CITY REFUSE COMPOST AND SODIUM DODECYL SULPHATE AS MODIFIERS OF DIAZINON LEACHING IN SOIL

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ABSTRACT

The effect of a city refuse compost (CRC) and of an anionic surfactant (sodium dodecyl sulphate (SDS) on the leaching of diazinon (0,0-diethyl 0-2-isopropyl-6-methylpyrimidin-4-yl-phosphorothioate) in the soil was studied using packed soil columns. Breakthrough curves showed the existence of various regimes of pesticide adsorption related to the pesticide and organic material nature and the soil properties. Leaching rate and mass transfer of diazinon decrease following the addition of CRC to the soil and increase after the addition of SDS. The degree of increase or decrease was found to depend strongly on the amendment dose added, especially in the case of SDS. The results afford basic data on which to base the possible use of the organic amendments studied in physicochemical methods designed to prevent the pollution of water by hydrophobic pesticides (immobilization) or to restore soils contaminated by these compounds (leaching).
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INTRODUCTION

The increasing presence of hydrophobic organic pollutants (HOPs) in surface and ground waters (1-3) demands continued research about the effects of soil properties on their transport and also about the development of physicochemical and biological methods aimed at the prevention of pollution by these compounds and the decontamination of soils and waters.

The importance of soil organic matter in the adsorption and mobility of HOPs has been stated in many works (4-7). Research has also been carried out on the effects of organic materials (8-10) and surfactants (11-14) added to the soil on the adsorption and mobility of HOPs . The main aim of those researchs was initially to elucidate the modifications occurring in the adsorption and mobility of HOPs when these compounds coexist in

the soil with organic substances as a result of human activity. However, those works now also include the aim of investigating the potential use of organic materials and surfactants to solve problems of the pollution of soils and aquifers due to the presence of HOPs (15-17).

In this context, we studied the effect of the addition to the soil of a city refuse compost and of an anionic surfactant (sodium dodecyl sulphate) on the mobility of diazinon. City refuse compost is available in large quantities and its nature and composition differ considerably from that of other humic substances of animal and plant origin.

Diazinon is an organophosphorus insecticide (0,0-diethyl 0-2-isopropyl-6-methylpyrimidin-4-yl-phosphorothioate) that is sparingly water soluble. Several authors have reported its detection in ground waters (1) and others have studied its persistence in the soil relative to other pesticides (18). Previous works by the authors of this investigation have shown that the organic matter content of the soil is the main parameter governing the adsorption and mobility of diazinon (19) and that the presence of peat, liquid humic acid and hexadecyltrimethylammonium bromide (a cationic surfactant) affects its mobility in the soil (20).

MATERIALS AND METHODS

The soil used was a cambic Arenosol (horizon A) containing 0.69% organic matter, 9.9% clay, 3.0% silt and 86.4% sand.

^{14}C-labelled diazinon with a specific activity of 185 MBq mg^{-1} 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 mgL^{-1} and is soluble in most organic solvents (21).

City refuse compost (CRC) from the treatment plant at Valdemingómez (Madrid, Spain) and sodium dodecyl sulphate (SDS) from Aldrich Chemical Co. (Milwaukee, Wi) were used. The organic carbon content was 28.1% for CRC and 22.1% for SDS.

Diazinon leaching experiments were conducted in a glass house, using packed soil columns unamended and amended with two different doses of CRC and SDS: 2t ha^{-1} and 15t ha^{-1} (as total carbon) and also amended simultaneously with the high doses of CRC and SDS. The pore volume (PV) of the packed columns was determined by the weight difference of water-saturated columns *versus* dry columns. The columns employed were made of PVC (35 cm long x 5 cm inner diameter) and experiments were carried out following the method proposed by Weber et al. (22). 5 mL of 200 µgmL^{-1} diazinon in ethanol (5Kg ha^{-1}) with a specific activity of 36 kBq mL^{-1} were added to each column, previously conditioned to a humidity equivalent to field capacity. The columns were leached with 60 mL of water every two days (3.1 cm) up to a total of 1200 mL. Column leachates were also monitored every two days for insecticide content. After draining for some time, the columns were cut breadthwise at 5 cm intervals. To quantify the ^{14}C in the different segments, a Harvey OX-

500 biological oxidizer was used and the activities of the radioactive solutions were determined on a Beckman LS scintillation counter. Each experiment was performed in duplicate.

