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Soil thin-layer chromatography and pesticide mobility through soil microstructures
New technical approach

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Abstract

Soil thin-layer chromatography with water or water–methanol as solvents allows observation and measurement of the mobility of labelled pesticides through soil microstructures. Eleven different sieved matrices were studied: pure humine, pure clays, schists and soils. Ionized compounds (paraquat, glyphosate) were tightly bound to these matrices. The other compounds, lipophilic and generally non-ionized ones, migrated in the same order on most of the studied matrices, either mineral or organic: R_F atrazine=isoproturon>diuron=fipronil>phenmedipham. This order was roughly correlated to log P but much more complex correlations were suggested. The rate of water movement, WR, widely changed from one matrix to another. Therefore, the pesticide movement, M, in soil microstructures under the action of rain may be described by the equation $M = WR\,R_F$.

Keywords: Soil; Environmental analysis; Pesticides

1. Introduction

Xenobiotic compounds and especially pesticides are abundantly spread on soil or water surfaces. For instance, 10^8 kg of organic pesticides are spread each year on cultivated areas in France and 4×10^8 kg in the USA [1]. What happens to these compounds is an object of great concern for agronomy, environment and human health. Leaching of these substances in soils may lead to groundwater contamination. Therefore, at the present time, in order to obtain the legal authorization for pesticides and their agronomic uses, detailed information about leaching of the products inside several types of soils and under different conditions is required [2]. For this purpose, several techniques have been developed, first under agronomic conditions, with a large variability and heterogeneity of answers, and, secondly, under controlled conditions with lysimeters generally respecting the initial soil structure but also with soil columns, some of which are very similar to true chromatographic columns, where a thin and homogenous granulometry is obtained. Another technique, which is theoretically similar to soil columns, has been developed over the last 30 years, since the pioneering work of Helling and Turner [3]. This is soil thin-layer chromatography, which has been used under numerous conditions [4–12]. Surprisingly, since the work of Helling, the theoretical bases of

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this method were never clearly discussed and never compared to the results of classical thin-layer chromatography, using homogenous, well-defined adsorbants and several optimized solvents rather than water only [13].

The purpose of this report is to try to contribute to a better understanding of this method, as well as of its uses and limitations.

2. Experimental

2.1. Soils and substrates

Three representative surface soils from the Southeast of France were collected at one given depth between 0 and 10 cm in cultivated fields (CSA and TNM were sandy loam soils and FAY was sandy clay loam). Some of their physico-chemical characteristics (pH, percentage of clays, and percentage of organic matter) were, respectively: CSA: 6.2, 18% and 2.8%; FAY: 7.5, 40% and 2%; and TNM: 7.2, 21% and 5.5%. Four schists from different origins were collected in the Alps from different places: La Mure, Le Murier, Mens and Chamonix. The three different clays used were purchased from Fluka: H^+-montmorillonite K10 (200 $m^2 g^{-1}$, 300 $g l^{-1}$ density), H^+-montmorillonite KSF (30 $m^2 g^{-1}$, 800 $g l^{-1}$ density) and H^+-kaolinite (SiO_2 46%, Al_2O_3 39%).

2.2. Soil thin-layer chromatography

After collection, the soil samples were air-dried and sieved through a 2-mm screen before being powdered with an electric mill (Polymix PX-MFC). The powder obtained was sieved through a 100-μm mesh screen. Before being pulverized and sieved (100 μm), the schists were previously manually broken with a hammer. Commercial powdered clays were sieved at 100 μm before use. Then 30 g of powdered substrate were suspended in a dioxan–water (1:1, v/v) solvent to make a slurry which was then spread as a 0.7-mm thick layer on a 20×20 cm glass plate with the help of a thin-layer spreader (Desaga, Heidelberg). The plates were dried at room temperature and stored until being used for chromatographic tests. When necessary, pyrolysed matrices were obtained after a 3-day period in an oven at 600°C.

