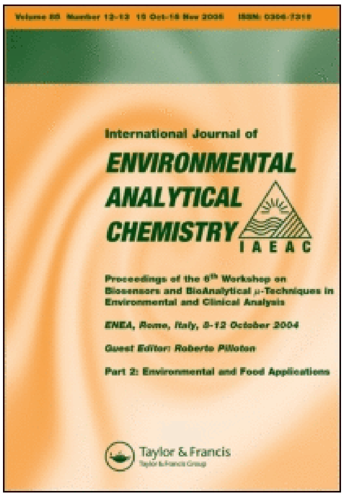

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Volatilization of ^{14}C-Labelled Fenpropimorph after Application to Plants and Soil under Simulated Outdoor Conditions

N. Staimer[a]; T. Müller[a]; R. Kubiak[a]
[a] Staatliche Lehr-und Forschungsanstalt für Landwirtschaft, Weinbau und Gartenbau, Breitenweg, Germany

To cite this Article Staimer, N. , Müller, T. and Kubiak, R.(1996) 'Volatilization of ^{14}C-Labelled Fenpropimorph after Application to Plants and Soil under Simulated Outdoor Conditions', International Journal of Environmental Analytical Chemistry, 65: 1, 183 — 191

To link to this Article: DOI: 10.1080/03067319608045553

URL: http://dx.doi.org/10.1080/03067319608045553

Intern. J. Environ. Anal. Chem., Vol. 65, pp. 183–191
Reprints available directly from the publisher
Photocopying permitted by license only

VOLATILIZATION OF ^{14}C-LABELLED FENPROPIMORPH AFTER APPLICATION TO PLANTS AND SOIL UNDER SIMULATED OUTDOOR CONDITIONS

N. STAIMER, T. MÜLLER and R. KUBIAK

Staatliche Lehr- und Forschungsanstalt für Landwirtschaft, Weinbau und Gartenbau,
Breitenweg 71, D-67435 Neustadt/W.str., Germany

(Received, 9 September 1995; in final form, 15 April 1996)

The volatility of fenpropimorph was investigated in a laboratory chamber constructed for studying the volatilization of ^{14}C-labelled pesticides from plant and soil surfaces. Summer barley was cultivated on experimental platforms (0.5 m^2) filled with soil and treated in an application chamber with ^{14}C-labelled fenpropimorph formulation (Corbel^R) at the beginning of ear emergence. After application, the platform was transferred into the volatilization chamber where a 96 h outdoor weather scenario was simulated. The results of three experiments demonstrated that up to 60% of the initial total radioactivity could be released from the plant-soil system within 96 h, most of it being the unchanged ^{14}C-fenpropimorph which undergoes a fast oxidative (degradation by solar irridation in the atmoshpere. Furthermore, $^{14}CO_2$ was detected in quantities of 1.1 to 1.8%. After plant extraction, however, mainly polar metabolites, such as fenpropimorh acid, were found four days alter application by Radio-HPLC-analysis. In order to evaluate the volatilization behaviour of fenpropimorph sprayed to bare soils, three additional experiments were carried out showing a volatilization rate of 11.4% at most, much lower than those of plant surfaces.

KEY WORDS: Volatilization, laboratory studies, ^{14}C-labelled fenpropimorph.

INTRODUCTION

The systemic morpholine fungicide Corbel^R with fenpropimorph ((±))-*cis*-4-[3-(4-*tert*-butyl-phenyl)-2-methylpropyl]-2,6-dimethylmorpholine) as the active ingredient is widely used for the control of *Erysiphe graminis, Rhynchosporium secalis* and *Puccinia spp.* in cereals. Outdoor lysimeter studies with formulated ^{14}C-labelled fenpropimorph applied on wheat at the beginning of ear emergence showed that 56 days after treatment only 30% of the radioactivity that reached the plant/soil system of the lysimeters could be recovered in plants, soil and leachate[1]. Therefore, 70% of the radioactivity applied was missing 8 weeks of application, possibly released into the atmosphere as fenpropimorph or as volatile transformation compounds like $^{14}CO_2$ after mineralization. So laboratory experiments in a volatilization chamber described in detail by Kubiak *et al.* (1993)[2] were carried out in order to get exact information about the volatility behaviour of ^{14}C-labelled fenpropimorph and possible volatile degradation products setting up an exact mass balance. Since it is well known that climatic parameters may have a decisive effect on volatilization and metabolism of pesticides a four day weather scenario was simulated in the volatilization chamber reflecting a typical climate of the main application time of fenpropimorph with respect to variable wind speeds, air humidities and temperatures. In addition, a computer-controlled lighting system generating light intensities with a maximum of 1500 W/m^2 was installed in order to mimic natural sunlight conditions from sunrise to sunset.