Conservative tracer transport, using chloride as ion tracer, was implemented to describe the dispersive characteristics of each column used for pesticide transport studies. The amount of chloride ion applied was 30 mg and the water flow rate was the same as that used in the pesticide leaching studies.

RESULTS AND DISCUSSION

Figure 1 shows the percolation and cumulative curves of diazinon leaching in the unamended soil columns and in columns amended with the two doses of CRC. The Figure also shows the curves corresponding to the leaching of the chloride tracer ion, these were almost identical for the amended and unamended columns.
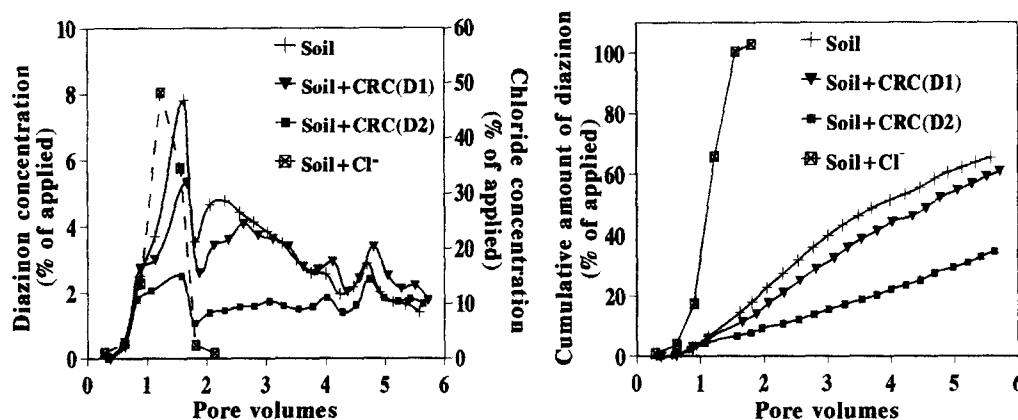

Figure 1. Breakthrough and cumulative curves for diazinon leaching in unamended soil and in soil amended with 2t ha^{-1} (D1) and 15t ha^{-1}(D2) of sodium dodecyl sulphate.

The percolation curve of chloride, which is a conservative ion and thus does not undergo any retention or degradation in soils but does signal the movement of water, showed a maximum concentration peak at a leachate volume of 1.20 PV, close to 1PV as generally occurs in the percolation of conservative ions (23).

The percolation curves of the pesticide in natural soil and in CRC amended soil are highly asymmetric and show a similar and very unusual shape; they display an inflection on the upward stretch followed by a maximum concentration peak and a long tail with small maxima. In all of them, the inflection occurs at a leachate volume very close to that corresponding to the maximum concentration peak of the percolation curve of chloride ion. This indicates that in all cases part of the diazinon applied to the columns is leached as the chloride ion with the water and that no adsorption occurs. The diazinon concentration corresponding to this inflection is 3.7% for the natural soil; this decrease to 3.0% and 2.1% for the soils amended with the low and

high doses of CRC respectively, showing that the amount of diazinon percolating with the water decreases with the increase in the amount of organic matter added to the column.

The maximum concentration peak of the three curves appears at similar leachate volumes. These are higher than the volume corresponding to peak in the percolation curve of chloride. This, together with the decrease in diazinon concentrations of the maxima of the curves when the dose of CRC is increased, indicates that during percolation the pesticide is adsorbed by the organic matter added to the soil, without excluding the possible adsorption of the pesticide by the mineral fraction of the soil. In all three cases, the descending part of the curve points to a gradual elution of a fraction of adsorbed pesticide up to a leachate volume of 1.8PV. After this point, a slow and irregular elution is seen, as reflected by the different peaks seen in the tail of the curve. The diazinon concentration of the peaks in the 1.8-3.8 PV zone decreases as the amount of organic matter present in the soil increases and must correspond to the leaching of other fraction of diazinon more strongly adsorbed by the organic matter. However, in the 3.8-5.8 zone all curves display two peaks whose concentrations, unlike what happens in the above-mentioned maxima, varies little from one curve to another. The same occurs with the volume of leachate at which they appear. These peaks, which reflect the elution of more strongly retained diazinon, must correspond to the leaching of pesticide adsorbed by the smectite present in the soil; the amount of this clay is the same in both the amended and unamended soils.

