

Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: overview

Carole BEDOS*, Pierre CELLIER, Raoul CALVET, Enrique BARRIUSO, Benoît GABRIELLE

Institut National de la Recherche Agronomique, Unité Environnement et Grandes Cultures, 78850 Thiverval-Grignon, France

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Abstract – Volatilization may represent a major dissipation pathway for pesticides applied to soils or crops, accounting for up to 90% of the application dose in some cases. This paper collects and discusses recent data in the literature about this process. On the day of application, pesticide volatilization rates ranged from 0.1 g·ha⁻¹·h⁻¹ for prometton compound to 80 g·ha⁻¹·h⁻¹ for fonofos, for example. In general, pesticides are volatilized from plant surfaces to a greater extent and faster than from the soil. Volatilization continues for from a few days to several weeks (or sometimes even more), occasionally displaying a diurnal cycle. According to the experimental studies reported in the literature, the main factors affecting this process during the first few days after treatment have been identified as follows: the physico-chemical characteristics of the compound and the environmental conditions (temperature, soil moisture, nature of the soil or the crop) are key parameters, along with management practices.

pesticides / volatilization rate / physico-chemical factors / environmental factors / agricultural practices

Résumé – **Transfert de masse des pesticides dans l'atmosphère par volatilisation à partir des sols et des plantes : une synthèse.** La volatilisation des produits phytosanitaires appliqués sur le sol ou les cultures peut représenter une voie de dissipation majeure, pouvant atteindre dans certains cas 90 % de la dose appliquée. Cet article présente et analyse les données récentes relatives à l'estimation des flux de transferts de masse liés à ce processus. En ce qui concerne les pertes ayant lieu le jour de l'application, les taux de volatilisation sont compris entre 0.1 g·ha⁻¹·h⁻¹ à près de 100 g·ha⁻¹·h⁻¹ selon le pesticide considéré. En général, la volatilisation depuis la surface foliaire est plus importante et plus rapide que depuis la surface du sol. La volatilisation s'échelonne de quelques jours à plusieurs semaines (parfois plus), suivant parfois un cycle diurne. Les principaux facteurs conditionnant ce processus quelques jours après le traitement sont présentés à travers divers résultats expérimentaux présentés dans la littérature. Les facteurs clés sont les caractéristiques physico-chimiques du composé, ainsi que les conditions environnementales (température, contenu en eau du sol, nature du sol et de la culture) et les pratiques culturales.

pesticides / taux de volatilisation / facteurs physico-chimiques / facteurs environnementaux / pratiques culturales

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* Correspondence and reprints
Carole.bedos@grignon.inra.fr

1. INTRODUCTION

After field application, pesticides enter the various environmental compartments: the ground and surface waters, soil, plants and the atmosphere [44]. Their occurrence in the atmosphere [4] can occur as a result of drift during application or, subsequently, volatilization from soil, plants or surface water and by wind erosion. Pesticides may still be observed in the atmosphere after the treatment period has apparently ended in a region. Many observations and experimental studies highlight the contribution of volatilization to atmospheric contamination. Indeed, this process may continue for several days or weeks after treatment, and even go on for several months in the case of particularly persistent pesticides (organochlorines for example). As a result, it causes the transfer of significant fractions of applied chemicals [40] from the treated surfaces into the atmosphere. Once they enter the atmosphere, chemicals may be transported over large distances. In some cases, (e.g. atrazine, mecoprop or azinphos-methyl), subsequent atmospheric deposition may significantly contribute to surface water pollution [12].

Before going any further, the definition of the term *volatilization* as used in this paper should be clarified.

Strictly speaking, volatilization is the physico-chemical process by which a compound is transferred to the gas phase. It can result from evaporation from a liquid phase, sublimation from a solid phase, evaporation from an aqueous solution or desorption from the soil matrix. The transfer of a compound from a compartment (soil or plant) into the atmospheric compartment involves several steps, including not only these phase transformations but also transport processes. The term *volatilization* as used here represents the global outcome of all the processes leading to the transfer from the soil or plant compartment into the atmosphere.

As illustrated in Figure 1, volatilization is one of the pathways of the pesticide after it has penetrated the soil or plant. The involved processes include interactions with the soil matrix, and transport and transformation processes. Some of these processes are competitive, leading to the restriction, delay or conversely, promotion of other processes. Pesticides are low-volatile to semi-volatile compounds (except fumigants, which are volatile). They are therefore distributed into all phases: solids, liquids and gases. This partition depends on the physico-chemical properties of the compound. It determines the main routes of the pesticide transport. The volatilization process can thus be expected to be directly and