MATERIAL AND METHODS

Physical-chemical data application details of fenpropimorph are shown in Table 1. The radiochemical purity of the ^{14}C-labelled compound was > 97%. ^{14}C-fenpropimorph was mixed with non-labelled fenpropimorph and blind formulation in order to obtain labelled Corbel^R.

In the laboratory volatilization experiments the 1.1 fold amounts were applied with a specific radioactivity of 76 kBq/mg a.s. to take into account the application losses of the spraying system. The application losses consisted of side wall contamination in the application chamber and contamination of the spraying equipment These losses were determined exactly after extraction with acetone. The total amount applied to the plant stands or bare soil could be calculated by subtracting the losses from the total amount used for application. Summer barley was cultivated under outdoor conditions in experimental platforms (0.5 m^2) and sprayed in the application chamber with formulated ^{14}C-labelled fenpropimorph at the beginning of ear emergence. Experimental duration was 96 h for all experiments. In the volatilization chamber the climatic conditions measured before in outdoor experiments

Table 1 Physicochemical data and application details of fenpropimorph.

	fenpropimorph[3]
IUPAC-name	(±)-*cis*-4-[3-(4-*tert*-Butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine
^{14}C-labelling	phenyl ring
Mol. formula	$C_{20}H_{33}NO$
Mol. weight	303.5
Vap. pressure	3.5 mPa at 20°C
Solubility in water	4.3 mg/l (pH 7, 20°C)
Henry's law constant	1.0×10^{-7}
K_{ow} logP	4.1 (pH 7, 22°C)
K_{oc}	862–4500
pKa	6.98
g a.s./ha	750
Amount of water/ha	400 L
Formulation	EC
Nozzle-type	Tee-Jet E 8001
Spray pressure	2.0 bar
Experiment. platform	0.5 m^2
Summer barley	'Alexis'
Stage of growth	ear emergence
Soil-types	loamy clay (pH 6.8, Corg 1.1%, clay 29%) sandy loam (pH 6.7, Corg 1.5%, clag 13%) loamy sand (pH 6.1, Corg 0.8%, clay 7%)

were simulated (Figure 1). In this context a computer controlled solar simulation apparatus (K. H. Steuernagel GmbH) was available above the volatilization chamber emitting light intensities with a maximum of 1500 W/m^2 and a spectral distribution similar to the natural sunlight. A special glass plate on the top the volatilization chamber allowed the passing of the photolytical relevant wavelengths of 200–400 nm. Furthermore, an irrigation system was available to adjust the soil moisture to 50% of the maximum waterholding capacity (WC$_{max}$) during the experiments with three different bare soils (Table 1).

