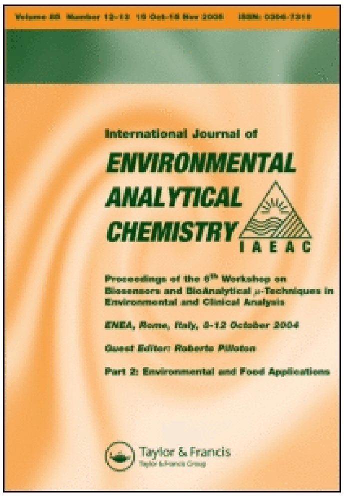

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A New Laboratory Protocol to Monitor the Volatilization of Pesticides from Soils

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A NEW LABORATORY PROTOCOL TO MONITOR THE VOLATILIZATION OF PESTICIDES FROM SOILS

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A laboratory set-up is developed to measure the volatilization of pesticides from soils. It allows the simulation of field conditions and the control of all the parameters that can influence the volatilization phenomenon. These parameters consist of micro-climatic factors such as temperature, soil and air humidity, wind-speed, and also by physicochemical factors like the nature of pesticides and soil types. A preliminary study of the volatilization is conducted on lindane adsorbed on an Alsatian soil (France): the loess. The influence of soil moisture on the volatilization rate is assessed. Lindane appears to volatilize faster from a loess at field capacity (12.4% m/m of the dry soil) than from a dry loess. Indeed, 11% of the lindane initially adsorbed on the soil was volatilized after 26 days from the wet soil against only 0.8% from the dry soil during the same period. This difference is probably due to a soil-water extraction of the lindane adsorbed on the soil or to a competition between water and pesticide molecules for the adsorption sites on soil surfaces.

Keywords: Volatilization; pesticide; lindane; γ-HCH; soil; atmosphere

INTRODUCTION

The last years have seen an increasing interest in soil, water and air pollution. In these fields, pesticide contamination plays an important part as these chemicals can be found in all environmental compartments. In fact, once spread, the pesticides laying on plant and soil surfaces can first evaporate, or be carried to surface waters by runoff with water and erosion of soil solids. Pesticides that enter the soil can be either degraded by biological or chemical action, leached to ground water or stay in the field adsorbed on soil particles. In turn, the

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*Corresponding author. Fax: +33-388-358484. E-mail: wortham@illite.u-strasbg.fr adsorbed pesticides can be carried towards ground water or volatilize in the atmosphere. Runoff and leaching considered together rarely exceed 5 to 10% of the total amount of pesticides applied on the soil.[1,2] In contrast, evaporation and volatilization can, within a few days after application, carry away 80 to 90% of the pesticides initially spread.[3] Numerous studies have been conducted in natural field conditions during the latter decades to estimate the amount of pesticides volatilized from soil.[4–6] Mainly, these field studies have provided information on the actual rate of pesticide's passing into the atmosphere. Nevertheless, during field experiments, environmental parameters such as temperature, soil and air humidity, that influence the volatilization of pesticides, are not very well controlled. Consequently, rapid fluctuations can occur to each of the parameters which reduces the duration of the experiment to between one and three hours. Moreover, as environmental parameters are in constant evolution, the field experiments are difficult to reproduce. All things considered, it appears almost impossible to evaluate the influence of each parameter on the volatilization rate and to understand the different steps of the volatilization mechanism by field measurements only. For these reasons, some laboratory experiments have been built up such as micro-agro-ecosystems[7–9] and specific volatilization chambers.[10–12

Our aim is to study separately each of the parameters that can influence the volatilization of pesticides. For that purpose, we have elaborated an experimental protocol which includes:

- A volatilization chamber according to the principle suggested by Spencer *et al.*[12].
- A peripheral equipment which controls and measures the physico-chemical parameters.
- A soil preparation from its sieving to pesticide adsorption.
- An analytical procedure.