2.3. Pesticides

Seven radiolabelled pesticides, six herbicides and one insecticide were used in this study (Fig. 1). Five of them were neutral chemicals from the following families: triazines (atrazine), phenylureas (diuron and isoproturon), biscarbamates (phenmedipham), phenylpyrazols (fipronil). In addition, two ionic pesticides, the cationic paraquat and the anionic glyphosate were used. These two latter compounds were water-soluble. Some physico-chemical characteristics of these compounds are presented in Table 1. Stock solutions were prepared in distilled water for glyphosate and paraquat and in ethanol for the other pesticides. Approximately 50 000 dpm of each ^{14}C-labelled molecule were spotted with a microsyringe at 2.5 cm from the bottom edge of the plates. After depositing the spots (distance between two spots: 2.5 cm), the plates were allowed to develop in a closed plastic chamber using distilled water (in a first attempt, 0.01 *M* $CaCl_2$ was used as a developing solvent. Since the results were exactly the same with pure water, $CaCl_2$ was suppressed) or water–methanol (4:1 or 3:2, v/v) as solvent. A sheet of filter paper dipping into the developing solvent fed solvent continuously to the substrate at the base of the plate, thus leading to a relatively uniform flow. During development with solvent the whole device was held in a horizontal position. Solvent migration occurred at a distance 17.5 cm from the baseline. The plates were then dried at room temperature.

The migration lasted between 2.5 and 9 h. The labelled compounds were incubated concurrently with the studied matrices for 10 h, then eluted with methanol, concentrated in vacuo, and chromatographed on silica-gel Merck 60 F with lipophilic solvents such as light petroleum (b.p. 40–65°C)–ethyl acetate–formic acid–acetic acid (40:40:1:1, v/v) in order to look for the possible formation of metabolites on autoradiograms. No significant amount of metabolites was detected under our experimental conditions.

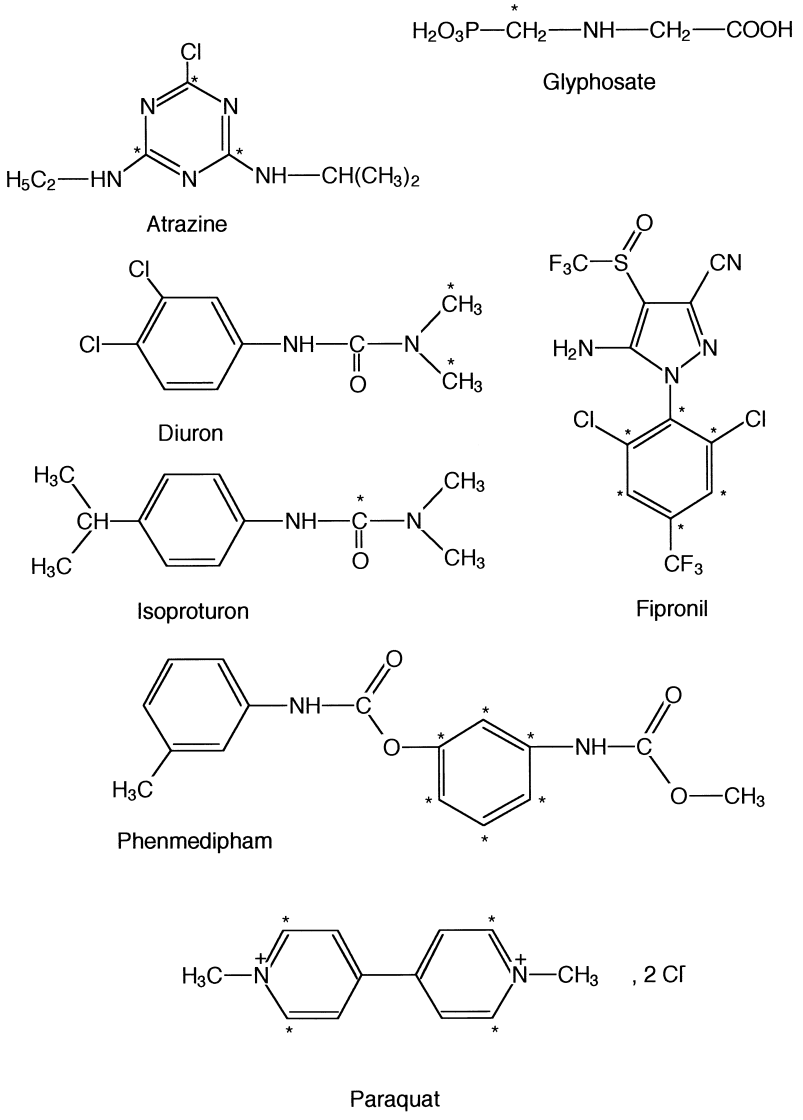

Fig. 1. Structure of the studied pesticides. Asterisks refer to ^{14}C-labelled positions.

