

Predicting and Measuring Environmental Concentration of Pesticides in Air after Soil Application

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ABSTRACT

Pesticides can volatilize into the atmosphere, which affects the air quality. The ability to predict pesticide volatilization is an essential tool for human risk and environmental assessment. Even though there are several mathematical models to assess and predict the fate of pesticides in different compartments of the environment, there is no reliable model to predict volatilization. The objectives of this study were to evaluate pesticide volatilization under agricultural conditions using malathion [*O,O*-dimethyl-*S*-(1,2-dicarbethoxyethyl)-dithiophosphate], ethoprophos (*O*-ethyl *S,S*-dipropylphosphorodithioate), and procymidone [*N*-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide] as test compounds and to evaluate the ability of the Pesticide Leaching Model (PELMO) to calculate the predicted environmental concentrations of pesticides in air under field conditions. The volatilization rate of procymidone, malathion, and ethoprophos was determined in a field study during two different periods (December 1998 and September 1999) using the Theoretical Profile Shape (TPS) method. The experiments were performed on bare silty soil in the Bologna province, Italy. Residues in the air were continuously monitored for 2 to 3 wk after the pesticide applications. The amount of pesticide volatilized was 16, 5, and 11% in December 1998 and 41, 23, and 19% in September 1999 for procymidone, malathion, and ethoprophos, respectively. In both these experiments, the PELMO simulations of the concentration of ethoprophos and procymidone were in good agreement with the measured data (factor ± 1.1 on average). The volatilization of malathion was underestimated by a factor of 30 on average. These results suggest that volatilization described by PELMO may be reliable for volatile substances, but PELMO may underpredict volatilization for less-volatile substances.

OVER THE PAST YEARS pesticides have been measured in precipitation and air at many sites worldwide (Dubus et al., 2000). In Italy, Trevisan et al. (1993) measured concentrations of alachlor up to $10 \mu\text{g L}^{-1}$ in a forest 2 km from agricultural fields. Broglia and Mastropasqua (1999) measured dithiocarbamate residue up to $10 \mu\text{g L}^{-1}$ in air in an urban center close to a vineyard area. This and other evidence has led to growing concerns about health and the environment.

The main routes of introduction of pesticides into the atmosphere after normal agricultural applications are volatilization from soil and plant surfaces and drift. The rate of pesticide flux into air is influenced by various factors, such as the physicochemical properties of the pesticide, application techniques, meteorological conditions, dissipation processes, characteristics of the treated surface, and the season of the application. Volatilization from the soil surface may be influenced by the amount

of organic matter and by the mineralogical particles on which pesticides are adsorbed.

Many field measurements performed with different techniques report volatilization from fallow soil higher than 20% (Table 1). In fallow soil, if the moisture is adequate, pesticides initially volatilize at rates proportional to the vapor pressure of the chemical. If the moisture remains constant, volatilization is a function of the solar energy that influences the diffusion: solar-induced temperature changes affect the vapor pressure and, hence, the volatilization rate. If the soil dries out adsorption becomes a more important process, although this change is reversible and volatilization restarts when the soil is rewetted (Glotfelty et al., 1984; Willis et al., 1972; Glotfelty and Schomburg, 1989; Cliath et al., 1980). Also, other physical factors (e.g., aerodynamic resistance, atmospheric stability, and pressure changes) affect volatilization without affecting vapor pressure. More than 90% of the volatilization seems to occur from the topsoil layer, which is a few millimeters deep, during the first week after pesticide application.

Currently, a number of mathematical models such as PELMO (Klein, 1995), PRZM (Carsel et al., 1998), and MACRO (Jarvis, 1994) are used to assess the fate of pesticides in different compartments of the environment. For pesticide authorization, the European Community (EC Directive 91/414) requires measurement and prediction of the concentration of the pesticide in air.

Considerable experience has been gained with some pesticide fate models, mainly in the field of ground water protection (Vanclooster et al., 2000). Some of these models also calculate volatilization fluxes, but they need an improvement of accuracy. For most uses of these models, volatilization is set to zero as input data are lacking to parameterize volatilization modules (Tiktak, 2000). The precise simulation of volatilization behavior as an integral component of a complete pesticide transport model is important especially as a module that can be integrated into existing predicted environmental concentration ground water models such as MACRO, PEARL, and PELMO. Further development and improvement of the existing volatilization models are therefore indispensable. In previous model approaches and approximation procedures the relevant processes (e.g., transformation, diffusion, and convection) are described with varying degrees of accuracy. Some of the models (e.g., BAM and PESTLA) are suitable for screening volatilization behavior, but cannot replace a model validated by field studies (Jury et al., 1983). Currently there is a need for deterministic models validated

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Table 1. Cumulated volatilization from fallow soil measured with different techniques.

Pesticide	Surface moisture conditions	Experiment duration	Cumulated volatilization	Air temperature	References
		d	% of dose applied	°C	
Triallate	moist	14	29	10	Bor et al., 1995
Ethoprophos			24		
Parathion-ethyl			4		
EPTC	dry	14	26	16.5	Bor et al., 1995b
Triallate			19		
Parathion-ethyl			2.4		
Trifluralin	moist	4.2	13	12	Pattey et al., 1995
Triallate			21		
Lindane	moist	2	17.5	12	Siebers et al., 1993
Lindane			28		
Chlorthal-dimethyl	moist	21	18	19	Majewski et al., 1991
EPTC	moist	3	32	20	Clendening et al., 1990
Atrazine		17	0.6		
Chlorthal-dimethyl	moist	21	10	18.5	Ross et al., 1990
Trifluralin	dry	2.1	25	ND†	Taylor et al., 1976, 1977
	moist	7	90		
Heptachlor	dry	2.1	40		
	moist	6	90		
Lindane	dry	2.1	12		
	moist	6	90		
Chlordane	dry	2.1	2		
	moist	2.5	50		
Dacthal	moist	1.4	2		
Chlorpyrifos-ethyl	dry	3.2	0.64	25	Majewski et al., 1989, 1990
Diazinon			0.13		
Lindane			9.9		
Alachlor	moist	21	19	20	Gloffely et al., 1989a
Toxaphene			31		
Atrazine			2.4		
Simazine			1.3		
Chlorpropham	moist	7	37	24.5	Turner et al., 1978
Heptachlor	moist	1	14	22 to 33	Nash, 1983
		11	60		
Trifluralin		1	8		
		11	60		
Fonofos	moist	4	18	-3 to 18	Whang et al., 1993
Chlorpyrifos-methyl			7		
Atrazine			0.7		

† Not determined.

at the field scale that are capable of calculating hourly and daily predicted environmental concentrations.