All these steps were not totally original but were improved upon or associated with each other in a new way. The volatilisation chamber was filled with a selected soil on which pesticides were adsorbed. The experiments were carried out under conditions that simulated the *in situ* volatilization as correctly as possible even if the experimental constraints made it necessary to use some parameters not totally realistic. For the first study, we chose to present the influence of soil humidity alone on the volatilization process of lindane (γ-HCH) adsorbed on an Alsatian (France) loess at 30°C. This pesticide was chosen because it had already been studied by Spencer *et al.*[11,13,14] with the same type of volatilization chamber. This first study made it possible for us to compare our results

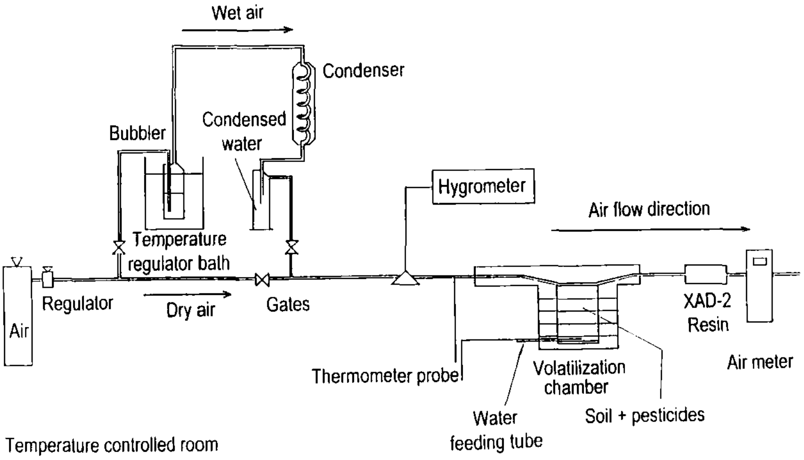

FIGURE 1 Schematic diagram of the experimental set up.

with those previously obtained[11,13,14] and consequently to validate our experimental procedure before study of new pesticides.

After a description of the experimental procedure, results concerning the volatilization will be presented. The experiments were carried out with two soil moistures: field capacity (12.4% m/m of the dry soil) and dry soil. This latter condition is unrealistic compared to the one encountered in the field but akes it possible to understand the volatilization mechanism.

MATERIAL AND METHODS

The volatilization chamber consisted of two parts: the chamber as such and the peripheral equipment which controled the environmental parameters such as temperature, air and soil humidity.

Chamber Description

The chamber's form consisted of a rectangular box (internal section: 3 cm wide and 10 cm long). Its height could vary from 2 to 10 cm by addition of 2 cm high sections. During the experiments the chamber was filled with a soil on which the pesticides were adsorbed (Figure 1). To avoid external pesticide contamination and the dispersal of soil particles, a pure and laminar air flow (about 1 $L.min^{-1}$) swept the soil surface throughout the experiments and carried the volatilized pesticides towards an XAD-2 resin trap preceded by a glass fibre prefilter (1.8μm nominal, Prefiltres AP40, Millipore) to avoid eventual soil contamination of the resin trap. This latter was a styrene divinylbenzene copolymer characterised by reversible adsorption due to its macroreticular porosity, its wide adsorption surface, and its non-ionicity. Before use, the XAD-2 resin was cleaned by a double period of 24 hours extraction with soxhlet (200 g.L^{-1} with hexane/dichloromethane: 85/15). The resin trap was removed daily then analyzed to determine the quantity of pesticides volatilized per unit of time. The air flow circulation took place in the hollow lid of the chamber ($3 \times 10 \times 0.5 = 15$ cm^3), designed to obtain a laminar flow, particularly by removing angles greater than 12 degree.[15] All the constituents of the volatilization chamber including the box, the sections and the lid, were made of Teflon to avoid wall effects.