2.4. Autoradiograms and R_F values

Autoradiographic films (Eastman Kodak, DFE 5) were applied to the dried plates for 3 days. The distances covered by the products on the thin layer compared to that covered by water, i.e. the R_F value, were measured on the radiochromatograms. Where possible, the visualization of movement was obtained using a linear analyzer (Berthold LB 282) with a multichannel analyzer, and smoothed radiograms were plotted.

3. Results and discussion

3.1. Making a soil thin-layer chromatogram

A soil can be seen as a mixture of three types of

Table 1
Some physico-chemical characteristics of the pesticides used

Name	Chemical name	pK_a	Log P	Water solubility (mg l^{-1})[c]	Activity by spot (dpm)
Phenmedipham	Methyl 3-(3-methycarbaniloyloxy) carbanilate	None	3.75[d]	4.7	50000
Atrazine	6-Chloro-N^2-ethyl-N^4-2,4-isopropyl-1,3,5-triazine-diamine	1.71[a]	2.5[d]	33	52500
Diuron	3-(3,4-Dichlorophenyl)-1,1-dimethylurea	None	2.7[d]	42	
Isoproturon	3-(4-Isopropylphenyl)-1,1-dimethylurea	None	2.5[d]	70	44700
Glyphosate	*N*-(Phosphonomethyl)-glycine	2.3−5.9 10.9[b]	−4	12000	60000
Paraquat	1,1′-Dimethyl-4,4′-bipyridinium	11	–	–	76000
Fipronil	(±)5-Amino-1-(2,6-dichloro-4 4-(trifluoro methyl)phenyl-(trifluoro methyl) =sulfinyl)-1 H-pyrazole-3-carbonitrile	None	2.8[d]	1.9	50500

[a] Ref. [21].
[b] Ref. [35].
[c] Ref. [36].
[d] Personal results obtained using the partition method described in Ref. [37].

components: (1) compact poorly absorbing compounds, such as sand and pebbles; (2) mineral components with absorbing properties, such as clays, possibly including mineral ions (Ca^{2+}, Mg^{2+}, PO_4H_{2-} . . .); and (3) organic compounds such as insoluble humines, traces of more or less water-soluble humic and fulvic acids, and native plant organic compounds (lipids, lipophilic proteins and polymers such as lignin, cellulose or starch). Moreover, a living biomass is present inside the soil, mostly constituted of microorganisms. However, this biomass does not grow during thin-layer storage and is constituted mainly of spores and cysts. For TLC use, the distribution of the different thin particles acting as adsorbing substrates has to be strictly homogenous. This explains why the coarse elements have to be discarded through sieving. Another way of preparation may involve crushing the coarse components (root and bark fragments, rock pieces . . .). In such a case, the global composition of the layer differs slightly from that obtained through sieving only.

The dry thin layer may be very friable, generally preventing a vertical development. For this reason, our whole device was held in a horizontal position [Fig. 2(A)]. For routine use, 5% cellulose (poorly adsorbing fiber) was added, giving better cohesiveness to the layer without changing the R_F values. When the soil slurry is made with distilled water, the thin layer may crack during the evaporation of water. A better result may be obtained through the use of a mixture of dioxan or methanol and water for slurrying the powder.

3.2. What is the principle of soil thin-layer chromatography?

Two fundamental features contribute to the characterization of soil TLC. First, the layer is a mixture of solid particles the sizes of which are

