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Study of the effect of exogenous organic matter on the mobility of pesticides in soils using soil thin-layer chromatography

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Abstract

The effect of soil amendment using urban compost, agricultural organic amendments and surfactants on the mobility of two sparingly-soluble pesticides – diazinon and linuron – was studied by soil thin-layer chromatography. The modifications in R_f values due to the addition of the amendments were similar for both pesticides. No significant correlation was found between the R_f values and the content of total organic carbon in the amended soils. This fact indicated that not only the organic carbon content of amended soils but also the amendment nature, specially their content in soluble fractions must play a very important role in the pesticide mobility. The surfactants gave rise to important alterations in pesticide mobility; the pesticides changed from being slightly mobile in natural soil to being immobile in the soil sample modified with tetradecyltrimethylammonium bromide and to being mobile in the soil sample amended with sodium dodecyl sulphate.

Keywords: Soil; Environmental analysis; Pesticide mobility; Pesticides

1. Introduction

Information on the presence of agricultural pesticide residues in soils and waters has increased considerably in recent years [1–3]. The data available suggest the need for gaining further insight into the processes of adsorption and mobility of these compounds in the soil and for studies addressing new factors involved in such processes.

The organic matter of the soil is known to play a crucial role in the adsorption and mobility of hydrophobic organic compounds in general [4] and of hydrophobic organic pesticides in particular [5,6]. Additionally, the adsorption of these compounds by dissolved organic matter increases their solubility [7–9]. Accordingly, these two adsorption processes

may prevent or favour pesticide leaching from the soil.

Despite this, little research has been devoted to studying the potential effects on pesticide mobility of the exogenous organic matter that, as a result of anthropogenic activities, reaches the soil. Using packed soil columns, Zsolnay [10] and Guo et al. [11,12] studied the effects of an organic fertilizer and of carbon-rich residues on the mobility of atrazine and alachlor and Foy [13], using soil thin-layer chromatography (soil TLC), investigated the effect of certain surfactants on the mobility of selected pesticides.

Among the organic materials that may coincide with pesticides in the soil, the most important are organic fertilizers, solid or liquid organic amendments and surfactants used as adjuvants in pesticide formulations and also present in irrigation water and

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sludges. Owing to their specific properties, the latter compounds are able to increase the apparent solubility of hydrophobic organic compounds, especially at concentrations above their critical micellar concentration (CMC) [14–16].

In the present work we studied the mobility of two sparingly water-soluble pesticides – diazinon and linuron – in a natural soil and in a soil amended with different organic materials using the soil TLC technique. Diazinon (O,O-diethyl-O-2-isopropyl-6-methylpyrimidinyl phosphorothioate) is an organophosphorus insecticide and linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] is a herbicide belonging to the urea group. Both compounds are very persistent in the soil [17,18] and their residues have been detected in surface and underground waters [1,19]. Moreover, studies on the mobility of both pesticides using soil TLC in series of soils have shown that the organic matter is the main parameter affecting their mobility [20–22].

2. Experimental

2.1. Soil sample

A soil sample from the surface horizon (0–10 cm) of a eutric cambisol was used. The characteristics of the soil were as follows: pH, 7.5; organic matter content, 0.77%; clay, 18.1%; silt, 15.5; sand, 64% and cation-exchange capacity 9.4 cmol/kg. The mineralogical composition of the clay fraction was; illite, kaolinite and montmorillonite.

2.2. Pesticides

¹⁴C-Labelled diazinon of specific activity 610 MBq/g and 97% purity was purchased from International Isotope (Munich, Germany). Unlabelled diazinon of technical purity (98%) was supplied by Riedel de Haen (Hannover, Germany). The chemical is a liquid with a water solubility of 40 mg/l [23].

¹⁴C-Labelled linuron of specific activity 1310 MBq/g and 98% purity was purchased from Hoechst (Frankfurt, Germany). Unlabelled linuron of technical purity (99%) was supplied by Promochem

(Wesel, Germany). The chemical is a solid with a water solubility of 81 mg/l [23].

2.3. Organic materials

The organic materials employed were as follows: City refuse compost (CRC) from the solid residue treatment plant at Valdemingómez (Madrid, Spain), Grün Garant peat (GGP) (Deutsche Torfgesellschaft, Saterland Scharrel, Germany) used as agricultural amendment, Humimag liquid amendment (HH) (Braker Laboratories, Valencia, Spain) commercial humic acid from Fluka (FHA) (Fluka, Busch, Switzerland), sodium dodecyl sulphate (SDS) anionic surfactant (Aldrich, Milwaukee, WI, USA) and tetradecyltrimethylammonium bromide (TDTMA) cationic surfactant (Aldrich). The content of organic carbon of the amendments was as follows: 28.1% for CRC; 34.7% for GGP; 22.1% for HH; 47% for FHA; 50.0% for SDS; 60.6% for TDTMA.