Environmental Monitoring

Before the beginning of the experiments, the soil was wetted by means of a water feeding tube placed at the bottom of the volatilization chamber. About one week was needed to obtain the homogenization of the humidity throughout the soil. During the experiments, the amount of water evaporated was controlled by a daily weighing (maximum weight: 4100 g, precision: ± 0.01 g, Mettler PM4000) of the whole system (soil/pesticides and volatilization chamber). To keep constant the soil moisture, the missing water was added by means of the water feeding tube. The control of air humidity allowed the setting of the evaporation rate of water from soil. The air was a dry and pure mixture of N_2/O_2 (78/22) directly obtained from an air cylinder (less than 0.3% humidity, Prodair, l'Oxygène liquide). Wet air at about 100% relative humidity (RH) was obtained by dry air bubbling in water at 35°C to reach saturation followed by a cooling at experimental temperature (30°C). Finally, various air humidities were obtained by mixing dry and saturated air at different rates. The air flow humidity was constantly measured by an hygrometer that utilized the chilled mirror dew condensation principle to determine water vapor concentration (0.5% RH accuracy, 0.2% RH sensitivity between a temperature of -50°C and $+70$°C and a pressure of 0 and 14 Kg. cm^{-2}, EG & G moisture and humidity systems Model 911 Dew-all™) and placed just before the volatilization chamber. Considering the air flow velocity (about 1 L.min^{-1}) and the volume of the lid of the volatilization chamber (15 cm^3), the air above the soil was changed about 4000 times per hour which was sufficient to ensure first order kinetics. On the other hand, according to the cross section of the hollowed lid (3×0.5 cm) this rate of change corresponded to a wind speed of about 1.7 m.s^{-1}. Such velocity was

TABLE I Physico-chemical parameters of the soil.

$C_{organic}$	*Clay*	pH_{water}	*Bulk density* (ρ_T)	*Density* (ρ_S)	*Cation exchange capacity*	*Field capacity*
5% (m/m)	11% (m/m)	8.42	1.27 $g.cm^{-3}$	2.63 $g.cm^{-3}$	10.9 Cmoles +/kg soil	14.4% (m/m)

realistic even if it was low compared to wind speeds generally observed in the field. Nevertheless, this low speed was essential to limit the transport of the water used for air saturation towards the soil system and to avoid the dispersal of soil particles towards the pesticide trap. The velocity was controlled by a regulator and measured by a gas meter. All the system was placed in a temperature controlled room (30 ± 1°C). Additionally, two thermometer probes recorded the temperature steadiness in the soil and in the air flow.

Soil and Pesticide

The soil used was an Alsatian loess (France) essentially composed of silt (80%) and highly carbonated (5%). The soil parameters are described in details in Table I. We chose to determine the volatilization of lindane: 1α,2α,3β,4α,5α,6β-HexaChlorocycloHexane also named γ-HCH for which data are available in literature.[11,13,14] This preliminary study was carried out essentially to control the good working order of our experimental procedure. At 20°C lindane has a water solubility of 7 $mg.L^{-1}$[16] and a vapor pressure of 5.6 mPa.[17] At 25°C its henry's law constant is $1.33.10^{-4}$.[14]

Soil Preparation and Pesticide Adsorption

In order to have reproducible experiments, it was necessary to prepare an homogeneous and clean soil. Consequently, the soil samples collected in the natural environment were first softly disintegrated and 50 μm sieved. Then, a double period of 24 hours soxhlet extraction eliminated the extractable pesticides already adsorbed on the soil. Finally, a further double period of 24 hours heating at 105°C destroyed all bacterial activity in order to avoid biodegradation of the pesticides during the experiments.

Soil samples were prepared by adsorption of the pesticides in liquid phase. This method has less efficiency than the one using sublimation of pesticides, but was much less hazardous.[18] On the other hand, if we had sprayed directly onto the soil pesticides dissolved in the liquid phase, we would have had the effect of the size of these droplets which capable of influencing their persistence in soils.[19] We avoided these effects by using our method of adsorption by sonication of the soil with the pesticides in liquid phase. For this purpose, a solution containing given concentrations of pesticides (34 μmoles.L^{-1} or 10 mg.L^{-1}) in methanol (1L) was stirred in a sonicator for 12 hours with the clean and sterilized soil (350 g). The particles were then removed by filtration and dried under moderate vacuum.