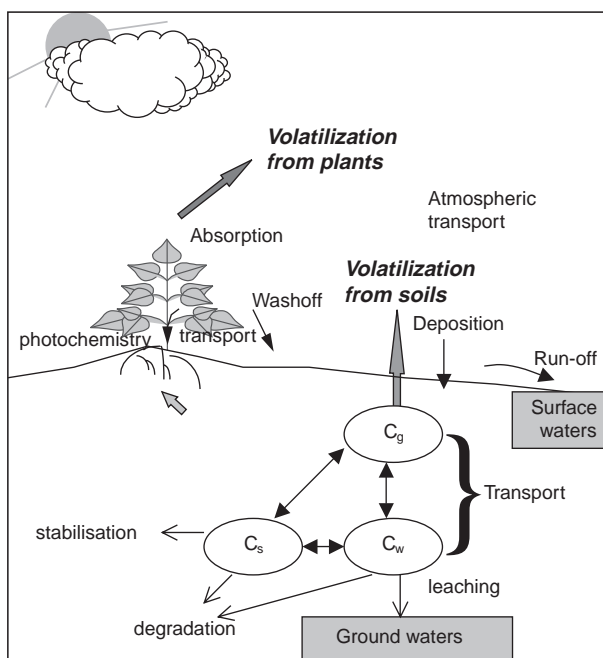


Figure 1. Major processes involved in the behavior of pesticides after their application to soil or plants. C_g , C_w and C_s represent the pesticide concentrations in the gas, aqueous and solid phases respectively.

indirectly controlled by physico-chemical, environmental and management-related factors.

Most of the studies on pesticide volatilization from soil or plants were carried out in the USA in the early 1980s [13, 18, 35, 40...]. They provided some information on the behavior of certain compounds, such as the organochlorine pesticides, for instance. New compounds may now be in use, which means that further investigations are called for. Since the early 90s, Van den Berg [41], Pattey et al. [31], Bor et al. [7] and Stork et al. [38, 39] extended the study of the volatilization process. However, these studies were done under different conditions and using different methods which makes it difficult to synthesize the different results obtained.

The purpose of this paper is to address the questions related to pesticide volatilization. The first part of this paper focuses on the order of magnitude of the emission flux and its time span. The second part of this paper addresses questions about the factors – meteorological and pedological conditions, management practices – governing the volatilization process and their interactions. We will try to answer these questions in the light of the different behavior patterns observed experimentally.

2. OBSERVED VOLATILIZATION RATE

Various methods have been developed for studying the volatilization of chemical compounds: micro-meteorological methods reviewed by Majewski [26], semi-field systems (volatilization chambers or wind-tunnels) and laboratory systems. Comparison of the results obtained by these different experimental methods (recently discussed by Van den Berg et al. [43]) falls outside the scope of this discussion. Volatilization can occur as soon as the surface has been sprayed. Little is known about this early flux, as measurements do not usually begin until a few minutes after the treatment. Consequently we cannot attempt to include the transfer occurring immediately after application in the discussion that follows. Fumigants are not included in this discussion.

2.1. Volatilization from soils

Taylor and Spencer [40] summarized cumulative losses, expressed as a percentage of the application dose, from studies carried out by several authors, mostly in the USA. Several of the compounds involved (such as the organochlorines) are now banned. Volatilization ac-

counted for as much as 90% of the application dose, depending on the compound and environmental conditions. For some compounds, such as trifluralin or lindane, as much as 90% of the application dose was lost within a week through volatilization. For others, such as atrazine, the cumulative losses after 24 days corresponded to about 2% of the application dose. This behavior could partly be explained by the physico-chemical characteristics of pesticides, such as vapor pressure or Henry's law constant (which is the partition coefficient between gaseous and aqueous phases), as will be discussed below. The volatilization of trifluralin or lindane is more intense than that of atrazine or simazine, presumably because of large differences in their Henry's law constant (4.03 and $0.134 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ for trifluralin and lindane respectively, versus 2.87×10^{-4} and 3.43×10^{-4} for atrazine and simazine respectively [25]). Even for a given chemical, total losses may differ due to differences in environmental conditions or agricultural practice (e.g. soil water content, soil type, tillage). For example, the cumulative volatilization of chlordane within 2 days reached 50% in the case of a moist fallow silt loam soil compared to only 2% from a dry fallow sandy loam [40].

Table I shows the values of average losses during the day of application reported by various authors [49]. Quantitatively, pesticide volatilization rates ranged from a few $\text{g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$ to nearly $2000 \text{ g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$, depending on the considered pesticide and the application dose. Bor et al. [7] used the aerodynamic method to estimate volatilization for 14 days after application of triallate, parathion and ethoprophos (applied separately) on a sandy soil. The highest fluxes were found on the day of application and can be summarized as follows: the order of magnitude of the measured fluxes estimated with a 1-h sampling on the day of application, one day after and 2-h sampling fourteen days later were respectively for triallate $42 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$, $6 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$, around $1 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ (for an application dose of $1480 \text{ g}\cdot\text{ha}^{-1}$); for ethoprophos $58 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$, $2.5 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$, around $1 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ (application dose of $1660 \text{ g}\cdot\text{ha}^{-1}$) and for parathion $5 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$, $0.5 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ and $0.4 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ (application dose of $1720 \text{ g}\cdot\text{ha}^{-1}$). At the end of the observation period, volatilization can continue, because a substantial fraction of pesticide remains in the topsoil.

Three weeks after application, Glotfelty et al. [15] observed a volatilization rate from bare soil of about $2 \text{ g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$ for alachlor, $0.6 \text{ g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$ for atrazine, $0.5 \text{ g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$ for simazine and $11 \text{ g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$ for toxaphene. However, as the environmental conditions on that day were unfavorable for volatilization, these values can be considered as low fluxes.