The main objective of this paper is to determine the volatilization of procymidone, malathion, and ethoprophos under agricultural conditions. The secondary objective is the evaluation of the ability of PELMO (Klein, 1995) to predict pesticide loss by volatilization in field conditions.

MATERIALS AND METHODS

Field Site, Weather Data, and Test Substances

The experiment was performed at the Rhône-Poulenc experimental station in the Emilia-Romagna region outside Bologna, Italy (44°31' N, 11°17' E). The field is situated on a flat alluvial plain in the Po River valley (Fig. 1). The soil (Vertisual Cambisol) is a silty loam with a 1.5% organic carbon content and pH 7.8. All measured physicochemical properties are reported in Table 2. The experimental field is surrounded by arable land, and a 1-m-deep ditch delimits one edge of the field.

An automated climatic station (Model AD2; Silidata, Modena, Italy) recorded air temperature, soil temperature (5- and 10-cm depths), wind speed, wind direction, precipitation, air humidity, and solar radiation on an hourly basis. It was installed within the field site. A daily summary of the weather data is shown in Table 3. Evapotranspiration was calculated from pan evaporation daily data.

Three test substances with different chemical properties were selected (Table 4): the insecticides malathion and ethoprophos and the fungicide procymidone. The test substances were applied for the purpose of this study in December 1998 and September 1999 (Table 4) onto fallow soil by a spray bar. This nonlabel application was justified because this was a scientific study to evaluate processes, not a regulatory study to assess risk. The pesticide application was performed with a hand-carried sprayer with a 5-m-wide boom in a quasicircle with a 25-m diameter and an area of 495 m² (Fig. 2a). Because considerable volatilization normally takes place immediately after application, the sample collection started 15 min after application. During the course of the experiment, no spray treatments were performed within 8 km of the experimental field.

Measurement of the Volatilization

Air Sampling

The air-sampling system adopted for the field study was developed by evaluating a number of different procedures. The field measurements of volatilization were performed with one air-sampling station consisting of a 20-mm-diameter glass tube sampler of containing a plug of polyurethane foam (PUF). This was connected by a Teflon tube to air-sampling pumps (Model 224-PCEX4; SKC, Eighty Four, PA), which were operated with an airflow of 2 L min⁻¹. The PUF sampling plug was positioned at the center of the circular plot at Z_{inst} height (Z_{inst} is described in the Calculation of Volatiliza-

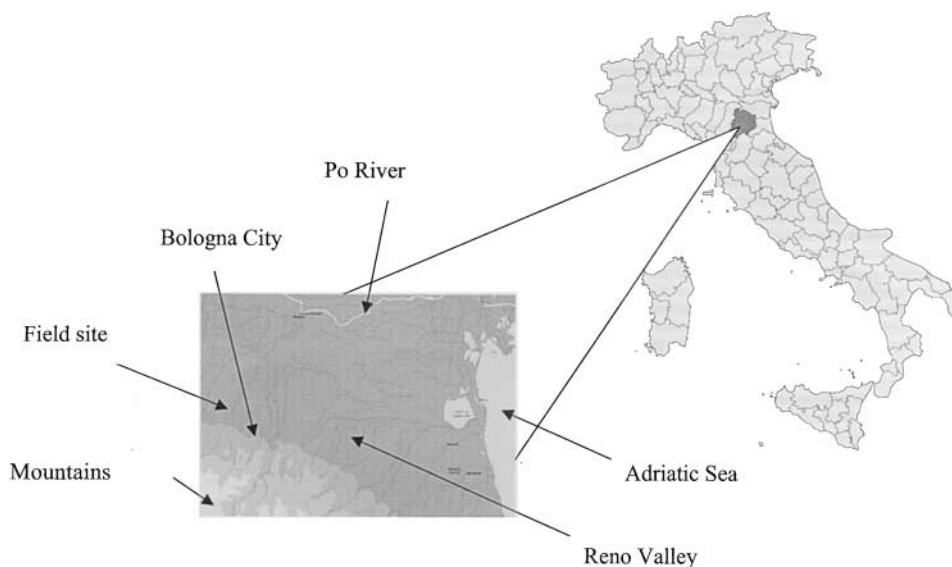


Fig. 1. Site map of the field experiment.

tion in the Field section, below) (Fig. 2). Replicate samples were collected, but with differing sampling intervals. After sampling, the plugs were returned to their sample jars and stored at -22°C until analysis.

Analysis and Validation of the Air Sampling Procedure

The extraction procedure of PUF was performed using a triple extraction with acetone (50 mL for each extraction) in an ultrasonic bath, followed by filtration with 10 g of anhydrous sodium sulfate. The extract was then concentrated under vacuum and finally evaporated to a volume of 1 mL under nitrogen flow. This 1-mL extract was used for the final gas liquid chromatography (GLC)–electron capture detector (ECD) and GLC–nitrogen phosphorus detector (NPD) analyses.

Determination of Ethoprophos, Malathion, and Procymidone by Gas Liquid Chromatography. A Model 8521 GLC (Dani Instruments, Cologno Monzese, Italy) equipped with a ^{63}Ni ECD and a fused-silica DB-17 capillary column (30-m length \times 0.25-mm i.d., 0.25- μm film thickness; J&W Scientific, Folsom, CA) were used for procymidone quantification. The GLC–ECD operating conditions were: injector temperature, 280°C ; detector temperature, 289°C ; initial temperature, 180°C for 3 min, $4^{\circ}\text{C min}^{-1}$ up to 210°C for 10 min, $15^{\circ}\text{C min}^{-1}$ up to 270°C , and held at 270°C for 10.5 min. The carrier gas was He at 4 mL min^{-1} , the injection volume was $1\ \mu\text{L}$, and the retention time of procymidone was 18.1 min.