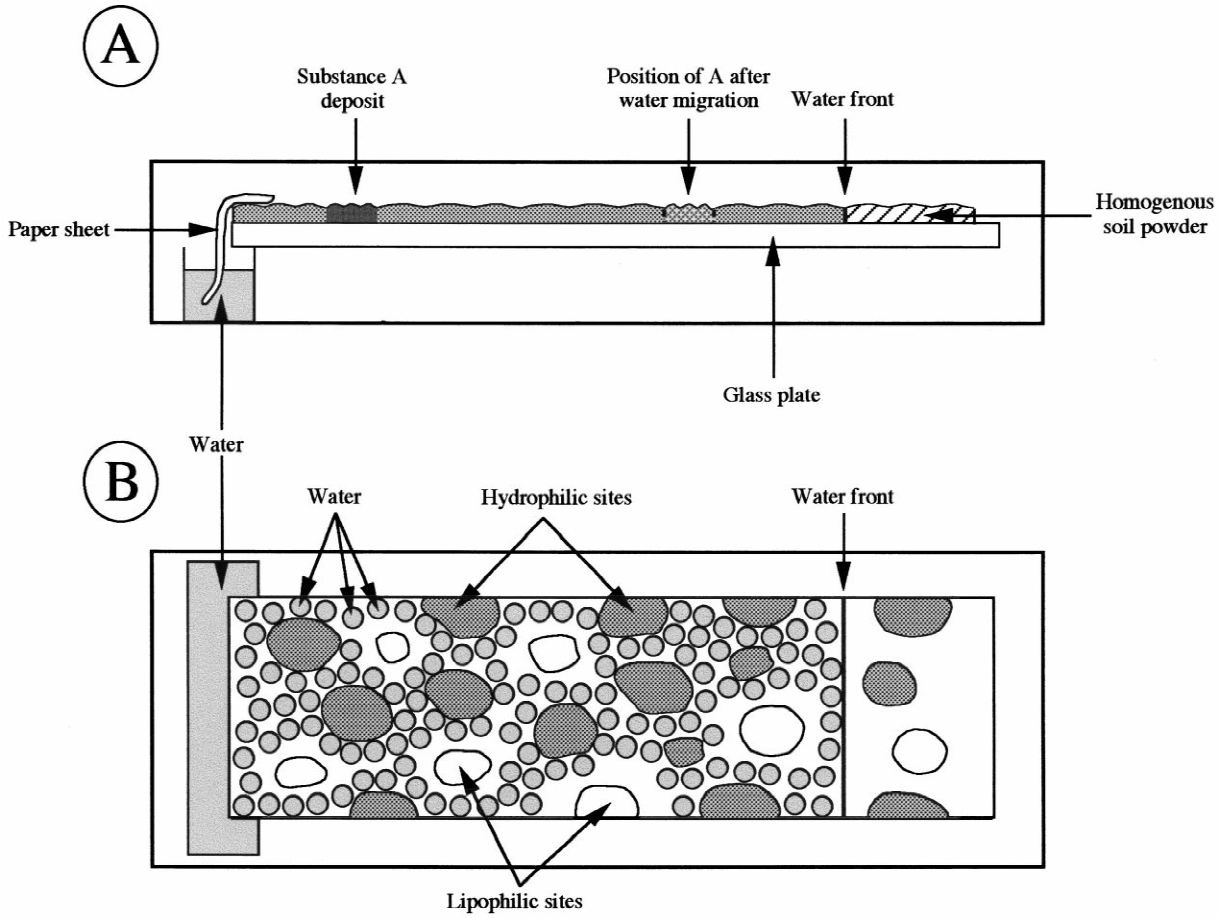

Fig. 2. Scheme illustrating the principle of soil thin-layer chromatography: (A) experimental device; (B) scheme tentatively illustrating water movement inside a heterogenous microporous layer containing hydrophilic and lipophilic sites.

lower than 100 μm in our experimental conditions. The chemical composition of the particles was not the same (clay, humine, sand . . .) but these particles were distributed randomly. Most of these particles have a high affinity for water, whereas others, or specific parts of them, do not. Secondly, the solvent chosen to move between these particles is water, in order to mimic rain movement in soil microstructures in the field (Fig. 2B). These features contrast strongly with classical TLC systems for which the chemical composition of the layer is homogenous and the solvent mixture is generally complex and chosen in order to optimize the separation of the studied chemicals. Under the conditions used, a soil thin layer is characterized by its water capacity and by the rate of water movement through the layer. As shown in Table 2, the water content, as a percentage of substrate dry mass, greatly differed, depending on the nature of the matrix used. Concurrently, the rate of water movement also greatly changed with the nature of the matrix but no simple relation seemed to exist between this characteristic and the water content.