Table I. Fluxes observed from soil just after treatment (within 12 to 24 h) after Woodrow et al. [49].

Compound	Flux (g·ha ⁻¹ ·d ⁻¹)	Application Dose (g·ha ⁻¹)	Wind (m·s ⁻¹)	Temperature (°C)	Method of determination
Herbicides					
Trifluralin	1440	2840	ns*	19–30	Micro-meteorological
Atrazine	20	2500	0.08	5–35	Residue analysis [√]
Insecticides					
Fonofos	1919	5300	ns	11–32	Micro-meteorological
Diazinon	6	1500	0.8–1.3	ns	Micro-meteorological
Lindane	242	1500	0.8–1.3	ns	Micro-meteorological
Chlorpyrifos	22	1500	0.8–1.3	ns	Micro-meteorological
p,p' DDT	11	1300	1.6–1.7	30–34	Micro-meteorological
Prometon	3	ns	0.3	25	Residue analysis
Dieldrin	69	2500	0.08	5–3	Residue analysis
Fungicides					
PCNB	958	2500	0.08	5–35	Residue analysis

[√] Residue analysis of treated matrix.

* ns: not specified.

Using the Relaxed Eddy Accumulation method, Pattey et al. [31] measured fluxes on the day of application of about 23 g·ha⁻¹·h⁻¹ (for an application dose of 1150 g·ha⁻¹) for trifluralin, and 31 g·ha⁻¹·h⁻¹ (application dose: 1700 g·ha⁻¹) for triallate, without incorporation. Maximum fluxes were observed during the 1-h sampling period following application by Cessna et al. [9], who reported a value of 6.3 g·ha⁻¹·h⁻¹ after trifluralin incorporation into the soil (application dose of 650 g·ha⁻¹).

2.2. Volatilization from plants

Pesticide volatilization from plant surfaces may occur very quickly after treatment [47]. Volatilization of more than 90% of the application dose was observed. Even though the rate of volatilization from plants seems to be higher than that from soil, little data is available, as pointed out by many authors [43]. Gottschild et al. [16] reported data collected by Siebers in 1993 showing that volatilization of lindane within the first 24 hours after treatment is much greater from sugar beet leaves than from bare soil (89% and 13% of the application dose respectively). Similar results were reported by Boehncke et al. [6] for deltamethrin and lindane, but the interpretation of their data is hindered by the fact that the experi-

mental conditions were unfavorable to pesticide volatilization from soil. Rüdél and Waymann [32] found that 38 to 58% of the application dose of lindane was volatilized from bean leaves versus 28% from soil in a wind tunnel. Rüdél [33] found that the volatilization rates of methyl parathion, endosulfan and fenpropimorph were 5 to 13 times greater from plants compared to soil. For lindane and trifluralin, this ratio was only to 2 and 1.5 respectively. Several possible explanations for these differences in the volatilization from soils and crops have been proposed [45]:

- turbulence above and inside the foliar coverage increases the convection exchange rate between leaves and air;
- pesticide/leaf interactions may be different from pesticide/soil interactions, with a much higher adsorption on soil than on plants. This explanation is also suggested by Boehncke et al. [6];
- water evaporation may also be different from leaves and soil (due to differences in temperature or moisture levels).

Cumulative volatilization fluxes, as a percentage of the application dose, were given by Jansma and Linders [19]. The authors quoted values for mevinphos, lindane and deltamethrin obtained by Boehncke et al. [6] using

an indirect method (residue analysis). Whatever the characteristics of the crop (species, canopy structure, plant age), the volatilization kinetics of lindane or mevinphos showed a similar pattern. 30 to 50% of lindane may disappear within one hour after treatment. This fraction rose to 88–97% after three days. These data were all obtained in the same study, which makes it possible to compare the behavior of deltamethrin, lindane and mevinphos. The degree of volatilization seemed to be quite closely correlated with vapor pressure (vapor pressure was about 2×10^{-6} , 5×10^{-3} , 8×10^{-2} Pa, respectively). Boehncke et al. [6] pointed out this correlation, which may only exist just after application. Over longer periods, the nature of the leaves seems to interfere.

Woodrow et al. [49] reported volatilization rates (Tab. II) observed on the day of application (within 12 to 24 h). The range of values is large. For a given chemical, these rates cannot be compared directly to the fluxes given in Table I for volatilization from soil, as the conditions and measurement methods are different (except for *p,p'*-DDT).

Smelt et al. [34] found a volatilization rate of fenproprymorph from sugar beet leaves of $20.7 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ during the first hour after treatment. This flux decreased slightly with time on the day of application (under rather constant meteorological and crop management conditions) and more rapidly on the next day ($2.2 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$). Van den Berg et al. [42] observed that the rates of volatilization of parathion applied to potato were highest just after application: $14 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ one hour after application

versus $2.4 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$, 6.6 hours after treatment (aerodynamic method). Seven days after application, fluxes ranged from $0.07 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ to $0.19 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$, and parathion residues on foliage were low, suggesting that volatilization may have been complete. For chlorothalonil, shortly after application fluxes were around $0.62 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ and decreased to $0.41 \text{ g}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ seven days later. At the end of the experiment, chlorothalonil residues on foliage were still high, suggesting that volatilization could carry on. These results show that chlorothalonil behaves quite differently from any of the previously mentioned compounds.