Ethoprophos and malathion were determined with a Dani Instruments GC 1000 instrument equipped with an NPD detector. The operating conditions were: splitless, injector temperature 250°C ; ZB5 Zebron column (30-m length \times 0.25-mm i.d., 0.25- μm film thickness; Phenomenex, Torrance, CA); $1\text{ mL helium min}^{-1}$; temperature program from 140 to 280°C in 30 min. The retention times were 6.1 and 11.5 min for ethoprophos and malathion, respectively. With these conditions the detection limit was 0.01 mg kg^{-1} and good linearity was achieved ($R^2 > 0.95$) for all the pesticides.

Active ingredients were recognized by comparison between sample and standard retention times and concentrations were determined by linear regression technique recovery tests. Air concentrations were obtained by considering the volume of sampled air (Capri et al., 1999).

Static Recovery, Retention Efficiency, and Sampling Efficiency. Results for static recovery, retention, and sampling

efficiency are presented in Table 5. Static recovery is the ability of the sampling medium to retain a spiked solution when the sampling cartridge is stored in clean, quiescent conditions for the duration of the test period. An aliquot of procymidone ($25\ \mu\text{L}$ of $122\ \mu\text{g mL}^{-1}$, $3.05\ \mu\text{g}$), malathion ($25\ \mu\text{L}$ of $187\ \mu\text{g mL}^{-1}$, $4.67\ \mu\text{g}$), and ethoprophos ($25\ \mu\text{L}$ of $187\ \mu\text{g mL}^{-1}$, $4.67\ \mu\text{g}$) solution was added to each PUF plug, so that the liquid spread out over the surface, then the extraction was performed (Table 5). The test was performed at room temperature (25°C and 45% relative humidity). There were three replicates of each sample, in addition to the control samples of laboratory blanks (untreated) and samples fortified with acetone alone.

Retention efficiency is the ability of the sampling medium to retain a compound when added in the form of a liquid solution. This test was performed to verify the capacity of PUFs to absorb the active compound during the sampling process and during air transmission. The PUF plugs were fortified and connected to the personal sampling pumps for 3 h in the dark, with a 2 L min^{-1} air flow (18.5°C and 53% relative humidity) (Table 5). Control samples consisted of

Table 2. Pesticide Leaching Model (PELMO) input for scenario characterization including measured physicochemical properties.

Input	Value
Latitude, $^{\circ}$	44.31
Snow melt factor	0.46
Calculate evapotranspiration with	pan evaporation data
Minimum depth for evapotranspiration, cm	0
Pan factor	1
Erosion	not calculated
Runoff	not calculated
Crop parameter	silty loam soil
Soil parameter	
Core depth, cm	110
Number of horizons	1
Thickness of layers, cm	10
Initial soil water, $\text{m}^3\ \text{m}^{-3}$	0.178
Biodegradation factor	1
Soil horizons parameters	
Bulk density, Mg m^{-3}	1.4
Dispersion, $\text{m}^2\ \text{s}^{-1}$	0
Sand content, %	47.3
Clay content, %	19.2
Organic carbon, %	1.495
pH	7.6

Table 3. Meteorological inputs used in the Pesticide Leaching Model (PELMO).

Day of month	Rainfall	Evaporation†	Temperature, 1400 h	Temperature, daily mean	Temperature, daily excursion	Relative humidity
	mm		°C			%
December 1998						
16	0.0	3.5	7.1	3.9	8.8	91.8
17	0.2	3.2	4.9	0.9	8.5	97.0
18	0.0	4.4	7.4	3.2	9.6	93.8
19	0.0	5.5	9.5	5.8	12.2	81.6
20	0.2	6.0	11.3	6.5	13.8	83.4
21	0.0	1.1	4.5	3.6	6.1	97.6
22	33.4	1.0	4.9	3.6	2.5	97.1
September 1999						
11	0.0	3.4	17.1	14.6	7.4	88.6
12	0.0	5.8	20.3	19.4	12.7	78.0
13	0.2	5.2	20.7	14.8	13.1	82.7
14	0.2	3.6	18.8	14.8	7.8	94.2
15	0.0	3.5	19.1	17.8	8.6	85.6
16	0.2	2.5	18.4	14.9	6.8	91.8
17	0.0	3.2	19.5	17.0	7.0	83.0
18	0.0	4.2	18.6	14.6	6.7	77.3
19	7.2	2.3	12.8	12.6	5.1	77.5
20	2.0	2.5	12.3	9.3	6.4	76.2
21	5.4	0.8	8.1	8.5	2.2	84.5
22	25.6	0.8	9.4	7.5	5.5	100.0
23	1.0	3.3	15.6	12.4	7.2	94.5
24	9.0	2.3	15.3	14.3	7.5	93.6
25	4.4	1.0	16.2	14.3	5.2	99.5
26	1.0	5.9	25.4	15.6	11.2	84.0
27	0.2	1.9	18.1	22.0	3.4	98.6
28	0.0	6.0	20.8	17.7	9.2	88.8
29	0.2	3.7	18.4	14.6	10.7	96.0
30	0.2	6.1	17.1	14.9	3.9	97.2

† Estimated by RadEst (Donatelli et al., 2003).

fortified PUF plugs, which were stored at a low temperature (<5°C), and by PUF plugs not connected to a personal sampling pump.

Sampling efficiency is the ability of the sampling medium to trap the vapor of a particular pesticide or metabolite. The proportion of the analyte of interest that is collected and retained by the sampling medium is determined by introducing the analyte as a vapor in air (or in nitrogen) into the air sampler. The sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended field use. This experiment allows a mass balance measurement of the pesticide distributed in the air phase and

on the wall of the flask used to generate the vapor. Furthermore, it gives a good indication of the sorption breakthrough curve of the sorbent by means of different PUFs positioned along the tube. To evaluate the sampling efficiencies, several tests were performed on the active ingredient (in the form of the analytical standard) in different conditions of temperature and relative humidity (Table 5).

Calculation of Volatilization in the Field

The volatilization of pesticides from the soil surface is calculated with the Theoretical Profile Shape (TPS) method de-

Table 4. Chemical inputs used in the Pesticide Leaching Model (PELMO).