A fraction of the soil (15 g) was set apart and used as a control to determine the initial pesticide concentration. It was determined, respectively for the dry and the wet experiment, that an amount of 5.1 ± 0.6 μg and 5.8 ± 0.7 μg of lindane per gram of dry soil was adsorbed. These values represented a total amount of pesticide adsorbed on the 350 g of soil of 1780 ± 210 μg and 2020 ± 240 μg for instance a yield of 18 ± 2% and 20 ± 2.7% respectively for the dry and the wet experiment. The remaining soil (335 g of dry soil) was introduced in the volatilization chamber and wetted as previously described.

Pesticide Analysis

The extractions of lindane from the soil and XAD-2 resin were carried out with soxhlet apparatus as suggested by numerous authors.[7,20–24] We avoided the use of methanol[21,22] which dissolves the XAD-2 resin and the use of water incompatible with the gas phase chromatography analysis. To minimise the impact of systematic errors, the same solvent was used for both materials (soil and XAD-2). It was constituted by a mixture of hexane/dichloromethane (85/15) following the procedure developed by Bossan *et al.*[25].

The extracts were concentrated to 1 mL in a rotary evaporator at 30°C. Finally lindane was analyzed by Gas Phase Chromatography with electron capture detector on a Carlo Erba 6000 gas chromatograph fitted with a ^{63}Ni radioactive source (Carlo Erba ECD-80). An on-column mode (2 μL) and DB-5 (J & W Scientific) capillary fused silica column (0.317 mm i.d. × 30 m, 0.25 μm thickness) were used. The carrier gas was helium and the make-up gas was argon/methane (90/10). Their flow rates were respectively 2 mL.min^{-1} and 35 mL.min^{-1}. All these conditions of analysis have already been presented in a previous study.[26] The detection limit of the gas chromatograph was 0.04 μg.mL^{-1} with a relative standard deviation of 5.2%. This detection limit, obtained in liquid samples after the different preparatory steps corresponded to a pesticide volatilization rate of 1.7 ng.h^{-1} assuming that the volatilization lasted 24 h and that the final sample volume was 1 mL. The yields of each step of the procedure and the total relative standard deviation will be presented in detail in the results and discussion section.

Experimental Conditions

The first experiment was made at 30°C during 26 days and the pesticide used was lindane (min. 99.0%, Analytical standards, The Promochem group). The XAD-2 resin was changed every 24 hours in order to analyze the volatilized pesticides trapped on it. The soil moisture was kept at field capacity (12.4% m/m of the dry soil) which represented a water volume of 41.54 cm^3 to wet the 335 g of dry soil introduced into the volatilization chamber. The air stream was at nearly 100% relative humidity (93–97% RH). The second experiment was made under the same conditions (30°C, 26 days) but both the soil and the air were kept dry. In the first experiment, only little water evaporation occurred: about 1.5 mL per 24 hours which represented a water evaporation rate of 0.05 $cm.day^{-1}$. With the dry soil experiment, no water evaporation was observed.

RESULTS AND DISCUSSION

Soil and XAD-2 Extractions

In order to determine the efficiency of the overall experimental procedure i.e. extraction trapping, concentration and analysis, we proceeded with several tests. First, the lindane extractability with soxhlet was tested for the XAD-2 and the soil used. To reach this objective, four extractions of 12 hours were successively conducted on the same sample and the test was repeated five times. It appeared that, during the second 12 hours extraction of the XAD-2 resin, we obtained only two per thousand of the quantity extracted during the first 12 hours extraction. Consequently, a single 12 hours soxhlet extraction was sufficient to extract quantitatively the lindane trapped on the XAD-2 resin. For lindane the yield of each of the four 12 hours successive extractions is presented in Figure 2 and one can see that the sum of the quantity of lindane extracted during the four experiments represented 100%. We noted that lindane was well extracted in the first 12 hours with recoveries ranging between 65 and 94%. Nevertheless, the soil extraction was never complete with one extraction and full quantitative recoveries required a second 12 hours extraction. On the other hand, the third and fourth extractions did not result in the desorption of additional pesticide. This variation in the extraction yield of the two supports, XAD-2 and soil, was probably due to a stronger adsorption of lindane on the soil. Previous studies[18,25] conducted on polyaromatic hydrocarbons (PAH) and pesticides adsorbed on several supports postulated that these organic compounds were adsorbed in two ways: physi-sorption and chemi-sorption. According to their conclusions, the pesticide adsorbed on XAD-2 was essentially physi-sorbed and