In some cases, no volatilization was detected. Kubiak et al. [22] studied the volatilization of isoproturon sprayed on French beans both in the field and in a volatilization chamber. No fluxes were detected in the field, and only a low flux in the volatilization chamber.

3. FACTORS GOVERNING THE VOLATILIZATION PROCESS

Most of the pesticide volatilization rates and time courses described above were observed in the field. Consequently, they reflect the combined influence of several factors: the physico-chemical properties of the compounds, the environmental conditions and the management practices. Figure 2 summarizes the main factors involved in volatilization from soil. A similar diagram could apply to volatilization from plant foliage. As these

Table II. Fluxes observed from plants just after treatment (within 12 to 24 h) Woodrow et al. [49].

Compound	Flux ($\text{g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$)	Application dose ($\text{g}\cdot\text{ha}^{-1}$)	Wind ($\text{m}\cdot\text{s}^{-1}$)	Temperature ($^{\circ}\text{C}$)	Method of determination
Herbicides					
2,4-D (wheat)	160	500	2.6	23–31	Micro-meteorological
Pendimethalin (turfgrass)	247	3400	ns*	22	Micro-meteorological
Trifluralin (weedy turf)	381	2500	ns	ns	Residue analysis [√]
Insecticides					
Diazinon (dormant peach orchard)	218	4500	0.8–1.1	ns	Residue analysis
<i>p,p'</i> -DDT (cotton)	11	1300	1.6–1.7	30–34	Micro-meteorological
Toxaphene (cotton)	47.7	3730	1.6–1.7	30–34	Micro-meteorological
Dieldrin (weedy turf)	41.25	2500	ns	ns	Residue analysis

[√] Residue analysis of treated matrix.

* ns: not specified.

parameters are closely linked and interact with each other, their combined effects on the volatilization process are far from linear. We will now analyze the contributions of the main factors determining the volatilization rate and dynamics. This will be done on the basis of data obtained in semi-field systems such as volatilization chambers [35], micro-agroecosystems [27–30] and wind tunnels [17, 22, 33, 38, 39, 42, 45]. These systems allow the study of the determinism of the process of volatilization. The data obtained may be representative of fluxes on the field scale, provided some precautions are taken.

3.1. Physico-chemical characteristics of pesticides

The physico-chemical characteristics of the compound play a key role in determining how it behaves after application. Vapor pressure, water solubility (and thus the Henry's law constant) and adsorption coefficient (soil/water partition) are the most relevant. These

characteristics vary by several orders of magnitude from one compound to another: between 10^{-7} and 100 Pa for saturated vapor pressure and between 10^{-3} and 10^3 mg·L⁻¹ for water solubility. The importance of the physico-chemical properties of the pesticide can be outlined using the screening model developed by Jury et al. [20]. According to these authors, the duration, intensity and time course of the volatilization process from moist soil depends mostly on the Henry's law constant, K_h . On this basis, Jury et al. have defined 3 categories of pesticide: category I comprises highly volatile pesticides, with a non-dimensional $K_h \gg 2.65 \times 10^{-5}$; category II, moderately volatile pesticides with intermediate values of K_h and category III, slightly volatile pesticides with $K_h \ll 2.65 \times 10^{-5}$. For pesticides with a high K_h (category I), the volatilization rate is highest just after application, and then decreases at a rate dependent on whether soil water is evaporating or not. Most organochlorine pesticides belong to category I. Pattey et al. [31] found that the volatilization fluxes of trifluralin and triallate (class I) decreased by a factor of three within 4 days. Such

