Stage of growth	blossom	blossom
plants/m^2	28	28

blind formulation. The parathion-methyl formulation (^{14}C-labelled as well as not ^{14}C-labelled) was available ready for use. In the field experiments the concentrations given in Table 1 were used. In the corresponding laboratory experiments the 1.8 fold amounts were used to take into account the application losses of the spraying system. The application losses consisted of side wall contamination in the spraying chamber and contamination of the spraying equipment. These losses were determined exactly after extraction with suitable organic solvents. The total amount applied to the plant stand was calculated exactly after substraction of these losses from the total amount used for application. Because of the higher dosage used for application the resulting amounts corresponded to the required amounts given in Table 1. Experimental duration was 24 h for all experiments. During the two field experiments the following parameters were measured:

- wind speed in and above the plant stand using an anemometer (A 100 R; Vector Instr.)
- air temperature using a temperature sensor (SKH 2011; Skye Instr.)
- air humidity using a humidity sensor (W 200 P; Skye Instr.)

All data were continuously recorded using a data logger (Delta, T-Devices). It was cloudy during both field experiments and a 14 h lighting period (Quicksilver HQI, 400 W/m^2) was carried out during both laboratory experiments.

Plant samples were taken 5 min after spraying of the field plots to determine the initial A.I. concentrations. Therefore, 10 small plots of 0.5 m^2 were harvested separately in the case of isoproturon and 5 plots of the same size were harvested in the case of parathion-methyl. To determine the residues 24 h after spraying, another 10 plots were harvested in the isoproturon experiment. In the parathion-methyl experiment 5 plots were harvested after 1, 3, 6 and 24 h. The plants of each plot were extracted and analysed separately. For this purpose, the plant material was extracted using acetone and a homogenizer (Omni Int.) for 5 min.

After filtration of the solution, isoproturon was determined by HPLC (LKB) using a Lichrospher column (100 RP-18) and the solvent system ammoniumacetate (0.1 M)/acetonitrile. For detection, an UV-monitor (VWM 2141; Pharmacia) was used. Recovery by this method was 98% and the determination limit was 1 mg/kg.

In the case of parathion-methyl the organic fraction was cleaned up using a silica-gel column. Parathion-methyl was determined using a gas chromatograph (8320, Perkin Elmer) and a OV-1-DF-0.25 column. The flow rate was 1.3 ml He/min, injection temperature was 250 °C and oven temperature was 160 to 290 °C (temperature program). Recovery by this method was 95% and the determination limit was 1 mg/kg.

In the corresponding laboratory experiment the climatic conditions measured in the field experiments were simulated and plants grown under the same outdoor conditions were used. [phenyl-U-^{14}C] labelled isoproturon and parathion-methyl with a specific radioactivity of 32 kBq/mg isoproturon and 430 kBq/mg parathion-methyl were available for the experiments in the volatilization chamber. The total amount applied to the plant stand was calculated exactly after determination and subtraction of the application losses from the total amount used for application. Volatilization was investigated after extraction of PU-foams which served as a sufficient adsorption material for both compounds. Sampling times were the same as in the corresponding field experiments. Extraction was carried out by pressing and releasing the foam in acetone. For determination of the total balance of the radioactivity applied, plants were harvested at the end of the experiments and extracted as already described. In addition, in the two laboratory experiments the radioactivity not extracted from the plants was investigated by incinerating aliquots of the extracted and carefully (20 °C) dried material after homogenization using an oxidizer (Packard, 307). All measurements of radioactivity were carried out using a LSC 2550 TR/LL (Packard) and suitable scintillators.

Determination of isoproturon was carried out using the method described for the field experiment but radiodetection (LB 506; Berthold) was used instead of UV measurement.

In the case of parathion-methyl, aliquots of the organic extract were streaked onto a silica gel plate (60 F 254; Merck) which was developed using n-hexane/ethylacetate (70 + 30; v/v) and radio-chromatograms were recorded using a Linear Analyzer (LB 284; Berthold). The detection limit of radioactivity was 2 kBq/kg.

All experimental results are expressed as percentage values on the base of the initial A.I. concentration at the beginning of each experiment.

RESULTS

Experiments with isoproturon

The climatic data recorded during the field experiment and simulated for the corresponding experiment in the volatilization chamber are given in Figure 1. The experimental results of