Characteristic	Ethoprophos	Malathion	Procymidone
Molecular mass, g mol ⁻¹ †	242.3	330.3	284.1
Application data			
Application	soil application	soil application	soil application
Date of first application	16 Dec. 1998	16 Dec. 1998	16 Dec. 1998
Date of second application	11 Sept. 1999	11 Sept. 1999	11 Sept. 1999
Application rate, kg ha ⁻¹	1.00	0.64	0.75
Application depth, cm	0	0	0
Plant uptake factor	0	0	0
Volatilization data			
Henry's constant	calculated	calculated	calculated
Vapour pressure, Pa†	0.0465	0.0053	0.019
Aqueous solubility, mg L ⁻¹ †	700	145	4.5
Diffusion coefficient in air, cm ² s ⁻¹	0.05	0.05	0.05
Volatilization depth, cm	0.1	0.1	0.1
Sorption data			
K _{oc} , mL g ⁻¹ †	70	1800	1900
Freundlich exponent‡	0.9	0.9	0.9
pH during study	7.6	8.6	9.6
pK _a §	20	20	20
Limit for Freundlich‡, µg L ⁻¹	0.01	0.01	0.01
Annual increase, %	0	0	0

† Tomlin (1994).

‡ Default value.

§ Default value for totally undissociable molecule.

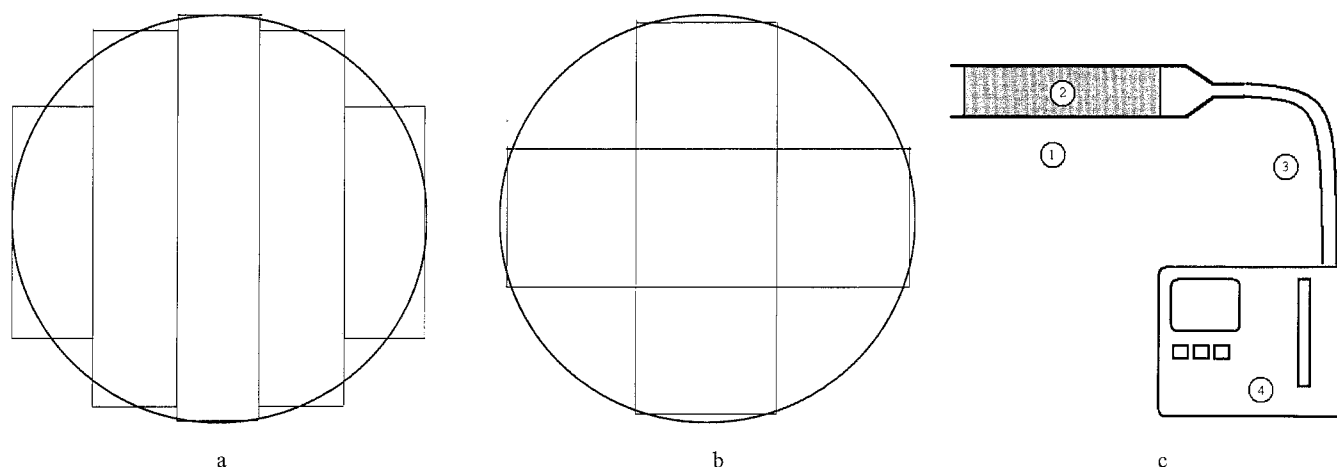


Fig. 2. Representation of the pesticide-treated area in Bologna. (a) The pesticides were applied in 5-m segments (rectangles) with a total area of 495 m² reproducing a quasicircle (dashed line) with an area of 491 m². (b) Representation of the soil sampling grid: each soil sample was collected in each square cluster. (c) The sampling instrumentation for air: 1, glass cartridge; 2, polyurethane foam (PUF) plug; 3, tygon pipe; and 4, programmable pump.

scribed by Wilson et al. (1982), which is used to determine the gaseous mass transfer from field experiments conducted in a circular plot. The TPS method has the advantage over the aerodynamic method (Yates, 1996) in that (i) the large fetch requirement is not necessary, (ii) measurement of the air concentration and wind speed are needed at only one height, and (iii) the sensor is placed at a height that is relatively insensitive to the atmospheric stability so temperature, wind gradients, and stability correction are unnecessary. This approach is based on the Trajectory Simulation Model (TSIM) (Wilson et al., 1982) and was used (Yates, 1993) to simulate movement of pesticides away from a treated field.

Volatilization, *V*, is calculated according to:

$$V = \frac{[u(t)c(t)]}{\Omega} \Big|_{Z_{inst}} \quad [\text{mg m}^{-2}\text{s}^{-1}] \quad [1]$$

where *u*(*t*) is the wind speed during the sampling time (m s⁻¹) and *c*(*t*) is the pesticide concentration in the air during the

Table 5. Air sampling validation.

Trial	Fortification	Recovery	Volatilization
	(25 μL) μg mL ⁻¹		
		Procymidone	
Static recovery	3.05	89 ± 9	
Retention efficiency	3.05	91 ± 5	
Sampling efficiency			
40% RH†, 25°C	3.05	89 ± 5	5 ± 1
40% RH 45°C, N‡	3.05	76 ± 21	31 ± 22
100% RH 25°C	3.05	66 ± 7	30 ± 7
		Malathion	
Static recovery	4.67	86 ± 3	
Retention efficiency	4.67	106 ± 11	
Sampling efficiency			
40% RH, 25°C	4.67	95 ± 11	2 ± 1
40% RH 45°C, N‡	4.67	90 ± 10	6 ± 2
100% RH 25°C	4.67	81 ± 9	10 ± 5
		Ethoprophos	
Static recovery	4.67	101 ± 21	
Retention efficiency	4.67	110 ± 14	
Sampling efficiency			
40% RH, 25°C	4.67	97 ± 12	3 ± 3
40% RH 45°C, N‡	4.67	85 ± 16	11 ± 8
100% RH 25°C	4.67	82 ± 10	12 ± 8

† Relative humidity.
‡ Under N flux.

sampling time (mg m⁻³) at sampling height *Z*_{inst} (cm). The ratio of the horizontal to vertical flux, *Ω*, is obtained using the “trajectory simulation method.” The terms *Ω* and *Z*_{inst} depend on the surface roughness, *Z*₀, and the upwind fetch distance (i.e., the radius of the treated surface).