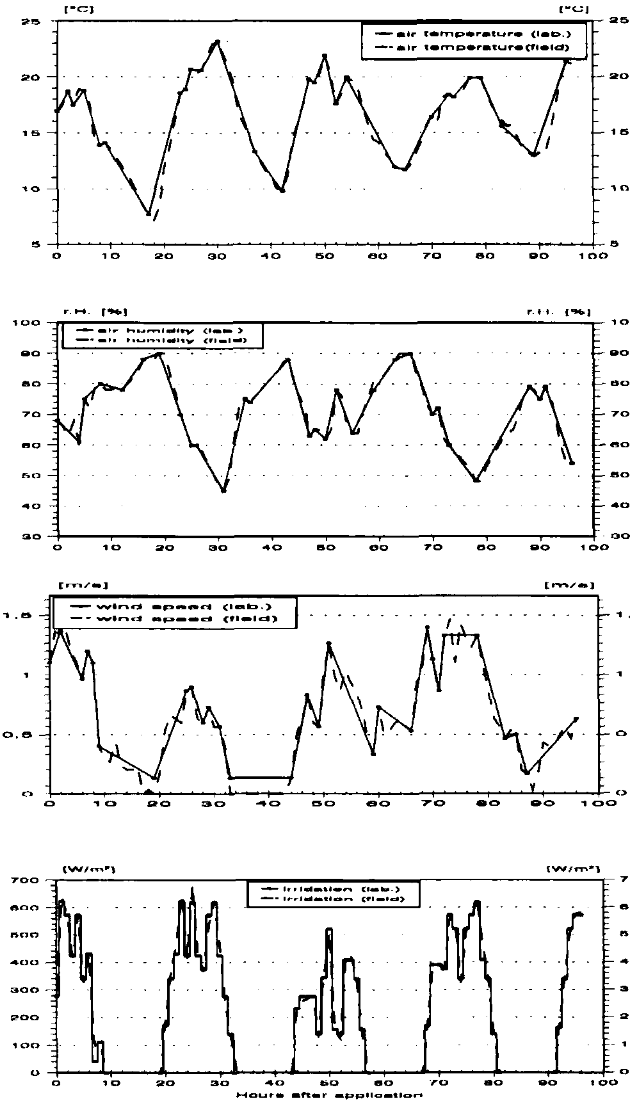

Figure 1 Climatic conditions measured directly above the plant stands during outdoor experiments with ^{14}C-fenpropimorph and simulated in the volatilization chamber.

Shortly after application, the experimental platforms (5 cm deep experiments with bare soil, 10 cm deep for experiments with plants) were transferred into the volatilization chamber. The conditioned air was converted into two parallel streams before entering the volatilization chamber. The upper channel (10 cm high) simulated outdoor wind speeds up to 1.5 m/s above the plant stands (Figure 1). The lower channel (80 cm high) simulated air exchange rates up to 0.3 m/s in the plant stands. The two air streams reached mixing channels after having passed the volatilization chamber in which the air is homoginized. At last the air streams passed both a filter system holding back radioactive compounds and a blower discharging the air out the system. A part of the total air stream (> 5%) was taken for further analysis from both channels. For exact investigation, a separation in volatile active ingredient and apolar metabolites adsorbed on polyurethan (PU)-foams, in polar metabolites detected by freezing traps and in $^{14}CO_2$ traps for measuring mineralized compounds was carried out. The PU-foams were exchanged 1,3,6,24,48,72, and 96 hours after application of ^{14}C-fenpropimorph and extracted with methano(11). An exact volume measurement allowed a total balance of radioactive substances in the air in combination with the analysis of the ^{14}C residues in plants and/or soil at the end of each experiment, a total balance of the initial total radioactivity applied was possible. To set up these mass balances, plants were harvested at the end of the experiments and extracted with methanol using a homoginizer for investigating the extractable radioactivity on the plants. In addition the non extractable pesticide residues were quantified by incinerating aliquots of the extrated and dried (30°C) plant material after homogenization using an oxidizer (Packard, 307). Furthermore the soil was taken from the platforms at the end of the experiments and homoginized. Then 50 g of dried soil (25°C) was extracted for 3 h in duplicate with a Bleidner-apparatus modified by W. Heizler[4]. The chloroform extracts (50 ml) of the soil samples were concentrated and then dissolved in methanol (5 ml). Bound radioactivity in soil samples was investigated after combustion as described above for non-extractable ^{14}C residues in plants. The ^{14}C-activity of all extracts was determined by a LSC 2550 TR/LL (Canberra Packard) and suitable scintillators. ^{14}C-fenpropimorph was identified by Radio-HPLC (Pharmacia, Sweden) using a Lichrospher column (100 RP-18, Merck) and the solvent system acetonitrile (85%), bidistillated water (15%) and ammonia water (0.25%). A FLO-ONE/Beta Radio HPLC Detector A-525 (Canberra Packard) is used for detection of the ^{14}C-labelled analyte.