For TLC, a deposit of a substance (or a mixture of substances) *A* is effected on a small surface of the starting line of the soil plate (Fig. 2A). This deposit is made in such a way that *A* is finally adsorbed on the small calibrated soil particles. Under satisfactory conditions, compound *A* is quickly and completely dissolved in water and moves with it. At the end of

Table 2
Water capacity and rate of water capillary movement for the studied matrices

Matrix	Water capacity (ml g^{-1})	Rate of water movement (cm h^{-1})	
		Initial rate	Average rate
Schists of Le Mûrier	0.47	1.50	0.5
Schists of Chamonix	1.27	1.75	1
Pure humine	2.3	4	3.6
Soil (FAY)	1.52	3	1.3
Soil (CSA)	0.58	7.7	6.7
Clay (K10)	0.99	5.2	3.1
Clay (KSF)	0.86	6.5	4.8
Clay (kaolinite)	0.26	3.5	2.2

the chromatographic run, each molecule of *A* is found at a characteristic place corresponding to an R_F value situated between 0 and 1. The higher the absorbing forces of the matrix for *A*, the lower the R_F value. As a consequence, one can see that a theoretical correlation does exist between R_F and K_d values. Hamaker [14] tentatively expressed this correlation between R_F and the standard distribution coefficient K_d through the formula $R_F = 1/1 + K_d B(1/v^{0.67} - 1)$, in which *B* is the density of the soil and *v* is the fractional soil volume filled with water under the conditions used by the author. However, this interesting attempt did not give rise to further developments.

K_d represents the quantitative equilibrium existing, under standard conditions, between the amount of product dissolved in water and that adsorbed on the studied matrix. As shown by sorption isotherms in most cases, the linear relation between the adsorbed amount and the initial concentration in water is only valid in a small range of concentrations. This point might explain the 'tailing' and streaking of products on soil TLC, first described by Helling and Turner [3] and that we have also observed in several cases. We first thought that this might originate from a saturation of the high affinity binding sites on the deposit area but it was easy to demonstrate, for instance in the case of fipronil or atrazine (Fig. 3), that the limiting factor was the water solubility of the studied compound. 'Tailing' occurred, whatever the nature of the matrix, when the compound deposited on the starting line could not be fully dissolved in the water front. Therefore, with lipophilic compounds, 'tailing' occurred for small amounts of product. This was not the case for more hydrophilic ones such as sucrose (results not shown). For obtaining a TLC without 'tailing', the deposit amount had to be decreased when the lipophilicity of the compounds increased. For example, no tailing occurred with fipronil (log $P = 2.8$) or atrazine (log $P = 2.5$) when the deposit did not exceed, respectively, 2 and 5 nmol/30 mm^2 (Fig. 3).

Soil TLC was used first of all for measuring the movement of a xenobiotic compound through soil microstructures. Therefore, the solvent had to be water. However, with water as solvent, many compounds have an R_F value of 0 on soil matrices after a 20 cm chromatographic run. Nevertheless, the strength of the binding to the soil of these compounds may differ widely and it was interesting to obtain an evaluation of this strength. For that purpose, it was decided in this work to decrease the solvent polarity progressively by adding small amounts of methanol to water. The results shown in Table 3 demonstrate that for ionic compounds such as glyphosate or paraquat, the change in solvent composition practically does not affect the R_F values. For lipophilic compounds, having almost the same R_F in water (0.12, 0.09, 0.13), the use of a less polar solvent allowed classification of their respective binding strengths (Table 3).

3.3. R_F values of seven pesticides on different matrices

Phenmedipham was the most lipophilic compound (log $P = 3.75$) and the four other neutral products had comparable log *P* values (between 2.5 and 2.8). The phenylurea family was represented by two derivatives: diuron with a 3,4-diCl on the phenyl ring and isoproturon with a 4-isopropyl, log *P* values being, respectively, 2.7 and 2.5. Three types of agricultural soils, three types of pure clay, pure humine, and four types of schists were chosen to make thin-layer plates. Samples of the different soils and schists used here were also submitted to a pyrolysis process in order to give another series of plates. The R_F values measured for the studied pesticides on all these substrates are shown in Tables 4–6.