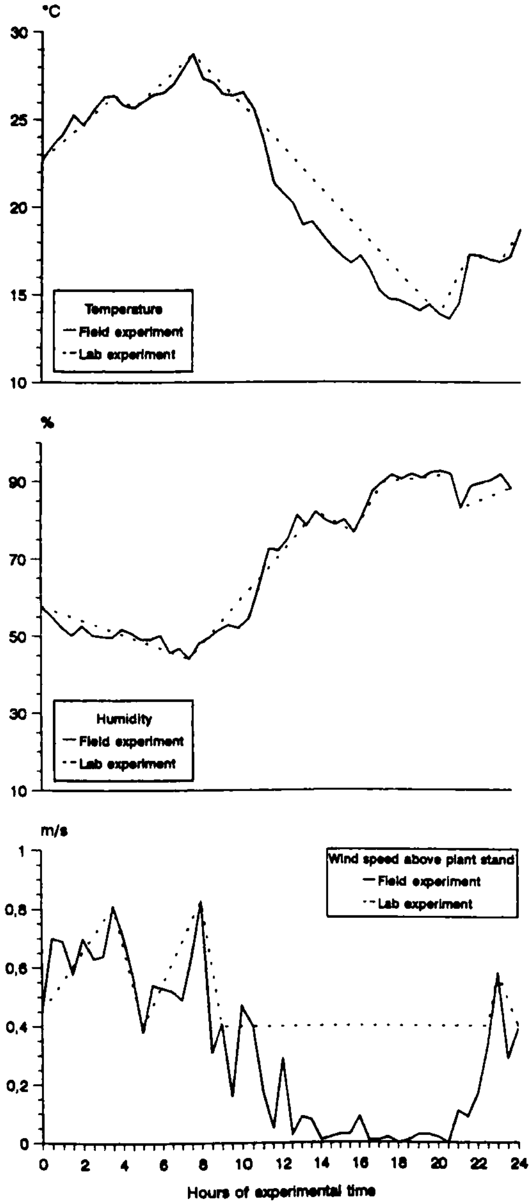

Figure 1 Climatic conditions measured during the field experiment with isoproturon and simulated in the corresponding laboratory experiment (Field measurements are half-hourly mean values)

both experiments are given in Table 2. More than 99% of the extractable residues from plants as well as of the volatilized ^{14}C was unchanged isoproturon.

Table 2 Balance of isoproturon applied to plants (Initial value applied to the plants = 100% SD = 12%)

		Field		*Laboratory*
		A.I.	SD[1]	A.I.
		%		
After 24 h:	*plant analysis*			
	a) extractable	101.7	16	97.0
	b) not extr.	—		3.4[2]
	air analysis	—		0.6
	Balance	**101.7**		**101.0**

—: not determined
[1]: Standard deviation
[2]: calculated as A.I. equivalents

Experiments with parathion-methyl

The climatic data recorded during the field experiment and simulated for the corresponding experiment in the volatilization chamber are given in Figure 2. The experimental results of both experiments are given in Table 3. More than 99% of extractable residues from plants as well as of the volatilized ^{14}C was unchanged parathion-methyl.

DISCUSSION

Since it has been well known that dissipation of pesticides form plant surfaces is influenced not only by volatilization, it was important for this comparative study to choose compounds which are not metabolizing during the 24 hours period under the experimental conditionas described and which are well extractable from plants. Furthermore, compounds had to be used which differ clearly in terms of their volatilization behaviour. From our own studies it was known that isoproturon[6] as well as parathion-methyl[7] fulfilled these requirements.

Concerning isoproturon no volatilization could be observed in the field experiment because 101.7% of the initial A.I.-value were determined after 24 hours in the plants. More data were available in the laboratory experiment showing a negligable volatilization rate of 0.6%. Very low volatilization rates can not be shown in a field experiments because high standard deviations are possible (Table 2). The extractable plant residues were in the same range as measured in the field and the radioactivity not extractable was very small. A sufficient balance could be calculated for the laboratory experiment (Table 2).

Concerning parathion-methyl the lack of the plant residues compared with the initial value determined in the field experiment by residue analysis after 1, 3, and 6 hours were in good accordance with the volatilization rates measured directly in the collected air samples of the corresponding laboratory experiment. The investigation after 24 hours again showed conformity between the field and the laboratory having in mind the restriction that no information could be given concerning the nature of the evaporated portions in the field experiment. The ^{14}C-residues not extractable from plants were small and again a sufficient balance could be calculated for the laboratory experiment after 24 hours (Table 3).