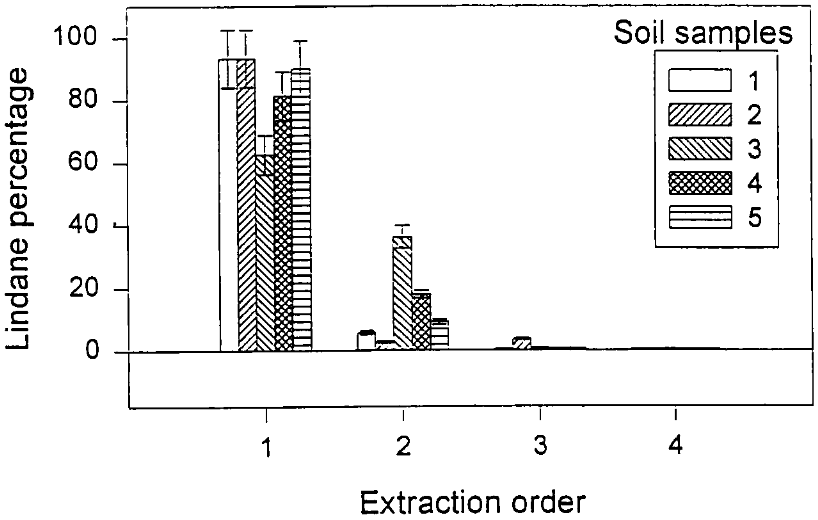

FIGURE 2 Results of the successive extractions (12 hours) of lindane from five soil samples.

consequently easily extractable while pesticide adsorbed on soil was both physisorbed and chemi-sorbed, which made them difficult to extract.

Secondly, to test the trapping of lindane on the XAD-2 resin, we used two identical XAD-2 resin traps in series. The pesticides trapped during 24 hours on the two traps were separately analysed to determine the yield of trapping. This experiment was carried out 3 times and the average yield was of 82 ± 13%.

Finally, the analytical method supposed that the extracts were concentrated by rotary evaporation. During this solvent evaporation, a certain amount of lindane was lost which greatly affected the final result. To determine the yield of the evaporation process, three different concentrations of lindane in hexane/dichloromethane (24, 48 and 96 $\mu g.mL^{-1}$ in 250 mL) were evaporated to 1 mL five times each. The average yields depended upon the initial concentrations and were respectively 37 ± 4%, 48 ± 8% and 74 ± 8%. Consequently, considering the yields of the different experimental steps (extraction, trapping, evaporation and analysis) the overall efficiency of the experiment was 30 ± 8%, 39 ± 13%, 61 ± 16% respectively for the three concentrations used above. All the results presented below in the text will take into account the overall efficiency.

Experimental Results

In order to validate our experimental set up, we conducted two main experiments under well controlled conditions. For each of these experiments, which lasted a total of 26 days, we followed the volatilization of lindane on the same soil (loess)