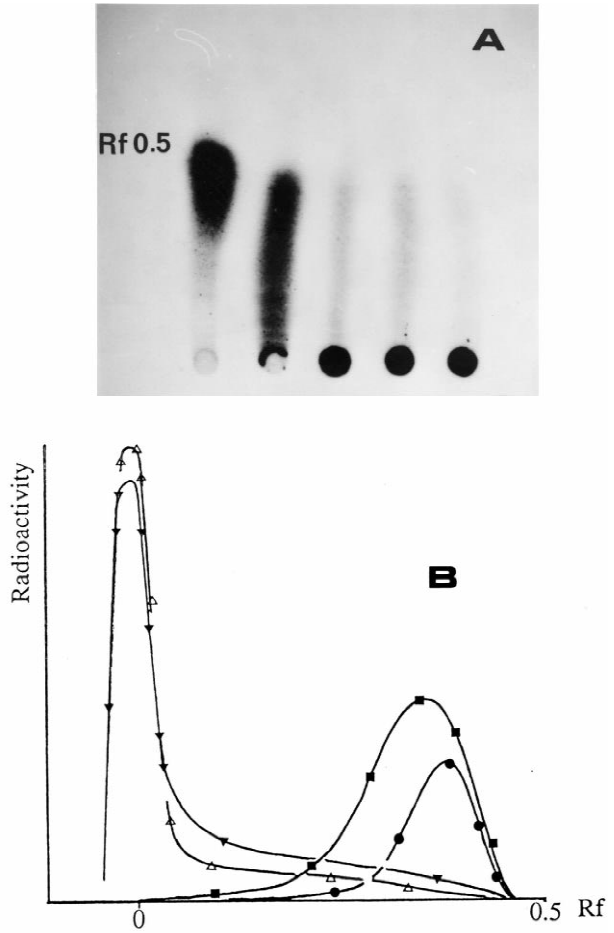

Fig. 3. Occurrence of tailing when the amount of the deposit is too high for obtaining an immediate and total water solubility: (A) Autoradiography of five spots of fipronil applied at different amounts (1.25, 6.25, 46.25, 100 and 500 μmol) on a CSA plate (solvent: water–methanol, 3:2). For each spot the same amount of ^{14}C-labelled fipronil (1.25 nmol) was deposited. (B) Smoothed radiochromatograms of atrazine in a soil thin layer (CSA) as a function of the amounts deposited (5, 10, 50 and 100 nmol/spot); 5 and 10 nmol corresponded to pure ^{14}C-labelled product, 50 and 100 nmol contained only 10 nmol of labelled compound; ●, 5 nmol; ■, 10 nmol; ▼, 50 nmol; △, 100 nmol. Solvent: water.

3.3.1. Chromatographic behaviour of paraquat and glyphosate

On each type of matrix studied here, the two types of ionic pesticides chosen were shown to be completely motionless in spite of good solubility in water. This situation seems clearly understood in the case of quaternary N compounds such as paraquat, which are present in soil solution as cationic species and react with negatively charged matrices, either mineral [15] or organic [16]. The mechanism of such an ionic binding was previously described, for instance by Weber [17]. In the case of the glyphosate, which is *N*-(phosphonomethyl)glycine, it is possibly present under a mono-, di- or trianionic form (Table 1) depending on the pH value of the matrix. It interacts with inorganic cations in soil colloids, via electrostatic forces, thereby competing with inorganic phosphates [11,18]. Such an interaction leads to a very low mobility of glyphosate. A possible role of precipitates of $Fe(OH)_3$, $Al(OH)_3$, $Al_2SiO_3(OH)_4$ at neutral and alkaline pH was also considered [8]. When the soils, clays and schists

Table 3
Changes in R_F values for seven pesticides chromatographed on CSA soil thin-layer plates with different solvents

Pesticide	Water	Water–methanol (4:1, v/v)	Water–methanol (3:2, v/v)
Atrazine	0.43	0.63	0.90
Fipronil	0.12	0.23	0.47
Phenmedipham	0.09	0.13	0.26
Glyphosate	0.04	0.05	0.05
Paraquat	0.00	0.04	0.04
Diuron	0.13	0.30	0.44
Isoproturon	0.41	0.58	0.77

studied here were pyrolysed, the high ionic binding of glyphosate or paraquat was maintained, with one exception (glyphosate on pyrolysed schists of La Mure, $R_F = 0.37$). In that case, the pH value of the substrate was acidic enough to maintain glyphosate under its monoanionic form, in contrast with the other pyrolysed schists which had higher pH values (>5.8) leading to the dianionic form increasing the binding.