2.4. Preparation of amended soils

Soil mixtures (<2 mm fraction) were prepared with amounts of the different organic materials equivalent to those that are intentionally or unintentionally added to soils and the mixtures were homogenized in an orbital shaker. Part of the mixture was separated for use with no further treatment (Soils A) while the other part (Soils B) was incubated in a chamber with humidity conditions equivalent to 80% of the field capacity at 28 °C over 60 days. The contents in organic carbon of the mixtures before and after incubation, determined by the Walkley–Black method [24], are shown in Table 1.

Table 1
Organic carbon content (%) of natural and amended soils before (soils A) and after incubation (soils B)

Organic materials	Soils A	Soils B
None	0.43	0.38
CRC	1.25	0.98
GGP	1.73	1.73
HH	0.62	0.45
FHA	1.52	1.54
SDS	1.77	1.62
TDTMA	1.62	1.46

2.5. Preparation of the soil plates

Soil plates for TLC were prepared by grinding the soil samples in a mortar, followed by sieving through 160 μm mesh. Soil (7.5 g) and distilled water (15 g) were slurried and spread as a 0.5 mm thick layer onto $20 \times 5 \text{ cm}^2$ glass plates with the aid of a Desaga TLC spreading device. Five plates were prepared for each soil, of which the first and fifth were not used. The plates selected were dried in a chamber at room temperature and subsequently stored in a desiccating chamber at a relative humidity of 70%.

2.6. Soil TLC procedure

The plates were marked with two horizontal lines at distances of 2 and 12 cm, respectively, from the base. A 5 μl droplet of (^{14}C)-labelled pesticide (175 Bq) was spotted onto the baseline of the three plates with the aid of a micropipette. The plates were placed in closed individual glass chromatographic chambers 22 cm in length and 5 cm wide. After the distilled water had migrated to a distance of 10 cm from the baseline, the plates were allowed to dry at room temperature. The movement of (^{14}C) pesticide was detected using a Berthold TLC Tracemaster 20 linear detector.

The mobility factor, R_F , is given by $R_F = R_1 / 10$, where R_1 is the frontal distance travelled by the pesticide.

3. Results and discussion

3.1. Mobility of diazinon in natural and amended soil

The results obtained in the determination of the mobility of diazinon in natural soil and soil amended with the different organic materials are shown in Table 2 as R_F values (mean of three determinations).

The R_F value for the mobility of the pesticide in the natural soil was 0.28; according to the classification of Helling and Turner [25], diazinon can be considered to be slightly mobile in this soil. In previous work on the effects of soil properties on the mobility of this pesticide, Arienzo et al. [20], using 25 soils with organic matter contents ranging from

Table 2

R_F for mobility of diazinon as a function of amendment (soils A) and of amendment–incubation (soils B)

Organic materials	Soils A		Soils B	
	R_F	S.D. ^a	R_F	S.D. ^a
None	0.28	0.06	0.28	0.01
CRC	0.23	0.02	0.20	0.04
GGP	0.18	0.02	0.18	0.02
HH	0.30	0.03	0.30	0.01
FHA	0.24	0.01	0.15	0.08
SDS	0.74	0.02	0.69	0.19
TDTMA	0.09	0.02	0.10	0.01

^a S.D. = standard deviation of three replicates.

0.47 to 10.28%, found R_F values between 0.07 and 0.27. Using six soils with organic matter contents in the 0.7–6.0% range, Somasundaram et al. [21] reported R_F values between 0.10 and 0.24. In view of the sandy nature and the low content in organic matter of the soil used here, the R_F value for the mobility of diazinon in the soil is close to the upper limit of the range found by these authors.

Following amendments of the soils with the organic matter, the R_F values decreased with the addition of CRC, GGP, FHA and TDTMA while it increased with the addition of HH and SDS. The maximum decrease was observed for the soil amended with TDTMA ($R_F=0.09$) and the minimum decrease for the soil amended with FHA ($R_F=0.24$). In soils amended with HH and SDS, the R_F increased to 0.30 and 0.74, respectively.

Although in all cases there were modifications in the R_F value, pointing to the effect of the organic materials on pesticide mobility, the compound continued to be slightly mobile in the amended soils, with the exception of those amended with TDTMA and with SDS in which became immobile and mobile, respectively [25].

No significant correlation was found between the R_F values and the content of total organic carbon in the soils. However, Arienzo et al. [20] did find a highly significant correlation between R_F and the organic matter content in a study of the mobility of diazinon in a series of soils with a broad range of organic matter contents. This is probably due to the fact that the organic material of the soils was more homogeneous in composition than the organic ma-

materials used in the present study. The organic carbon content should not be seen as the only criterion for assessing the adsorption capacity of a pesticide by the organic matter present; both the chemical structure and the properties of the organic constituents must also play a very important role. These constituents determine the type of bond, including hydrophobic bonds, that the pesticide can establish in its interaction with the organic matter.

In a study on the adsorption of diazinon by the same amended soils used in this study [26], no significant correlation was found between the Freundlich adsorption constant K and the content in organic matter of amended soils. However, there is a significant negative correlation between the K constant and R_f . This is because both parameters must depend on both the amount and the nature of the organic matter used.