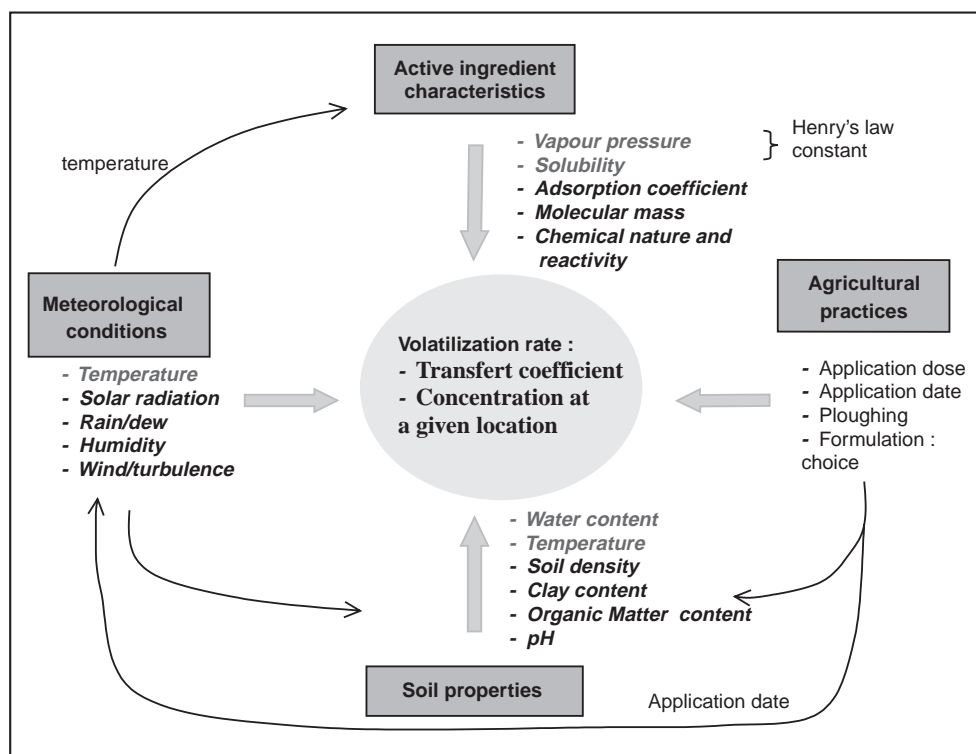


Figure 2. Parameters involved in the volatilization rate from soil. Arrows represent the different interactions. As vapor pressure, solubility or adsorption coefficient are temperature-dependent, an arrow joins the 'meteorological conditions' box to the 'active ingredient characteristics' box.

behavior in a study lasting two days has also been reported by Cessna et al. [9] for trifluralin, and by Majewski et al. [24] for trifluralin and triallate. According to this model, pesticides belonging to category III tend to accumulate on the soil surface as water evaporates from soil, so that volatilization increases with time, or slowly declines if water evaporation does not occur. Spencer et al. [36] and Spencer and Cliath [37] validated this classification into 3 categories for prometon and lindane.

Vapor pressure is also expected to be a key parameter governing pesticide volatilization. Nash [27] investigated its effect on the volatilization rate from soil, using a so-called "micro-agroecosystem". He found that all pesticides behaved similarly immediately after application, with the volatilization rate being halved after 8 hours. Compounds with higher vapor pressures (heptachlor, trifluralin and lindane) had initially high volatilization fluxes, ($>30 \text{ g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$) which decreased rapidly. In contrast, the volatilization of pesticides with lower vapor pressures (dieldrin, eldrin, DDT) was initially lower ($<10 \text{ g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$) and then decreased more slowly. All these pesticides belong to Jury's category I, and the behavior observed by Nash is consistent with Jury's classification.

Bor et al. [7] found that volatilization rates correlated with pesticide concentration in the air phase of the soil, but not with vapor pressure at 25 °C. Using the average daily volatilization rates, they estimated the following cumulative losses after 14 days: triallate (29%) > ethoprophos (24%) > parathion (4%), (triallate belongs to Jury's category I, whereas ethoprophos and parathion belong to class III). However, the cumulative fluxes shortly after application were not directly related to their Henry's law constant. According to the authors, this may be due to the three pesticides not being applied at exactly the same time. Consequently, the adsorption of the first pesticide applied to soil matrix may have already begun, limiting its volatilization.

When the adsorption of the pesticide molecules on the soil matrix is significant, the adsorption coefficient K_d or K_{oc} must be taken into account (K_d is defined as the partition coefficient of the pesticide between the aqueous and the solid phases of the soil; K_{oc} is the partition coefficient related to soil organic carbon). For this reason, Woodrow et al. [49] and Jansma and Linders [19] included K_d when determining a relationship between the volatilization rate and the physico-chemical characteristics of the pesticide.

To our knowledge, no such classification has yet been derived for volatilization from plants. The volatilization

flux during the first few hours after application often correlates with the vapor pressure of the compound [49]. However, using this kind of correlation, Jansma and Linders [19] found discrepancies with experimental data, and concluded that further investigations are needed. K_{oc} is also an important parameter that must be taken into account in describing the sink process of adsorption by plant foliage.

As a whole, the correlations between physico-chemical characteristics and the flux rates may be valid on the first day after application, because of the wide range of the physico-chemical characteristics of pesticide. They give an order of magnitude of the flux occurring after application. However, if one wants to describe its time course, on the diurnal scale for example, environmental conditions need to be considered, as described in the next section. These correlations are also limited by the fact that the pesticides applied to soil or crops are commercial formulations, whereas vapor pressure, aqueous solubility and adsorption coefficient are characteristics of the active ingredient. Since little is known about the differences between the physico-chemical properties of the applied formulation versus those of the active ingredient, volatilization predictions are highly uncertain.

3.2. Environmental conditions and agricultural practices

3.2.1. Atmospheric conditions

A higher air temperature tends to favor volatilization from plants and soils, because the vapor pressure of the compound over an aqueous solution is exponentially temperature dependent. A 10 °C increase in temperature leads to a three- to four-fold increase in vapor pressure for most pesticides [37]. Nevertheless, interactions with soil temperature and humidity may limit this effect as will be discussed below. In the case of an application on vegetation, an increase of 5 °C can lead to an increase in the volatilization rate by a factor of 8, in the case of 2,4-D applied to barley [8]. A similar pattern has also been observed by Van den Berg et al. [42] for parathion applied to a potato crop in a volatilization chamber and by Smelt et al. [34] and Stork et al. [38].