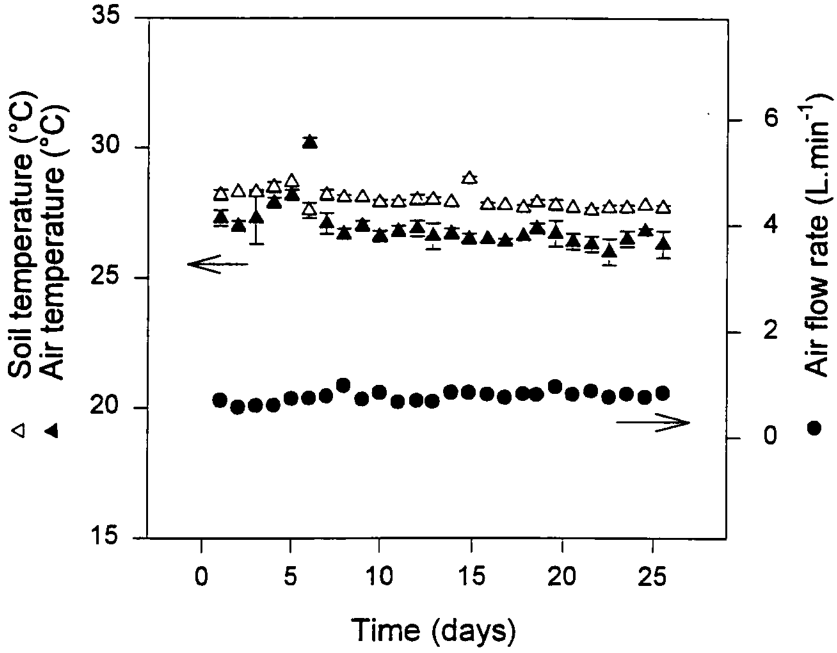

FIGURE 3 Conditions of the experiment conducted with dry soil.

at two different soil humidity levels, namely 0 % (dry soil, experiment 1) and 12.4% (soil at field capacity, experiment 2). Accordingly, the relative humidity (RH) of the air flow was set at 0 % and 95 % respectively. During these 26 days, the average air temperature (Figures 3 and 4) was 26.9 ± 0.8°C (exp. 1) and 28.3 ± 0.5°C (exp. 2). We noted in experiment 2, on day number 6, an anomaly due to the change of an air cylinder. All the other parameters: soil temperature (28.0 ± 0.3°C and 28.7 ± 0.3°C), air flow rate (0.77 ± 0.10 mL.min^{-1} and 0.67 ± 0.10 mL.min^{-1}) and for the experiment 2, RH of air (95 ± 2%), were almost constant during the experiments.

The analyses of the daily sampling of lindane on the XAD-2 resin made it possible to plot out the cumulative quantities volatilized (Figure 5). As it can be seen from this figure, volatilization decreased in time with or without soil moisture. Moreover, lindane escaped faster from a soil at field capacity than from a dry soil. More precisely, 11% and 0.8% of the lindane initially adsorbed on the soil was volatilized after 26 days from the wet and dry soils respectively. Considering the mass of lindane adsorbed on the soil (respectively 2020 ± 240 μg and 1780 ± 210 μg for the wet and the dry experiments) these two percentages represented an average vapor flux of 0.28 μg.cm^{-2} per day from the