RESULTS

Volatilization of ^{14}C-fenpropimorph applied to barley

In figure 2 the mass balances of three experiments under simulated outdoor conditions (Figure 1) showed that up to 60% of the initial total radioactivity could be extracted from the polyurethane-foams 4 days after application. Most of the radioactivity measured could be identified by Radio-HPLC as the unchanged active ingredient (Figure 3a). Metabolites could not be found in the polyurethane and freezing traps of the air sampling system. After 96 hours, however, 1.1–1.8% of the initial total radioactivity were mineralized to volatile $^{14}CO_2$ in the experiments 2 and 1, respectively.

For setting up the total mass balances of the applied radioactivity the plants and soil were extracted at the end of each experiment. In addition the bound residues were determined by combustion. So about 40% of the total radioactivity which had reached the plant/soil system at the beginning of the volatilization experiments were almost equally distributed between plants and soil 4 days after application. Most of the recovered ^{14}C-labelled residues were extractable from plants and soil (Figure 2). The Radio-HPLC-chromatogram in Figure 3b demonstrates that at least 60% of the extracted radioactivity from plants consisted of fenpropimorph acid and other polar metabolites. In the soil extracts, however, only the unchanged ^{14}C-fenpropimorph could be detected (Figure 3c).

Volatilization kinetics

Figure 4 characterizes the results of the volatilization kinetics of ^{14}C-fenpropimorph from the plant/soil systems obtained after replacing and investigating the PU-foams 1,3,6,24,48,72 and 96 hours after treatment. The volatilization of ^{14}C-fenpropimorph increased very quickly within 24 hours of application in all three experiments. Then the volatilization rates decreased more and more indicating that 48 hours after spraying of radioactively labelled fenpropimorph, the volatilization processes were almost complete.

Volatilization of ^{14}C-fenpropimorph applied to bare soil

In order to study the volatilization of fenpropimorph from bare soils three additional experiments were made. The mass balances in Figure 5 show the results. Therefore, most of the applied radioactivity was left in the three investigated soils 4 days after application. Most of it could be extracted and identified as ^{14}C-fenpropimorph. Five

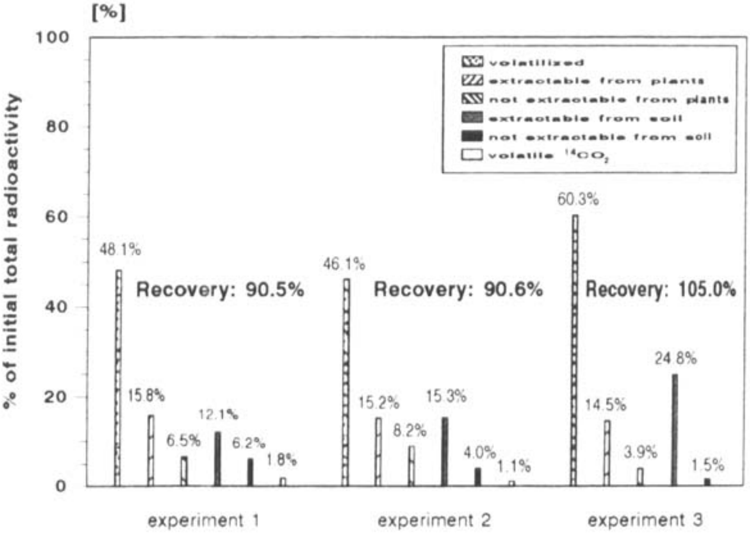

Figure 2 Mass balances of three volatilization experiments with ^{14}C-fenpropimorph 96 h after application to barley at the beginning of ear emergence.