The strong decrease in the mobility of diazinon in the soil amended with TDTMA (the R_f represents 33% of that corresponding to the natural soil) is probably due to the cationic nature of this compound. This surfactant must be adsorbed via cation-exchange mechanism by the soil, and the adsorbed molecules must in turn adsorb the diazinon via hydrophobic bonds, giving rise to a decrease in the mobility of the pesticide. The strong adsorbent power of the organic matter derived from the quaternary ammonium cations has been reported in studies on the adsorption of hydrophobic organic compounds in general [27,28], and hydrophobic pesticides in particular [29,30] using clays and soils saturated with these organic cations.

The slight increase in the mobility of diazinon in the soil amended with HH is due to the presence of soluble organic fractions in this material. As mentioned in the introduction of this work, dissolved organic matter is able to increase the apparent solubility of hydrophobic organic compounds and favour their mobility in the soil [7–9]. The solid fraction of the HH amendment should give rise to a decrease in the mobility of diazinon, as do CRC, GGP and FHA, since its active component is humic acid, like that of these latter solid amendments.

The dramatic increase in the mobility of diazinon in the soil amended with SDS (the R_f represents 264% of that corresponding to the natural soil) is due to certain specific properties of surfactants [14–16].

In view of the solubility of SDS and the amount of this compound present in the soil, its concentration in the leaching water must be higher than its CMC (2.38 g/l). As a result, the surfactant will be found in the solution in the form of spherical micelles whose hydrophobic nuclei will adsorb herbicide molecules and these will be leached out with the water-soluble surfactant.

Previous incubation of the natural soil over 60 days does not lead to any alteration in the mobility of diazinon in the soil (Table 2). Neither does incubation modify the mobility of the pesticide in the samples amended with GGP and HH. However, mobility is slightly altered in the soils amended with CRC, FHA and SDS. The lowest R_f value continues to correspond to the soil amended with TDTMA and the highest one to the soil amended with SDS. The slight changes observed with some amendments would depend on the sensitivity of these to the incubation process, which may elicit transformations and/or rearrangements of the components of the organic matter to give a more humified material and, in general, one with a greater adsorption capacity [31]. In this sense, in a study of the mobility of diazinon in columns of soil amended with an oxidized carbon and with leonardite, Sánchez-Martín et al. [32] found that previous incubation of the soil with the amendments considerably decreased the mobility of the pesticide in them.

As in the cases of the non-incubated soils, no correlation was found between the R_f values and the total organic carbon content of the incubated soils. However, a significant negative correlation was appreciated between the R_f values and the Freundlich K constant of the pesticide adsorbed by the amended and incubated soils [26].

3.2. Mobility of linuron in natural and amended soils

The R_f values shown in Table 3 indicate that linuron can be considered to be slightly mobile in the soil studied [25]. The value obtained is close to that reported by Pestemer [22] on studying the mobility of this herbicide in soils with organic matter and sand contents close to those used in the present work.

Table 3
 R_F for mobility of linuron as a function of amendment (soils A) and of amendment–incubation (soils B)

Organic materials	Soils A		Soils B	
	R_F	S.D. ^a	R_F	S.D. ^a
None	0.37	0.06	0.34	0.03
CRC	0.23	0.03	0.20	0.00
GGP	0.15	0.02	0.15	0.02
HH	0.41	0.04	0.35	0.08
FHA	0.15	0.02	0.12	0.02
SDS	0.65	0.19	0.70	0.17
TDTMA	0.08	0.03	0.10	0.01

^a S.D. = standard deviation of three replicates.

The effects of the soil modifications induced by the different organic materials added to the soil in the mobility of linuron are similar to those found in the study of the mobility of diazinon. Thus, TDTMA is the organic material that gives rise to the greatest decrease in the mobility of the pesticide while SDS considerably increases its mobility. The mobility of linuron is equal to that of diazinon in the soil amended with CRC and slightly lower than that of the latter pesticide in the soils amended with GGP and FHA.

There is little effect on the modifications in the mobility of linuron by incubating the soils with organic materials, as in the case of diazinon.

No correlation was found between the R_F values and the organic matter content of the amended soils either before or after incubation. However, a negative correlation was found by Pestemer [22] between the organic matter content and the mobility of linuron on studying the mobility of this pesticide in six soils with different organic matter contents.

The hydrophobic nature of both pesticides, with very similar water solubilities, and the involvement of the organic matter–pesticide interaction – in both cases mainly through hydrophobic bonds – indicates that the behaviour of both pesticides is very similar, even though their chemical structures differ considerably.

The results obtained show that simultaneous addition of organic amendments and pesticides to soils in agricultural practice may alter the mobility of sparingly soluble pesticides, the degree of the modification depending on the nature of the amendment and, especially, on the presence of soluble fractions.

Likewise, depending on their cationic or anionic nature the coexistence of surfactants with pesticides in the soil may decrease or increase the mobility of such compounds to a considerable extent. Accordingly, both types of organic material may affect the presence and distribution of pesticide residues in soils and waters. The results also suggest the possibility of using organic materials and surfactants to develop physicochemical methods for preventing the pollution of soils and waters by pesticides and for eliminating pesticide residues from these media.

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