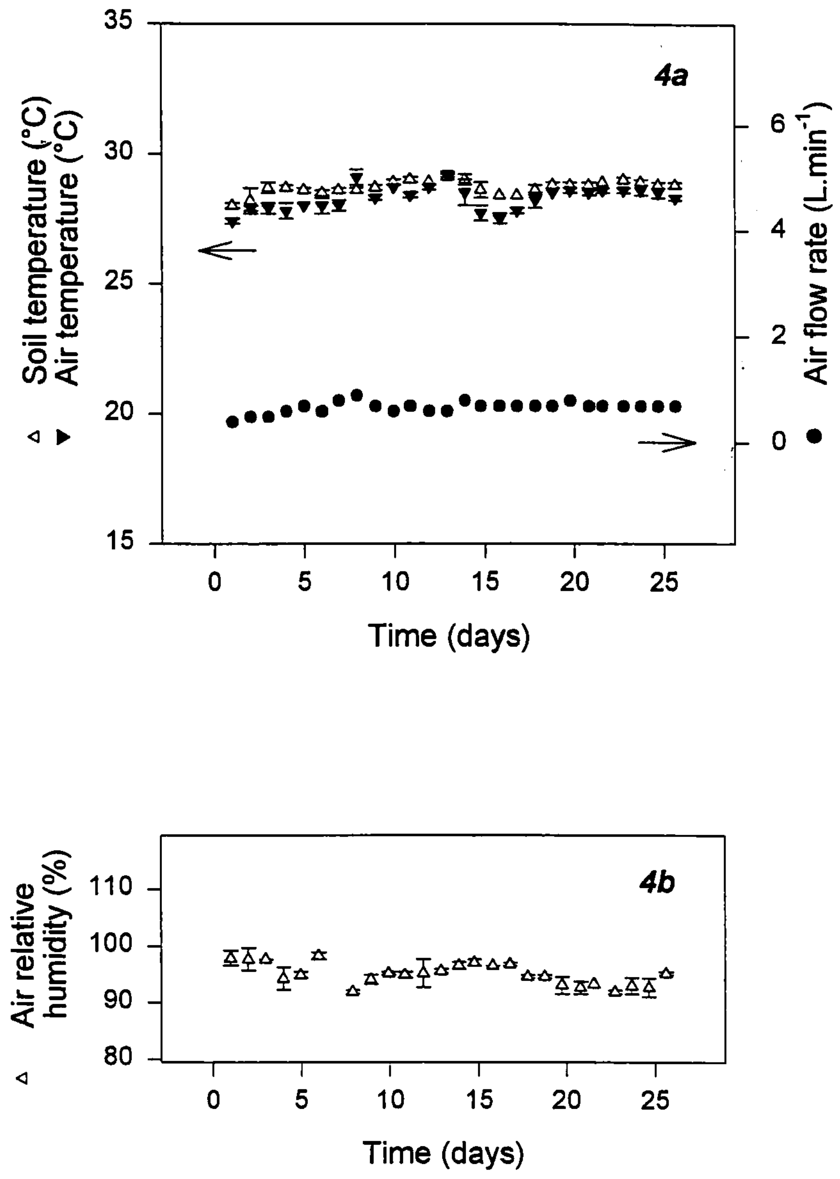

FIGURE 4 Conditions of the experiment conducted with soil at field capacity (12.4%, m/m of the dry soil).

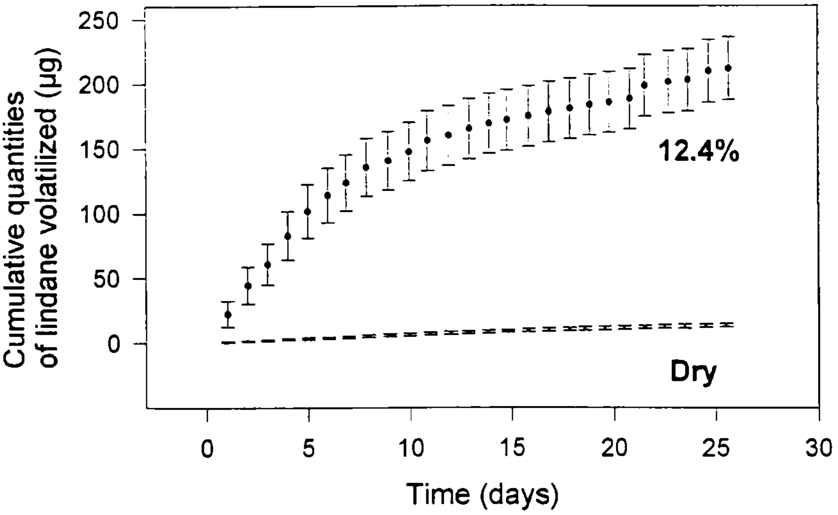

FIGURE 5 The influence of soil moisture on lindane volatilization.

wet soil and only of 0.02 µg.cm^{-2} per day from the dry soil. These results were consistent with several previous studies[11,27] showing that volatilization of lindane was more efficient from a wet than from a dry soil. On the other hand, the results obtained from the wet soil were in agreement with those obtained previously[14] [flux of 0.28 against 0.11 µg.cm^{-2} per day for the same pesticide and the same atmospheric relative humidity (about 100%)]. These two results were slightly different because some experimental parameters had been changed such as: the soil, the temperature (30°C against 25°C), the soil humidity (12.4% m/m against 19.9% m/m), the lindane concentration (5.8 µg.g^{-1} against 3µg.g^{-1}). Nevertheless, the harmony between our results and literature for both the influence of the soil moisture on the volatilization and the order of magnitude of the flux of lindane, validated our experimental procedure. It is now possible to study new pesticides in different experimental conditions to determine their behaviour.