With the TSIM, the hypothetical movement of the particles in the atmosphere is traced from the source to the point of measurement. Since the height profiles of the theoretical position of the volatilized pesticides cross each other for stable and unstable atmospheric conditions, it is possible to identify a single height, *Z*_{inst}, where measurements can be performed for all atmospheric conditions (Fig. 3). The value of *Z*_{inst} was calculated to be 67 cm, with a corresponding value of 7.0 for *Ω*. The curves in Fig. 3 were obtained using a Monin–Obukhov length (Wilson et al., 1981) of 500 and –500 cm for stable and unstable atmospheric conditions, respectively. The maximum horizontal length was set to 12.5 m according to the radius of the circle of the pesticide application area. Furthermore, to obtain sound curves, the horizontal length was divided into 1000 sections, and 2500 particles were released from each section for stable atmospheric conditions and 6000 for unstable conditions in the trajectory simulations. These particles represent each single cluster of air over the circular plot used by TSIM to simulate the hypothetical movement of the particles.

The roughness length, *Z*₀, was estimated by measurements of the wind speed at three heights continuously for two weeks

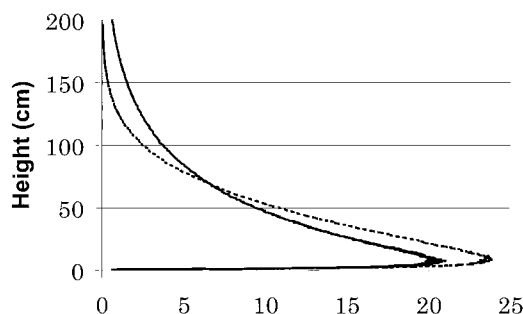


Fig. 3. Normalized flux of air (ratio of the horizontal to vertical flux) obtained using a Monin–Obukhov length of 500 and –500 cm for stable and unstable atmospheric conditions, respectively, for different heights at Bologna calculated with the trajectory simulation model. The full and dotted lines represent unstable and stable atmospheric conditions, respectively.

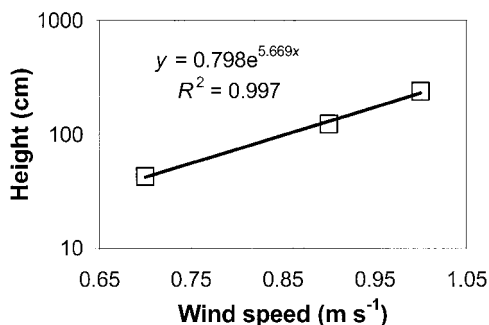


Fig. 4. Wind profile at 1700 to 1800 h on 11 Dec. 1998. Wind speed has been measured at three different heights from the soil (43, 124, and 240 cm). Open rectangles represent measured points (average) while the line represents a regression line. The constant (0.80) in the exponential function of the regression line corresponds to the roughness length, Z_0 (expressed in cm).

before the December 1998 sampling event. The roughness length was then obtained from the logarithmic wind profile where Z_0 is the intercept with the height axis. A constant value of 0.8 cm was obtained in December 1998 during the two weeks before the sampling events. An example of a wind profile from December 1988 is shown in Fig. 4. This value was used for both the December 1998 and September 1999 calculations.

The percentage of volatilization from the field was obtained from the ratio of the total amount of pesticides volatilized to the applied dose.

Soil Sampling

To verify the presence of test pesticides in the topsoil (i.e., 0- to 10-cm depth) before each treatment and to determine the concentration in topsoil at the end of same field trial, ethoprophos, malathion, and procymidone residue in soil were determined. Five topsoil samples were collected before each treatment and after each trial period using a random location inside an 8- × 8-m grid (composed of five clusters) located inside the treated area (Fig. 2b). Each sample was a mixture of three replicates. The holes in the ground caused by sampling were filled with bentonite pellets. The sampler used consisted of a stainless steel tube (10 cm long) with a "T" surface layer protection, which allows collection of soil samples without reciprocal sample contamination.

Simulating Volatilization

The one-dimensional PELMO (Klein, 1995) is a compartment model that simulates chemical movement in the unsaturated soil system within and below the plant root zone. Time-varying transport, including advection and dispersion, are included in the program. PELMO is based on PRZM-1, but processes have been added to it to overcome the limitations of PRZM-1 (Klein et al., 2000).

Prediction of pesticide volatilization in PELMO is based on Henry's and Fick's laws, using Henry's constant and the diffusion coefficient in air. To estimate the amount of pesticide that moves from the soil surface into the atmosphere, the assumption is made that the concentration of the pesticide in the air above the soil is practically zero. The user must specify the thickness of the active layer d . PELMO considers only volatilization from soil water and not from the sorbed phase. Based on these assumptions, volatilization is calculated according to the following equation:

$$J_v = -D(Hc_1/d) \quad [2]$$

where D is the diffusion coefficient in air ($\text{cm}^2 \text{d}^{-1}$), J_v is the volatilization rate ($\text{g cm}^{-2} \text{d}^{-1}$), d is the thickness of the active layer (cm), H is the Henry's constant (dimensionless), and c_1 is the dissolved pesticide concentration on the surface (g cm^{-2}). The thickness of the active layer of air was set as 0.1 cm by a calibration of the model against measured data (Table 6, Fig. 5). This agrees with the Forum for Coordination of Pesticide Fate Models and Their Use (FOCUS) ground water report where the depth for volatilization is set to 1 mm by default.

The version used in this study, FOCUS PELMO 1.1.1, is the application running on a Windows platform based on PELMO 3.2. The inputs required by the model are divided into three categories: scenario, pesticide, and weather. Some of these inputs were measured; others were estimated due to lack of information (e.g., Henry's constant was calculated from vapor pressure and aqueous solubility and diffusion coefficient in air was estimated as $0.05 \text{ cm}^2 \text{ s}^{-1}$, the default value). The simulations were run for each pesticide and for each season with no calibration except for the active depth for volatilization.

RESULTS AND DISCUSSION

Measurement of the Volatilization Rate in the Trials

The field experiments were performed in various meteorological conditions. In the December 1998 experiment, the average air temperature was 1.9°C (-3.3 to 12.7°C) and the air humidity was high (81–97%). It rained only on the last day of sampling (34 mm). The average wind speed was 0.6 m s^{-1} . In the September 1999 experiment, the average air temperature was 15.0°C (8.0 to 20.0°C) and the air humidity was between 77 and 100%. From 8 to 15 d after the pesticide application, 57 mm of rainfall was measured. The average wind speed was 1.4 m s^{-1} .

Pesticides were not detected in the topsoil samples collected before the applications (Table 7). At the end of the trials the concentration measured in soil ranged from 15 to 97% of the applied dose. A relevant part of the dissipation was due to volatilization processes: 15.9,

Table 6. Calibration of active layer input in the Pesticide Leaching Model (PELMO) (simulations run with different active layer heights) against measured volatilization data.