3.3.2. Lipophilic pesticides binding

These pesticides were strongly bound to: (1) montmorillonites; (2) schists of Mens, Chamonix and La Mure; and (3) pure humine. The binding was weaker for the three types of soils used here, for pure kaolinite and for one schist coming from Le Murier. With these matrices, pesticide migration gave R_F values between 0 and 1 and these values globally seemed to be anticorrelated to the log P values. The pyrolysis action on soils and schists was evidently responsible for the organic matter destruction but it

Table 4
R_F values for seven pesticides chromatographed on different soil thin-layer plates

Pesticides	Type of soil and solvent										
	FAY, water	FAY pyrolysed		TNM, water	TNM pyrolysed		CSA, water	CSA pyrolysed		Humine	
		Water	Water–methanol (3:2, v/v)		Water	Water–methanol (3:2, v/v)		Water	Water–methanol (3:2, v/v)	Water	Water–methanol (3:2, v/v)
Atrazine	0.63	0.71	0.96	0.39	0.98	11	0.43	0.60	0.93	0	0.43
Fipronil	0.20	0.49	0.94	0.08	0.50	0.96	0.12	0.60	0.95	0	0.20
Phenmedipham	0.10	1	1	0.06	1	1	0.09	0.37	0.91	0	0.10
Glyphosate	0	0	0	0.1	0	0	0.04	0	0	0	0
Paraquat	0	0	0	0.02	0	0	0	0	0	0	0
Diuron	0.23	0.60	0.94	0.13	0.95	1	0.13	0.51	0.91	0	0.13
Isoproturon	0.59	0.86	0.97	0.38	0.95	1	0.41	0.76	0.95	0	0.31

Table 5
R_F values for seven pesticides chromatographed on different unpyrolysed and pyrolysed schists

Pesticide	Type of schist and solvent											
	Schist of Mens			Schist of La Mure			Schist of Le Murier			Schist of Chamonix		
	Unpyrolysed		Pyrolysed, water	Unpyrolysed		Pyrolysed, water	Unpyrolysed		Pyrolysed, water	Unpyrolysed		Pyrolysed, water
	Water	Water–methanol (3:2, v/v)		Water	Water–methanol (3:2, v/v)		Water	Water–methanol (3:2, v/v)		Water	Water–methanol (3:2, v/v)	
Atrazine	0	0.19	0.34	0	0	0	0.43	0.63	0.86	0	0.09	0.94
Fipronil	0	0.08	0.29	0	0	0.20	0.15	0.50	0.57	0	0	0.47
Phenmedipham	0	0.04	0.11	0	0	0.10	0	0.30	1	0	0	0.51
Glyphosate	0	0	0	0.05	0.05	0.37	0.06	0	0	0	0	0
Paraquat	0	0	0	0	0	0	0	0	0	0	0	0
Diuron	0	0.08	0.23	0	0	0.31	0.10	0.34	0.91	0	0.05	0.85
Isoproturon	0	0.22	0.23	0	0	0.34	0.47	0.66	0.97	0	0.08	0.94

Table 6
R_F values for seven pesticides chromatographed on different clays (montmorillonites — KSF and K10 — and kaolinite)