Our results can be used to identify the slowest step of the volatilization, which in turn controls the overall kinetics. In this context, three major steps can be distinguished: the adsorption/desorption of pesticides on soil, their transport to soil surface and their evaporation into the atmosphere. The limiting step cannot be the evaporation from the soil surface because in that case, the curve of the cumulative quantities of lindane volatilized, obtained for the experiment with the wet soil, would have an exponential form and not a logarithmic one.[28] In the same way it has been observed previously that there is no accumulation of

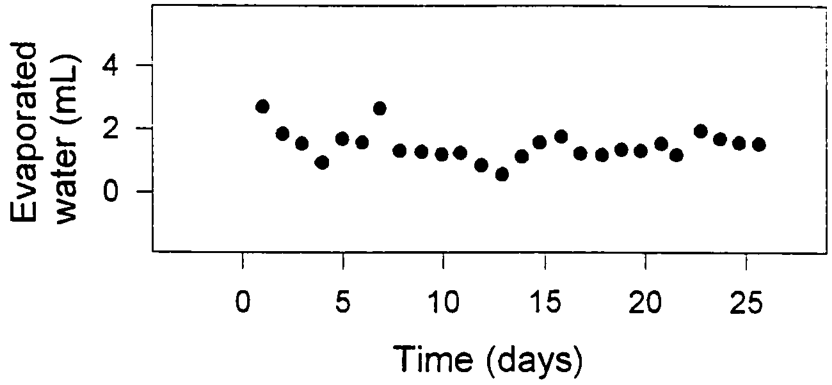

FIGURE 6 Evaporation of water during the 26 day experiment with wet soil.

lindane at the soil surface after 23 days of lindane volatilization.[14] In dry soils, the pesticides move by diffusion whereas in wet soils they can either diffuse or be carried by the water mass flow towards soil surface. In our wet soil experiment there was almost no water evaporation from soil (Figure 6), (about 1.5 mL.day^{-1}) but the evaporating water would only have to contain about 5 μg.mL^{-1} of lindane to obtain the 200 μg of lindane volatilized. Nevertheless, a reduction of the atmospheric relative humidity during more than 10 days which induces an increase of water evaporation (about 6 mL.day^{-1}) does not increase the volatilization rate of lindane. Consequently, the observed differences between the quantities of pesticides volatilized from wet and dry soil are not explained by the mass flow. As the diffusion coefficient of lindane in water is lower than that in air, the limiting step appears to be the desorption of pesticides from soil. The effect is a higher desorption of lindane in the presence of water, probably caused by a competition between water and pesticides for their adsorption sites on the soil surface or an extraction effect of water on the pesticides adsorbed on the soil.

CONCLUSION

This study has been carried out to control the good working order of our experimental procedure. The regularity of the physico-chemical parameters such as soil and air temperature, air flow rate, air relative humidity and water evaporation rate (Figures 3, 4 and 6) as well as the regularity of the lindane volatilization rate (Figure 5) shows that our experimental procedure permits a good control of the main parameters influencing the volatilization of pesticides from soil. Consequently, we now can study other pesticides frequently used in Western Europe.

It is observed that lindane volatilizes less from a dry than from a wet loess, at field capacity (12.4% humidity). As only low water movement in the soil is shown to take place, this difference in behavior is presumably due either to an extraction effect of water on the pesticides adsorbed on soil solids or on the competition of water and pesticide molecules for the adsorption sites on soil particles.

Finally, the volatilization chamber can be used for determining the specific influence of each parameter that affects the escape of pesticides from a soil, and among them the soil and pesticide type, moisture and temperature.

Acknowledgements

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