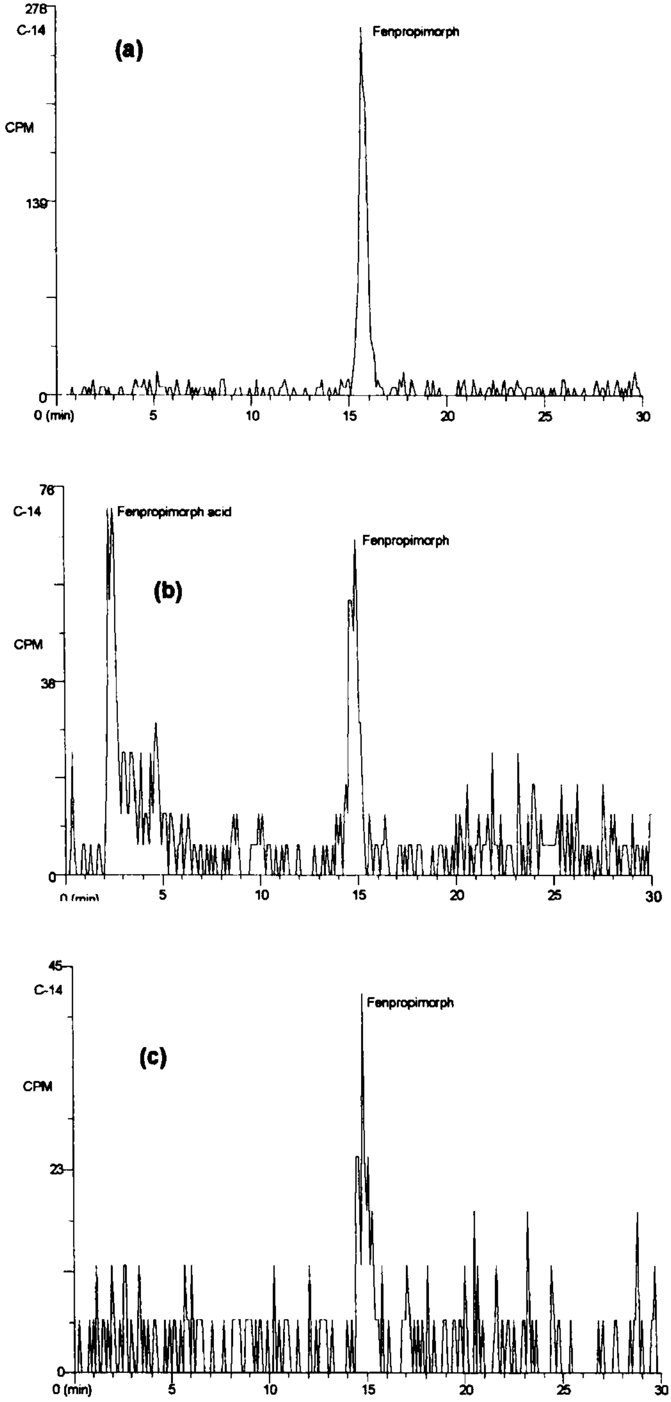

Figure 3 Examples of Radio-HPLC-chromatograms: (a) polyurethane-foam-extract 24 h after application; (b) plant and (c) soil extract 96 h after application.