Pesticide	Type of clay and solvent					
	KSF		K10		Kaolinite	
	Water	Water–methanol (3:2, v/v)	Water	Water–methanol (3:2, v/v)	Water	Water–methanol (3:2, v/v)
Atrazine	0	0	0.03	0.06	0.51	0.78
Fipronil	0.32	0.60	0.24	0.42	0.311	0.43
Phenmedipham	0	0.47	0.07	0.30	0.24	0.45
Glyphosate	0	0	0	0	0	0
Paraquat	0	0	0	0	0	0
Diuron	0	0.28	0.08	0.30	0.44	0.65
Isoproturon	0.10	0.26	0.14	0.27	0.50	0.72

also induced other structural changes in the mineral part of the matrices. This powerful treatment increased the R_F values of all the lipophilic pesticides. However, the increases were quite different depending on the pesticide nucleus. The soils studied here, which were mixtures of organic matter and of clays, showed a lower binding capacity than montmorillonites or schists or pure humine. This suggests that the surface area of the 100-μm sieved soils might be much lower than that of clays or powdered schists. In the same way, the difference in binding capacities of montmorillonites and kaolinite seemed to be associated with their structural characteristics, leading to widely different surface areas, as measured using the BET N^2 method ($30–800\times10^3$ $m^2\,kg^{-1}$ for montmorillonites and only $10–20\times10^3$ $m^2\,kg^{-1}$ for kaolinite [17]).

A striking point in this study was that the lipophilic pesticides considered here were classified in the same order of R_F, for most of the matrices, either mineral or organic. The products can be classified as follows, according to their R_F on different matrices: atrazine = isoproturon > diuron = fipronil > phenmedipham. In the case of montmorillonites the scheme was qualitatively different, with a specific high binding for atrazine (as shown in methanol solvents).

The general classification of R_F was roughly correlated to log *P*. A similar situation was described for triazole fungicides on soil TLC by Jamet and Eudeline [10]. Nevertheless, it has to be noticed that in several chemical series the correlation index between log *P* and electronic parameters (such as π) are far from negligible [19]. More commonly accepted explanations are based on physical attraction by Van der Waals forces [20]. The specific binding of atrazine seen here on montmorillonites seems to agree with previous experiments showing that the acidic pH of such clays would be responsible for protonation of atrazine. In fact, KSF and K10 show pH values of 2.3 and 2.75, respectively (in marked contrast with kaolinite, pH 5.25). This suggests that atrazine ($pK_a = 1.7$ [21]) would be for a large part found under its protonated form and tightly bound to montmorillonite by a ionic force as previously suggested [22–27]. Furthermore, Ainsworth et al. [28] suggested that protonated species were more easily adsorbed than neutral species even when the pH of the montmorillonite suspension was higher than the equilibrium constant (pK_a) of the pesticide. However, binding to montmorillonites seems not to be fully explained by such a phenomenon [29]. In the case of phenylureas, which are considered as hardly polarizable and quite hydrophobic molecules [30], the differences in R_F values on soil and humine between diuron and isoproturon seem clearly correlated to the differences in lipophilicity. On clays, the difference between montmorillonite and kaolinite suggests a possible protonation affecting the –NH– of the lateral chain in the case of montmorillonite. However, the difference in the external surface area of the two clays might also play a part. In contrast, isoproturon adsorption on clays seems not to be related to the kind of clay [30,31]. Gaillardon et al. [32] found that adsorption was also associated with log *P* among a phenylurea series (isoproturon,

metoxuron, linuron and diuron). Senesi and Testini [33] demonstrated also that adsorption depended on phenyl ring substitution in this series.

4. Conclusion

Soil TLC is obviously a method for measuring the relative movement of a molecule in a water stream, through a matrix having adsorbing properties. As the soil matrix is generally heterogenous, several types of adsorbing forces are evidently involved in this process, but only the highest forces probably play a significant role. The adsorbing forces in soil TLC seem to be mostly physico-chemical forces acting instantaneously, the biological retention forces ensured by the living biomass being drastically reduced and considered negligible.

Therefore, soil TLC seems to be representative of the possible movement, *M*, of a xenobiotic compound in the soil microporous phase when it rains. The R_F measured on soil TLC alone is not enough to describe this movement. As the rate of water movement, *WR*, widely changes from one matrix to another, this movement may be characterized by the equation $M = R_F WR$. As is now well-established, surface and groundwater contaminations mostly occur during the month following treatment [34]. The direct rain-induced rapid transfer of agronomical xenobiotics inside the soil in macroporous and microporous ways seems to play a pre-eminent role in this contamination process. Soil TLC is, therefore, an interesting technique, contributing to the evaluation of rapid microporous transfer. Sieving and mixing the soil powder allows us to obtain an average value of the microporous binding properties of the soil layer from which the sample was taken.

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