The volatilization rate increases with wind velocity. Waymann and Rüdell [45] found that for wind velocities increasing from 0.4 to 1.7 $\text{m}\cdot\text{s}^{-1}$, volatilization from soil increased from 12 to 31% of the application dose for lindane. Wind speed seems to have the same influence on pesticide volatilization from plants as from soil: an

increase in wind velocity increases the volatilization rate, even if atmospheric concentrations are lower. Waymann and Rüdél [45] found 62% of lindane volatilized from French beans over 24 h at a wind velocity of $2 \text{ m}\cdot\text{s}^{-1}$ versus 52% at a velocity of $0.4 \text{ m}\cdot\text{s}^{-1}$. A similar pattern was also observed by Breeze et al. [8] for 2,4-D applied to barley leaves. The impact of turbulence was observed by Harper et al. [18], who noted that in the case of toxaphene and DDT applied to cotton crop, lower turbulence led to lower volatilization.

Air humidity seems to favor volatilization from soil: Grass et al. [17] observed that at relative air humidities of 31, 49 and 78% in a wind tunnel, the percentage of trifluralin volatilized over the first day was 66, 64 and 96% respectively. However, we can assume that this effect is rather complex, and is related not only to relative humidity but also to surface dryness. When pesticide is applied to a crop, a low relative humidity will cause the leaves to dry out more quickly than they would at a higher air humidity. This favors adsorption of pesticide molecules on the leaf surface [42]. Higher air humidity therefore promotes both adsorption of the pesticide by plants and its volatilization.

Solar radiation affects pesticide volatilization from soil and plants and this aspect is discussed in the section dealing with the diurnal cycle. It is also involved in the photochemical degradation of the molecules on the surface, which is a sink process.

The impact of atmospheric factors all together may be non-linear. Data collected during one day in the case of trifluralin applied to bare soil in a wind tunnel reveal complex interactions between wind speed, air temperature and air humidity [17]. The lowest volatilization rate occurred under intermediate climatic conditions. Harper et al. [18], studying toxaphene and DDT volatilization from cotton plants, found that correlations between flux density and microclimate variables appeared to be weaker thirty days after application than during the first few days after treatment. According to the authors, volatilization at this stage seems to be governed more by pesticide residue on leaves and its distribution than by atmospheric variables. Moreover, any decrease in wind velocity increases the temperature of the leaves (a priori increasing volatilization), but at the same time it modifies the rates of transpiration and the evaporation of solvents in the herbicide droplet. The effects of these factors on pesticide uptake by leaves remain to be elucidated [8].

Rain and dew modify soil humidity by rewetting the soil surface, thus increasing pesticide volatilization (as observed by Majewski et al. [24] for trifluralin and

trifluralin), unless infiltration becomes significant and leaches the pesticides downward [7]. Rain washes out pesticide present on the leaf surface to an extent which is inversely proportional to the time between the application and the occurrence of rain. The amount of rainfall seems to determine the degree of pesticide washoff from plants to a greater extent than its intensity, especially if it occurs within 24 hours after application. In the case of methyl parathion and fenvalerate applied to cotton foliage, the mean amounts of pesticides washed off were related to the square of the mean insecticide loads on the plants and decreased with time [48]. Rain can also enhance pesticide penetration into the leaves, depending on the amount of rain, the time between its occurrence and treatment, the solubility of the pesticide or its formulation and the nature of the leaf [47]. This penetration process competes with the volatilization process.

3.2.2. Soil and leaf temperature

The temperature is a key parameter influencing pesticide volatilization as pesticide physico-chemical properties are temperature-dependent. A temperature increase can be expected to enhance volatilization, however this behavior is limited by soil dryness. Soil drying tends to promote the adsorption of the pesticide onto the soil matrix, thus limiting its availability for transport to the soil surface. Taylor and Spencer [40] pointed out the complex interactions between pesticide vapor density and temperature. They showed that, for a given increase in temperature, pesticide vapor density in the soil increases less above saturation than at saturation. Alvarez-Benedi et al. [1] investigated the competition between sorption and volatilization of terbutryn from two soils (a sandy and a loamy soil) and at two temperatures (15 and 25 °C), in a volatilization chamber for 50 days. The volatilization rate was clearly enhanced by an increase in temperature (cumulative loss of about 6% at 25 °C versus less than 1% at 15 °C for a sandy soil). Nash and Gish [29] observed that, between 5 and 35 °C, an increase of 10 °C in soil temperature increased the volatilization of halogenated pesticides applied to moist soil by a factor of 1.8. Similarly, Harper et al. [18] found a hyperbolic relationship between the volatilization rate (per unit of pesticide load) of toxaphene applied to a cotton crop and the leaf temperature ($r^2 = 0.79$).

Temperature gradient in soil is expected to influence pesticide volatilization because of its effect on water and pesticide movement. According to Jansma and Linders [19], there is a lack of data dealing with this process.