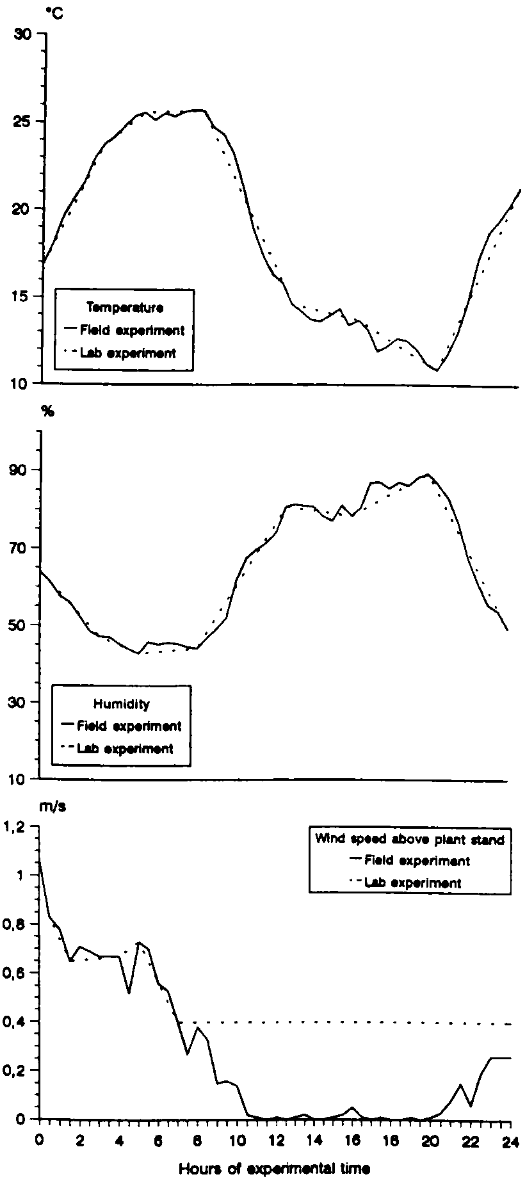

Figure 2 Climatic conditions measured during the field experiment with parathion-methyl and simulated in the corresponding laboratory experiment (Field measurements are half-hourly mean values)

It is well known that results from laboratory experiments (i.e. investigation of the degradation or leaching behaviour in soil) cannot be transfered to the actual field situation

Table 3 Reduction of initial value of parathion methyl on plants (Initial value applied to the plants = 100% SD = 17%)

		Field		Laboratory
		A.I.	SD[1]	A.I.
		%		
after 1 h:	plant analysis	86.1	23	—
	air analysis	—		84.1
After 3 h:	plant analysis	48.6	35	—
	air analysis	—		59.5
After 6 h:	plant analysis	29.8	32	—
	air analysis	—		46.6
After 24 h:	*plant analysis*			
	a) extractable	25.3	16	17.3
	b) not extr.	—		3.0[2]
	air analysis	—		22.8
Balance	total plant residues			20.3
(Lab)	total volatilization			77.2
	total			**97.5**

-: not determined

[1]: standard deviation

[2]: calculated as A.I. equivalents

without certain restrictions since small scale laboratory experiments carried out under standardized conditions may produce side effects[9]. The volatilization chamber used for the experiments reported here is capable of providing results that can be transferred to the real outdoor situation for either non-volatile or very volatile compounds because of a sufficient size of the plant stand (0.5 m^2), the use of plants grown under the same conditions, similar outdoor spraying procedure (Table 1), and the possibility of simulating real temperature and humidity fluctuations. Real wind speed conditions could also be simulated with the restriction that very low wind speeds (< 0.4 m/s above the plant stand) can not be realized (Figures 1 and 2).

High irridation can also not be simulated up to now. Because of this it would not have been possible to simulate the parathion-methyl experiment under sunny conditions since it is known that photolytical degradation of this compound may play a role[10]. This disadvantage will be overcome in future.

Having in mind this restrictions, this type of laboratory experiment gives more information compared with a field experiment, and analysis is more precise, because of the use of ^{14}C-labelled compounds. To prove this an experiment was carried out investigating the volatilization of ^{14}C-labelled dimethoate after application to bare soil. The results (Figure 3) showed that the compound was partly degraded by soil microorganisms during the experimental period of 24 hours showing that the biological activity of soils can be conserved during the experiment when freshly sampled soil is used and soil moisture can be controlled (50% of water holding capacity during this experiment). For this reason, 7.9% of the ^{14}C

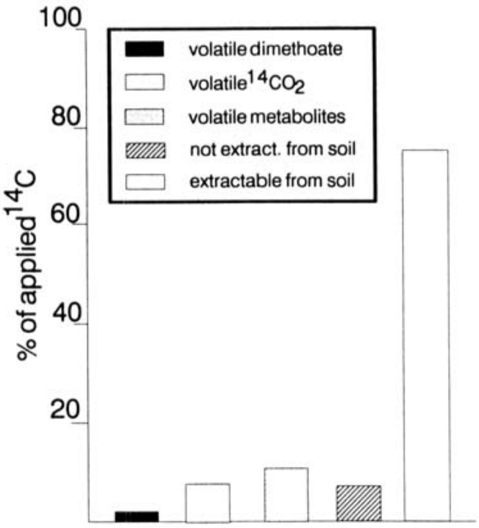

Figure 3 Balance of the volatilization experiment with ^{14}C-dimethoate 24 hours after application to bare soil

applied were detected as ${}^{14}CO_2$ in air samples indicating the mineralization of the [carbonyl-^{14}C]-labelling position of the A.I., 10.5% were determined as polar metabolites in the water, frozen out of air samples, 7.8% could no longer be extracted from the soil at the end of the experiment, 75.4% were extractable but only 1.3% of the compound applied were volatilized. The total balance of this experiment was 102.9%[11]. The result of the same experiment carried out under field conditions with unlabelled dimethoate would have lead to a possible misinterpretation if only the extractable soil residues had been taken for judging the volatilization.

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