The existence of different regimes of adsorption in the columns is in agreement with the results of previous works by the authors of this investigation and by other authors about the adsorption of diazinon and several organophosphorus pesticides (dithiophosphates) by soil and their components. Arienzo et al. (19) in a study on the adsorption of diazinon by a series of soils with organic matter contents ranging between 0.15 and 10.20% showed that the organic matter content was the main parameter involved in adsorption. Additionally, the adsorption isotherm of the soil used in the present experiments, also included in that work, was not linear and the isotherm of the soil amended with CRC was not linear either (24). This lack of isotherm linearity points to the notion that although diazinon, as a hydrophobic pesticide, is adsorbed by the active components of the soil and of the CRC (humic and fulvic acids) mainly through hydrophobic bonds (water organic matter partition), it must also be adsorbed by other specific mechanisms, such as interaction with the OH and COOH groups of the humic and fulvic acids or via interaction with the clay minerals of the soil. The adsorption of an organophosphorus pesticide, azinphosmethyl, also a dithiophosphate and sparingly soluble like diazinon on humic acid via interaction of the functional groups of the pesticide with the OH and COOH groups of humic acid has also been demonstrated by the authors of this work (25). Diazinon adsorption in the interlayer space of smectite via ion-dipole interaction, giving rise to stable complexes, has been demonstrated by Dios-Cancela et al. (26).

The retardation factors R, defined as the number of pore volumes necessary to leach 50% of the pesticide added to the columns (27) are shown in Table 1. The R value which is 1 PV for the ion chloride is shifted for the leaching of diazinon in the unamended soil to 3.81 PV and up to 8.20 PV in the soil amended with the high dose of CRC.

The amount of diazinon retained in the column amended with the high CRC dose was 3.42 times higher than that retained by the unamended column and that retained in the column amended with the low dose of CRC was 1.32 times higher than in the unamended column (Table 2). Regarding the distribution of the pesticide retained in the columns, in the column amended with the high dose of CRC 50% of the pesticide added remained in the first 5 cm of the column; in the column amended with the low CRC dose a slight accumulation was observed in the first two segments and in the unamended soil the first segment also accumulated the compound.

Table 1. Retardation factors, R, for the percolation of diazinon in the amended soil columns

Amendment	Dose[a]	R
None	--	3.81
CRC	D1	4.64
CRC	D2	8.20
SDS	D1	3.01
SDS	D2	0.54
SDS+CRC	D2	2.14

[a]D1, 2t ha^{-1}, D2 15 ha^{-1}

Table 2. Amounts of diazinon retained and leached (% of applied) in columns of soil modified with organic matters and surfactants. D1, 2t ha^{-1} and D2, 15t ha^{-1}.

Segment	Soil Treatment					
cm	Control	CRC(D1)	CRC(D2)	SDS(D1)	SDS(D2)	CRC(D2)+SDS(D2)
0-5	5.19	5.73	50.03	4.29	2.39	13.26
5-10	3.27	5.11	5.13	2.17	1.20	4.33
10-15	2.83	3.54	3.51	2.15	0.46	3.31
15-20	2.69	3.91	2.97	3.86	1.40	3.86
20-25	3.01	4.55	2.89	3.73	1.02	2.95
25-30	2.71	3.23	2.85	3.40	0.87	2.71
Soil (retained)	19.70	26.07	67.38	19.60	7.34	30.42
Water (leached)	65.34	60.92	34.59	66.10	85.97	54.56
Total	85.04	86.99	101.97	85.70	93.31	84.98

The results show that the addition of CRC to the soil decreases the leaching rate and mass transfer of the pesticide owing to increased adsorption of the compound by the active components of the organic matter via

different mechanisms, as shown by the complexity of the percolation curves. The magnitude of these modifications depends on the CRC dose added. These findings have important environmental implications for the prevention of water pollution by hydrophobic pesticides since they point to the possibility of decreasing the leaching of such compounds in the soil in a controlled fashion by the addition of selected doses of CRC.