3.2.3. Soil water content and water transfer

Volatilization tends to increase with increasing soil water content. Several authors noticed this behavior [7, 14, 21, 23, 37, 40]. Using a volatilization chamber, Chérif and Wortham [10] found that after 26 days 11% of the lindane initially adsorbed had volatilized from a wet soil versus 0.8% from the dry soil. When the soil is dry, volatilization is generally low and may become negligible, leading Jansma and Linders [19] to mention a “dramatically” reduced rate under dry conditions. The explanation for this is not straightforward and depends on the chemical nature of the pesticide. The increase in volatilization with soil moisture may be a consequence of a decrease in the number of adsorption sites available on the soil matrix (some being occupied by the polar water molecules) or due to the fact that these adsorption sites are not accessible, due to the presence of a water film, and that pesticide molecules, which have low water solubility, cannot reach them. According to Nash [27], the soil water content seems to have a greater impact on nonionic pesticides with low vapor pressures than on pesticides with high vapor pressures.

Water transfer contributes to pesticide transport inside the soil matrix. The dynamics of the volatilization flux is therefore influenced by all the parameters that govern water transfer. Stork et al. [38], studying the volatilization of terbutylazine and parathion methyl (Jury’s category III) applied to bare soil, observed a diurnal pattern following soil water evaporation (in a wind tunnel).

However, Grass et al. [17] could not find any correlation between trifluralin volatilization from soil and water evaporation rate in a wind tunnel. In this case, high water evaporation rates were associated with partial drying out of the upper layer of moist soil, and this could have led to a decrease in the volatilization rate.

The influences of atmospheric conditions, soil water content, water and heat transfer on pesticide volatilization are therefore all closely interrelated.

3.2.4. Consequences of the diurnal course of the volatilization flux

On the diurnal scale, a cycle has been reported by several authors for the volatilization of pesticides applied to soil, except on the day of application, when a peak of volatilization just after the treatment may mask a possible diurnal cycle [7]. Studying alachlor, toxaphene, atrazine and simazine volatilization, Glotfelty et al. [15] concluded that different patterns of diurnal behavior may be

observed, and that the key factors governing this cycle are primarily solar radiation and atmospheric stability, and also soil surface moisture: in a moist soil, the volatilization rate is higher around midday and early afternoon; whereas in dry soils, the rates are higher in the early morning or evening hours due to greater surface water content due to dew formation or capillary flux. Pattey et al. [31] found a correlation between the volatilization of triallate or trifluralin and latent heat flux, both peaking in the morning. These authors gave no indication of soil moisture. During their 5-day experiment, Majewski et al. [24] found a diurnal pattern, with high volatilization rates during the early morning hours just after sunrise, a decrease throughout the day and then a slight rise again just after sunset. This pattern was related to the moisture content of the topsoil layer, to dew formation in the morning and, in the early evening, to an increased movement of soil moisture to the surface. Clément et al. [11] observed a diurnal pattern for atrazine concentration in the atmosphere, with a peak value at mid-day (with no indication about soil moisture), as did Glotfelty et al. [15], when soil was moist. When the soil was dry, Glotfelty et al. [15] did not observe any decrease of the flux at midday for atrazine applied as a wettable powder formulation. However, in this case the transfer of pesticide into the atmosphere was not due to post-application volatilization but to wind erosion. The mechanism underlying this process, which is primarily mechanical, is totally different from that of volatilization and so the factors involved can be expected to be quite different.

Air temperature determines the evaporation of water from soil and consequently the pesticide volatilization rate for the pesticides which are primarily influenced by water transfer in the soil. This has been reported by Stork et al. [38] for terbutylazine (Jury’s class III) applied to bare soil, observing a diurnal pattern, with a higher volatilization rate during the day due to a higher temperature. Volatilization is often assumed to be negligible [7] during the night time.

A diurnal pattern has also been observed by Harper et al. [18] for the volatilization of DDT and toxaphene from cotton, with peak fluxes occurring midafternoon. Correlations were found between the rate of volatilization and temperature (air and leaf temperature), wind velocity, and net radiation. Van den Berg et al. [42] also found a higher volatilization rate from a potato crop in the afternoon of the first day after application, which was linked with high net radiation. Stork et al. [38] point out a similar pattern for the volatilization of fempropimorph and parathion-methyl from dwarf beans in a wind tunnel.

However, this diurnal cycle is not always observed. The complex interactions between the various parameters governing the volatilization process lead to various outcomes which may blur this general pattern. For example, Bor et al. [7] did not observe any diurnal cycle for triallate; this can be attributed to the climatic conditions with low radiation.

3.2.5. Factors related to the nature of the soil or the plant

Soil organic carbon content governs the adsorption of weakly polar or nonionic pesticides by the soil matrix, which conditions their availability for transport to the soil surface. Using a laboratory system, Lembrich et al. [23] compared the behavior of terbutylazine applied to two types of soil: a Brown soil (weakly loamy sand) and a Regosol (loamy sand). The first soil had a higher adsorption coefficient for terbutylazine (K_{oc} of 304 and 136 respectively), but its lower organic carbon content (1% versus 2.2% for the Regosol) resulted in a lower adsorption capacity. This could explain a greater cumulative volatilization. Over 10 days, 23% of the pesticide was volatilized from the Brown soil versus 7% from the Regosol. Clay minerals are involved in the adsorption of more polar or ionic pesticides. Alvarez-Benedi et al. [1] found that at a temperature of 25 °C, volatilization was enhanced against sorption in a sandy soil compared to a loamy one. Other factors, such as pH or the bulk density of the soil, can indirectly affect pesticide volatilization from soil.