Data	Active layer height cm	Cumulated volatilization		
		Ethoprophos	Malathion	Procymidone
Predicted	0.1	16.4	0.65	44.7
Predicted	0.2	7.50	0.19	18.0
Predicted	0.4	3.84	0.094	9.70
Predicted	1.0	1.56	0.036	0.42
Measured		19.4	14.5	31.1

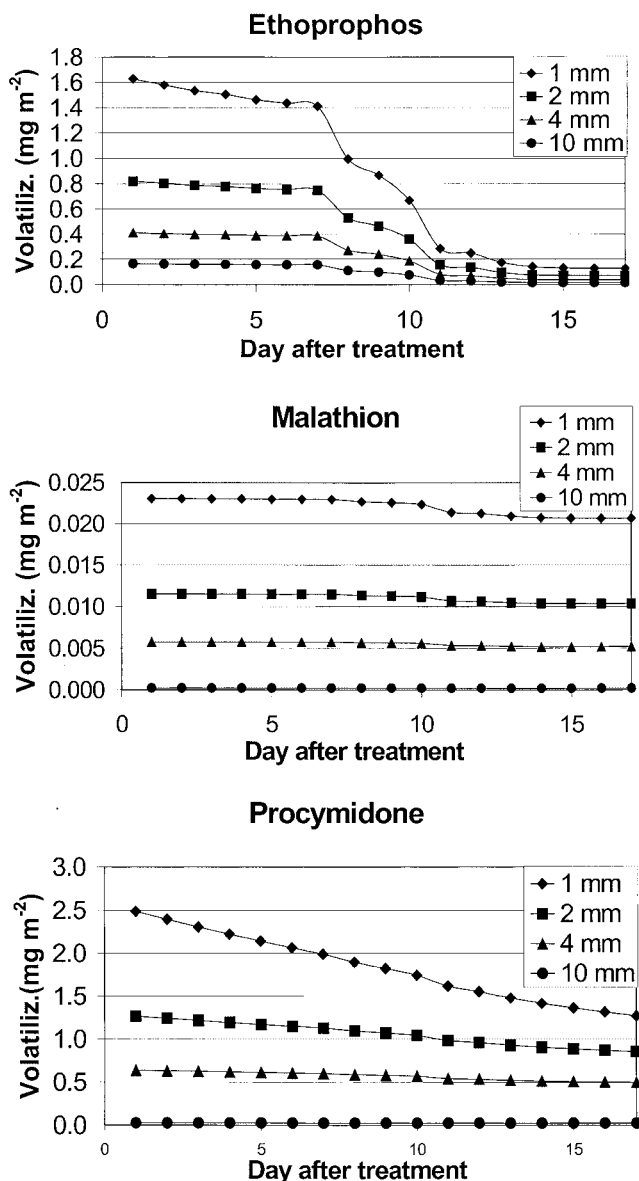


Fig. 5. Model sensitivity to different active air layer thicknesses (1, 2, 4, and 10 mm) on September 1999 simulations.

10.9, and 5.3% of the applied dose for procymidone, ethoprophos, and malathion, respectively, in December (6 d after treatment); and 41.5, 19.4, and 22.7% of the applied dose in September (16 days after treatment).

The differences between the pesticides are due to their chemical properties, while the differences between the seasons are due to the meteorological conditions influencing the volatilization process.

In Fig. 6 and 7, volatilization rates are presented for the December and September periods, respectively. In December a daily periodic variation of the volatilization was measured with an increase during the day and a decrease at night for ethoprophos and malathion. This process was stronger for the first 3 d after treatments with flux roughly proportional to temperature. Overall volatilization of ethoprophos, malathion, and procymidone was 5.8, 1.3, and 11.6 mg m^{-2} during the day and

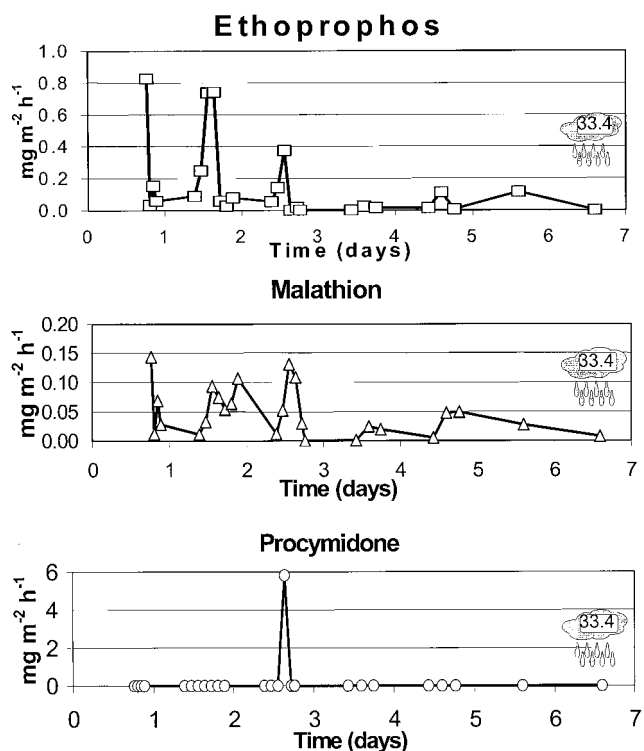


Fig. 6. Volatilization rate during the December 1998 study determined by the Theoretical Profile Shape (TPS). Day 1 corresponds to the end of the day of treatment (midnight). The cloud symbol represents a rainfall event in millimeters of rain.

2.2, 0.9, and 0.0 mg m^{-2} during the night, respectively. Differences were observed in the behavior of pesticides: procymidone in the atmosphere was detected only in one sample (in the daytime of the third day). Malathion and ethoprophos showed similar patterns, though the differences between days and nights were lower for malathion than for ethoprophos (Fig. 6). These data are evidence that light intensity or temperature may influence the volatilization flux.

In September the trend was similar to December in the first six days. The volatilization was still characterized by a daily periodic behavior lasting for most of the experiment, though the fluxes were lower than in the December experiment (4.7, 0.4, and 6.5 mg m^{-2} for ethoprophos, malathion, and procymidone, respectively, in the first six days after treatment; Fig. 7). Volatilization was high from the seventh to the tenth day after the application (58.5, 81.3, and 50.5% of total flux detected for procymidone, malathion, and ethoprophos, respectively). This may have been due to the influence of the climatic conditions, mainly rainfall and consequently increased soil moisture during this period (Fig. 6).