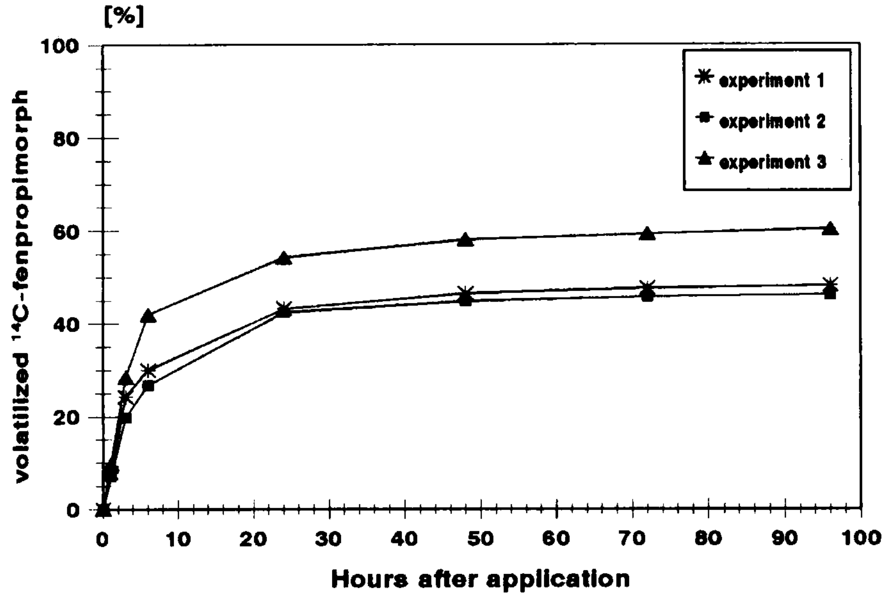

Figure 4 Kinetics of three volatilization experiments with ^{14}C-fenpropimorph applied to plant stands; applied redioactivity = 100%.

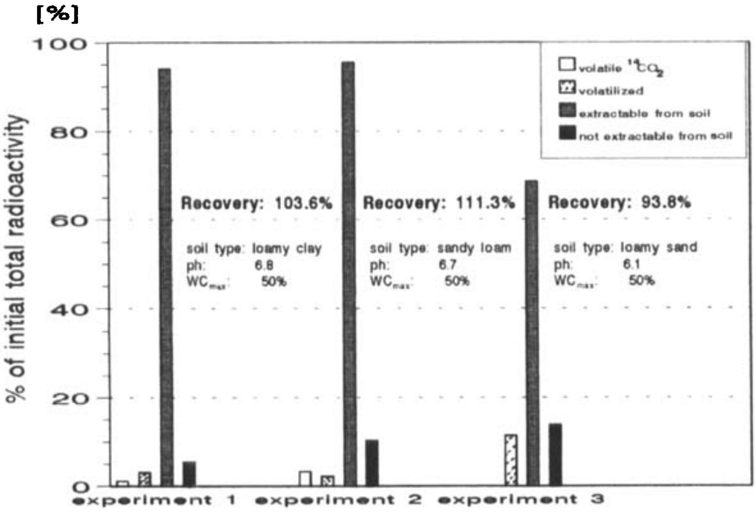

Figure 5 Mass balances of three volatilization experiments with ^{14}C-fenpropimorph 96 h after application to three bare soils0; WC_{max} = maximum waterholding capacity.

percent of the initial total radioactivity in experiments 1 and 2 (loamy clay and sandy loam, respectively) volatilized at most from the soils. In experiment 3 (loamy sand) 11.4% of the applied radioactivity volatilized from the bare soil 4 days after application with formulated ^{14}C-labelled fenpropimorph.

DISCUSSION

Volatilization from plant and soil surfaces defined as evaporation followed by movement into the atmosphere[5], does not only depend on the physico-chemical behaviour of the compound and its formulation. Besides the soil properties, the structure of plants and the pesticide concentration as well as climatic conditions may considerably affect the volatilization rates[6,7]. Thus a volatilization system was used in which a realistic outdoor scenario can be simulated[2]. Moreover the use of plants grown under field conditions and a sufficient size of the experimental plant stands (0.5 m^2) makes it possible to transfer the results of the volatilization chamber to a real outdoor situation[8]. In a lysimeter experiment with ^{14}C-labelled fenpropimorph under outdoor conditions published by Ebing *et al.* (1995)[1] only 30% of the applied radioactivity was found in plants and soil after the experimental period of 56 days. The experiments in the volatilization chamber reported here confirmed these results and in addition provided detailed information with respect to the fate of the missing radioactivity. Besides the unchanged fenpropimorph, $^{14}CO_2$ also appeared in the air sampling system indicating the mineralization of the [phenyl-^{14}C]-labelling position. Furthermore, an intensive degradation process of the ^{14}C-labelled fenpropimorph was observed during the experimental period of 4 days. On the one hand this fast metabolism of fenpropimorph is possibly due to photolytic processes on the leave matrices caused by the simulated natural sunshine conditions in the volatilization chamber. From earlier studies it is to be supposed that photodegradation on plant surfaces will be influenced by the nature of cuticular lipids depending on the concentration of unsatured and hydroxylated waxy biomolecules and the cutin content of plant cuticles[9]. On the other hand the systemic Corbel^R could be metabolized after plant uptake and translocation into the plant.