Regarding pesticide volatilization from plant surfaces, pesticide persistence on foliage depends on its wettability which is a function of the nature and age of the leaf, the stage of development of the leaf surface (waxy cuticle) and the density and height of the canopy. As already mentioned in the section dealing with physico-chemical characteristics, pesticide may adsorb on plant surfaces [40], and this is dependent on the characteristics of the leaf.

3.2.6. Agricultural practices

Crop management includes the date and dose of application, the choice of the formulation, spray droplet size, irrigation, pesticide incorporation and ploughing. The application date may be important with regard to atmospheric conditions. The effect of the application dose on volatilization from soil has been investigated by

Waymann and Rüdell [45] under semi-controlled conditions. The flux expressed in terms of mass per unit area is proportional to the application dose, whereas the flux expressed as a percentage of the application dose does not increase with the dose. The interpretation of such results is based upon the hypothesis of the existence of a thin layer at the soil surface through which transport is mediated solely by molecular diffusion. The validity of such a representation, in which a layer becomes saturated with pesticide is discussed by Van den Berg et al. [43].

Some guidelines have been issued regarding conditions of application for several pesticides. For example, trifluralin must be incorporated into the soil within 1 day after application. Whether the pesticide is incorporated or not will change its volatilization, as shown by results obtained in different studies reported by Taylor and Spencer [40], and Jury and Ghodrati [21]. After incorporation to a depth of 2.5 cm, trifluralin losses by volatilization reached only 22% in 120 days [40], which is rather low compared to the 90% losses for a surface application on moist soil referred to in the first part of this paper.

Formulation is also an important factor affecting the volatilization potential of an active ingredient [40, 46]. Microencapsulation, for example, seems to limit the extent of volatilization [40]. Using drop or spray applications can lead to different volatilization rates, as pointed out by Lembrich et al. [23]. Under laboratory conditions, the cumulative losses of terbutylazine from bare soil has been found to be higher after drop application than after spray application (11.4% vs. 9% respectively). Droplet size governs the competition between absorption by plant surfaces and volatilization: small droplets tend to evaporate more quickly than larger ones, and larger ones tend to be absorbed faster [3, 8].

Tillage modifies soil properties such as the porosity, the organic carbon content (incorporation of plant residues), the soil moisture distribution and the soil temperature. So it can be expected to have an impact on the intensity or the dynamics of pesticide volatilization [14, 46].

Pesticide distribution on foliage governs the intensity of volatilization: while the pesticide deposit still forms a continuous film over the whole surface, the volatilization flux is expected to depend only on the vapor pressure of the compound and on its molecular diffusion properties, whereas once the deposit breaks down and forms little islands, the volatilization flux will depend on the amount remaining [40].

4. CONCLUSION

The studies reviewed in this paper show that the pesticide mass transfer occurring by volatilization is a major dissipation pathway for some compounds, sometimes accounting for as much as 90% of the application dose. The general pattern of volatilization has been reported for several compounds under particular sets of conditions (environmental, agricultural practices). Volatilization may last for a period of several days to a few weeks (or sometimes even longer), and sometimes exhibits a diurnal cycle. The main factors affecting this process a few days after treatment have been identified as the physico-chemical characteristics of the compound, environmental conditions (temperature, soil moisture) and management practices. Diurnal pattern is correlated with temperature, solar radiation and atmospheric stability, but also with soil moisture in the case of volatilization from soil.

However, several questions remain. It is sometimes difficult to identify a single dominant factor. It is often difficult to compare data – sometimes due to a lack of data – such as the dose actually applied, or the environmental conditions of observation. A useful classification of the different pesticides on the basis of behavior patterns therefore remains to be produced. Some pesticides are persistent in the soil after being applied. We still do not know whether they can be transferred into the atmosphere a long time after their application, as discussed by Bidleman [5] in the case of organochlorine compounds. Even though volatilization seems to occur to a greater extent and at a faster rate from plants than from soil, there have been fewer studies on plants. We have also found that few fungicides have been investigated. Virtually nothing is known about the volatilization of metabolites. The effect of adjuvants is poorly documented, and this leads to some difficulties in interpreting the observations. Even the physico-chemical properties of the active ingredient are sometimes not well established and the ways they depend on temperature are not known with any accuracy. According to Asman [2], uncertainty by a factor of 10 is not uncommon. The lack of reliable data is pointed out by several authors, such as Bidleman [5] for example, who adds that these data are usually provided for only one temperature.

Progress could be made by means of a global approach covering all the processes of transport, sources and sinks that interact with volatilization. They have to be taken into account when attempting to identify other factors which may directly or indirectly affect volatilization. The interpretation of the different behaviors

observed experimentally calls for the development of mechanistic models. These are particularly relevant in the case of pesticides, due to the large number of compounds used. These models can be expected to be helpful in deriving a pesticide volatilization classification system.

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