The data obtained in the different seasons confirm that temperature and soil moisture affect the volatilization. Temperature is positively related with pesticide vapor pressure, so the higher the temperature, the higher is the volatilization when all other factors remain the same (Spencer et al., 1969; Grover et al., 1978; Grain, 1982; Glotfelty et al., 1989; Gueckel et al., 1982) (Fig. 6 and 7).

Table 7. Pesticide soil residual, application rate, and volatilization measured and predicted in the two trials.

Characteristic	Ethoprophos	Malathion	Procymidone
	mg m ⁻² ; %†		
	December 1998		
Pesticide soil residual before treatment	ND‡	ND	ND
Application rate	100	64	75
Pesticide soil residual after sampling	91.1 ± 11.3 (91.1 ± 11.3)	61.9 ± 7.3 (96.7 ± 11.4)	59.8 ± 9.7 (79.7 ± 12.9)
Volatilization measured (TPS§)	10.9 (10.9)	3.4 (5.3)	11.6 (15.5)
Volatilization estimated (PELMO§)	9.1 (9.1)	0.14 (0.1)	13.6 (18.1)
	September 1999		
Pesticide soil residual before treatment	ND	ND	ND
Application rate	100	64	75
Pesticide soil residual after sampling	15.8 ± 6.9 (15.8 ± 6.9)	55.3 ± 12.4 (86.4 ± 19.4)	38.1 ± 10.5 (50.8 ± 14.0)
Volatilization measured (TPS)	19.4 (19.4)	14.5 (22.7)	31.1 (41.5)
Volatilization estimated (PELMO)	14.6 (14.6)	0.65 (1.0)	32.3 (43.1)

† Mass in soil for soil residuals and application rate, cumulative flux for volatilization measured and estimated; percentage over applied dose.

‡ Not determined.

§ PELMO, Pesticide Leaching Model; TPS, Theoretical Profile Shape.

The data obtained in September (Fig. 7) after the rainfall confirm that an increase of the soil moisture increases the gas–liquid distribution of the pesticide and its diffusive transport (Smith et al., 1997; Glotfelty et al., 1984; Whang et al., 1993; Majewski et al., 1990; Bor et al., 1995a, b). At low moisture conditions the volatilization is highly reduced due to the equilibrium between the liquid–solid phase (Smith et al., 1997), but restoring of soil moisture can increase volatilization (Glotfelty et al., 1984; Whang et al., 1993).

Soil sorption plays an important role. It is well known that many pesticides increase the sorption at low moisture conditions and that sorption may be time-depen-

dent. This may justify the difference in volatilization fluxes between the pesticides tested and, in particular, the heterogeneity in behavior of the more soil-sorbed procymidone and malathion.

Simulation of the Volatilization Rate

The results of the simulations that were performed are reported in Table 7 (total amount data) and Fig. 8 (comparison between measured and predicted daily data). The statistical index root mean squared error (RMSE) calculated from observed and predicted data was used to express the overall fit of the model simulation:

$$RMSE = \frac{100}{\bar{O}} \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}} \quad [3]$$

where P_i is the predicted value, O_i is the observed value, \bar{O} is the average of the observed values, and n is the number of observations. With a perfect fit the value would be zero (Loague and Green, 1991).

The daily trend cannot be predicted because PELMO produces daily output, so the accumulated measured data were compared with the model predictions. In both experiments the model simulated the total flux of ethoprophos and procymidone in reasonable agreement with the measured data (Fig. 8). The RMSE for the ethoprophos was 123.8 and 125.5 while procymidone was 190.7 and 240.6 in December and September, respectively. On the other hand, volatilization of malathion was underestimated (Table 7) with the highest RMSE of 2759.5 and 223.1 in December and September, respectively.

The daily output is a limitation of the model because it cannot characterize the daily periodic behavior trend and the differences between the morning and night. However, the PELMO model was sensitive enough to simulate the mass balance after the soil moisture variation due to the rainfall. So in September 1999 after the rainfall, ethoprophos volatilization was reduced due to leaching, which reduced its availability for volatilization (Fig. 7). Given the limitations of the model, this trend is confirmed by the flux measured in September: after the eighth day of sampling the ethoprophos flux was

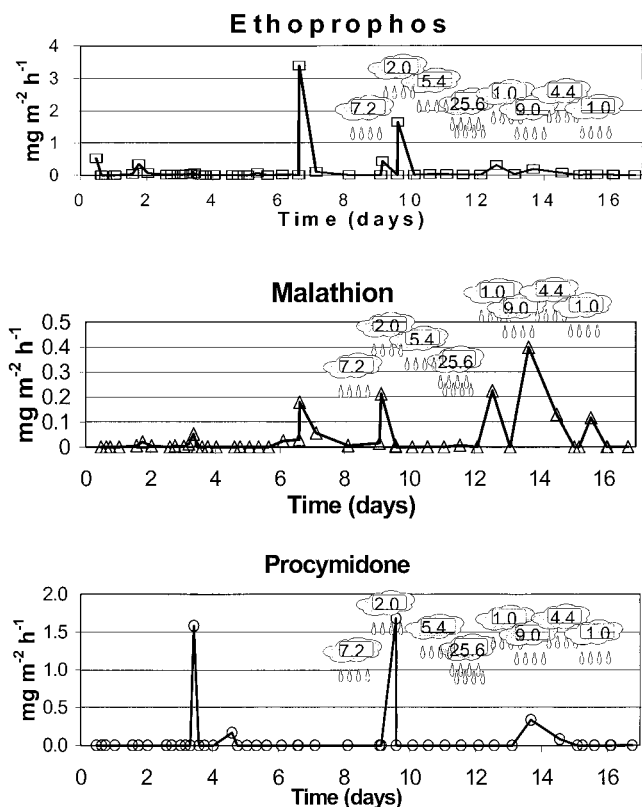


Fig. 7. Volatilization rate during the September 1999 study determined by the Theoretical Profile Shape (TPS). Day 1 corresponds to the end of the day of treatment (midnight). The cloud symbol represents a rainfall event in millimeters of rain.