The much lower volatilization rates of ^{14}C-fenpropimorph sprayed to bare soils corresponded to studies indicating considerably higher volatilization half-lives of pesticides on soil surfaces than those on plant surfaces[8,10,11]. The high K_{oc}-values for fenpropimorph (Table 1) result basically in a strong adsorption by the soil, lowering the vapor pressure of the fungicide dependent on soil moisture, soil type and the pH-value of the soil as well due to the weakly basic character of fenpropimorph (pKa = 6.98). In this connection the experiments with three different bare soils demonstrated that an increase in organic C and clay content of the soil led to decreased volatilization rates of fenpropimorph from moist soils with a maximum waterholding capacity of 50% (Figure 5). The large volatilization rates of fenpropimorph and other pesticides from plant surfaces, however, can be explained by less effective chemical adsorption reactions on the leaf surface. Therefore the vapor pressure rises to values close to that of the pure compound. That is the case especially if the spray film on the leaf surface is still liquid during the time directly after application. In this context the drying time of the spray film on leaf surfaces may be influenced by modified formulations or additives to commercial formulated pesticides[12,13].

Due to its high potential to evaporate from plant surfaces, fenpropimorph may be translocated off-site via the air. In comparison to a wide array of other commonly used agrochemicals, no elevated concentrations of fenpropimorph in rain water have been detected[14]. This is probably related to the short chemical half-life of the fungicide in the atmosphere where the compound is subject to rapid degradation by OH-radicals and possibly photooxidative conversion. Model calculations based on the Atkinson method[15] show fenpropimorph to have a tropospheric half-life of 1–3 hours. The theoretical results have recently been substantiated by experimental work[16].

Acknowledgements

The authors like to thank BASF AG and Ciba-Geigy AG for financial support and providing the ^{14}C-labelled fenpropimorph.

References

1. .W. Ebing, M. Frost, R. Kreuzig and I. Schuphan, *Nachrichtenbl. Deut. Pflanzenchutzd.*, **47**(1), 5-9 (1995).
2. R. Kubiak, T. Maurer and K. W. Eichhorn, *Sci. Total Environ.*, **132**, 115–123 (1993).
3. C. Tomlin (ed.), *The Pesticide Manual* (United Kingdom, 1994), 10th ed., 1341 pp.
4. Deutsche Forschungsgemeinschaft: *Methodensammlung zur Rückstandsanalytik von Pflanzenschutzmitten* (Verlag Chemie 1991).
5. W. F. Spencer, W. J. Farmer and M. M. Cliath, *Residue Reviews*, **49**, 1–47 (1973).
6. N. Burkhard and J. A. Guth, *Pestic. Sci.*, **12**, 37–44 (1981).
7. G. H. Willis and U. McDowell, *Rev. Environ. Contam. Toxicol.*, **100**, 23–73 (1987).
8. R. Kubiak, T. Müller and K. W. Eichhorn, *Intern. J. Environ. Anal. Chem.*, **58**, 349–358 (1995).
9. W. Schwack, W. Andlauer and W. Armbruster, *Pestic. Sci.*, **40**, 279–284 (1994).
10. U. Dörfler, P. Schneider and I. Scheunert, *Toxicol. Environ. Chem.*, **31–32**, 87–95 (1991).
11. A. W. Taylor, *J. Air Poll. Contr. Assoc.*, **28**(9), 922–927 (1978).
12. B. J. Wienhold, A. M. Sadeghi and T. J. Gish, *J. Environ. Qual.*, **22**, 162–166 (1993).
13. H. de Ruiter, M. A. M. Verbeek and A. J. M. Uffing, in: ACS Symposium Series **371** (B. Cross and H. B. Scher, eds., Washington, 1988) pp. 45–54.
14. J. Scharf and K. Bächmann, *Nachrichtenbl. Deut. Pflanzenschutzd.*, **45**(4), 82–87 (1993).
15. R. Atkinson, *Int. J. Chem. Kin.*, **19**, 799 (1987).
16. E. Stamm and T. Winkler, *Proc. of the Internat. SEFA Congress*, Rouen, September 13–15 (1995).