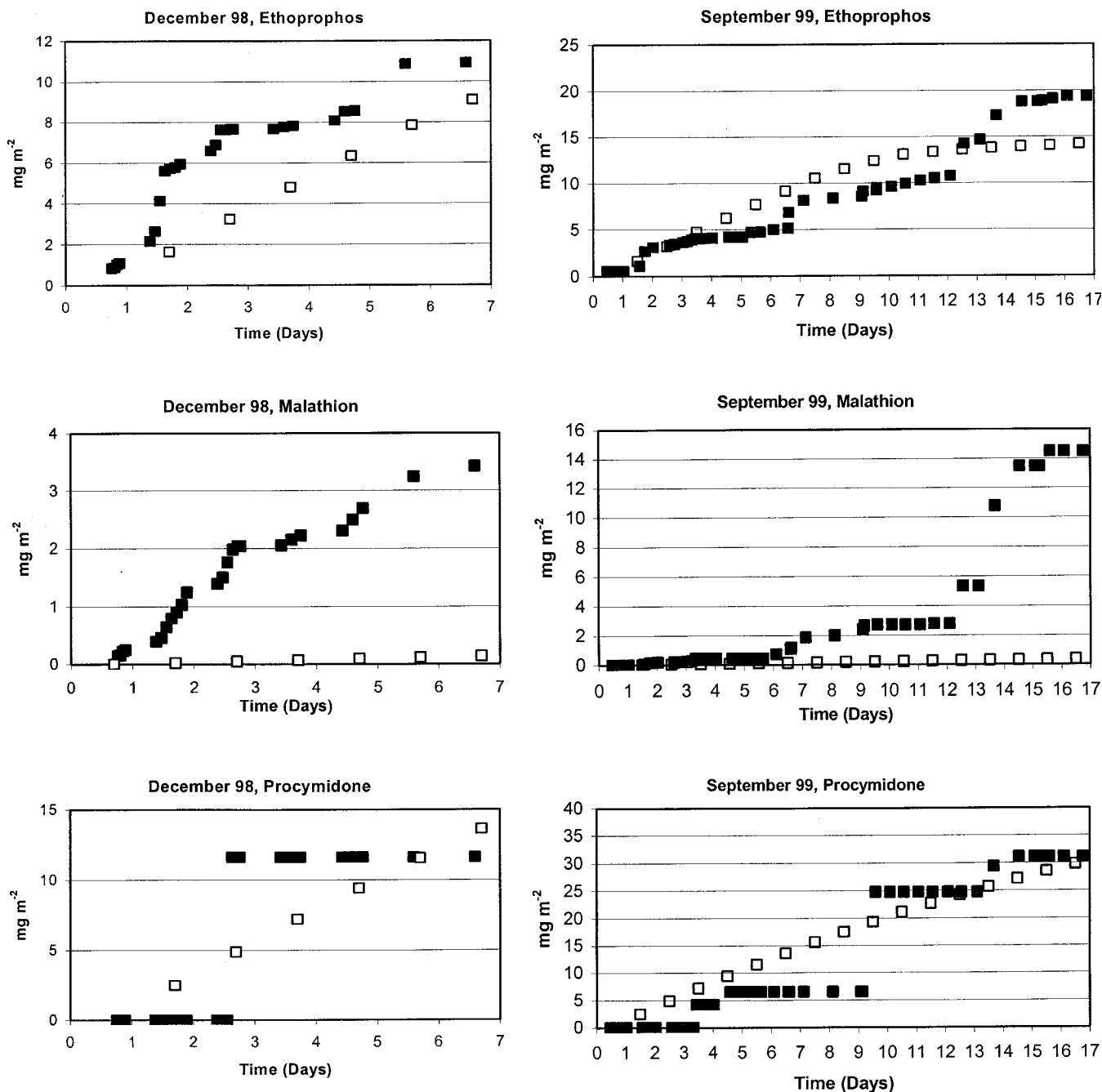


Fig. 8. Comparison of measured (solid squares) with predicted (empty squares) cumulative volatilization data. Day 1 corresponds to the end of the day of sampling (midnight).

65%, while the malathion and procymidone flux were 92 and 79% of the total flux predicted during sampling period, respectively (Fig. 7).

These results suggest that the description of volatilization in PELMO as based only on liquid-gas partitioning may be reasonably reliable for volatile pesticides such as procymidone and ethoprophos, but could not be applied for pesticides characterized by a vapor pressure of $<10^{-2}$ Pa, especially if it is strongly sorbed onto the soil. However, more experimental evidence should be collected. The present version of the model may be applied when a calculation of the predicted environmental concentration as percentage of the dose applied is

required in a low tier of a risk assessment. It could not be applied when a predicted environmental concentration is required over a time period. For this application, the sorption routine and gas-liquid partitioning should be revised including the time and moisture dependence of sorption, and a lower time-step calculation.

CONCLUSIONS

Pesticide volatilization after soil application is one of the most important processes for the environmental dissipation of xenobiotics and for risk assessment. Results reported in this paper demonstrate that in field

conditions, for pesticides with vapor pressures between 5×10^{-3} and 5×10^{-2} Pa, volatilization can represent up to 22.6% of the total fate in the environment. To this extent, volatilization may affect the air quality of the area surrounding the agricultural field, potentially exposing residents and bystanders to the pesticides. Most of these airborne residues are assumed to dissipate quickly in the air due to the photolytic activity of sunlight, but additional studies and measurements are needed.

Mathematical models can greatly help the interpretation of this process and in the assessment of exposure levels at different scales. Based on the experimental data reported in this paper, PELMO can be used for simulating the predicted environmental concentration in air, as required by the EU Directive, but it should be considered that its capacity may be limited, depending on the chemical and physical properties of pesticides. As such it is not meaningful to continue with a version of the model that gives such a poor description of the volatilization processes. The discrepancy between measured and predicted data is evidence that the current version of PELMO allows successful description of pesticide volatilization from soil only for volatile substances (vapor pressure $\geq 10^{-2}$ Pa) and over an intermediate to long time period (more than a few days). The model could be beneficially amended to take into account the influence of the hourly soil–air temperature variation during the day, a sorption routine including the effect of strong bonds and time-dependent sorption processes, and the temperature dependence of variables such as water solubility, vapor pressure, and Henry's constant. Though not studied here, volatilization from the crop canopy would also be helpful in the model.

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