Figure 2 shows the percolation and cumulative curves of diazinon leaching in the columns of natural soil and in the columns amended with both doses of SDS. It also shows the percolation curve of chloride ion in the amended columns; this was very similar for both doses of SDS. This curve is more asymmetric than the percolation curves obtained for the same anion in the column of natural soil and in the columns of soil amended with CRC. The slope of the ascending stretch is changed, however the maximum appears at almost the same volume of leachate, 1.1 PV, as in those curves.
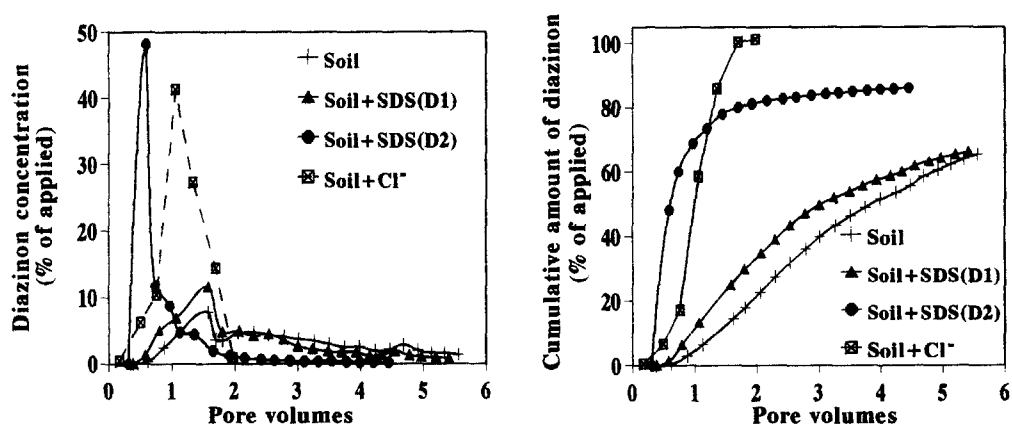

Figure 2. Breakthrough and cumulative curves for diazinon leaching in unmended soil and in soil amended with 2t ha^{-1} (D1) and 15t ha^{-1} (D2) of sodium dodecyl sulphate.

The shape of the percolation curve of diazinon in the column amended with the low SDS dose is very similar to the shapes of percolation curves of pesticide in natural and CRC amended soils showing the same peaks but with different diazinon concentrations. As in the case of the column of natural soil and CRC amended columns the inflection in the ascending stretch of the curve appears at the same leachate volume as the maximum of the percolation curve of the chloride ion. However, the concentration of diazinon corresponding to this inflection (5.0%) is higher than in those cases. The maximum concentration peak also appears at the same leachate volume as in those curves but also represents a higher concentration (11.6%). The peaks seen on the descending stretch of the curve appear at lower leachate volumes than in the natural soil and represent diazinon concentrations that are the same as or lower than in the natural soil. In principle, the percolation curve points to a faster leaching of diazinon than in natural soil.

The percolation curve of diazinon in the soil column amended with the high dose of SDS differs considerably from the other ones. It displays a very sharp peak at a leachate volume of 0.60 PV with a

corresponding diazinon concentration of 48.2%, indicating that an important amount of the pesticide is leached more rapidly than the chloride ion. This peak is followed by a tail exhibiting two maxima at leachate volumes slightly lower than those corresponding to the peak of the chloride on percolation curve and the maximum of the percolation curve of the natural soil, with diazinon concentrations of 8.8% and 4.4%, respectively.

The values of the retardation factors, R, for the leaching of diazinon in the columns amended with SDS (Table 1) were 3.01 PV for the column leached with the low dose and 0.54 PV in the case of the column amended with the high dose.

Regarding the amount of diazinon retained in the columns, in the one amended with the low dose this was 19.70% of the pesticide applied, close to that retained in the natural soil column; in the column amended with the high dose, this value was 7.34%.

The results show that addition to the soil of low doses of SDS alters diazinon leaching only moderately while the addition of high doses increases the leaching rate and mass transfer of the pesticide dramatically. These moderate or very marked changes in diazinon leaching in the presence of SDS are due to the solubility of hydrophobic organic compounds in the presence of anionic surfactants. This has been well documented for aromatic hydrocarbons by several authors (28, 29), who have attributed the phenomena to the adsorption of these compounds via hydrophobic bonds by the hydrophobic part of monomeric molecules or by the hydrophobic nucleus of surfactant micelles. At low surfactant concentrations, such as those that must be present in the soil solution for the low SDS dose applied to the column, the compound is in monomeric form and its effect on diazinon leaching is low. However, at concentrations above the critical micellar concentration (CMC), as must be the case of the soil solution following the addition of the high SDS dose, the surfactant molecules group to form micelles with a hydrophobic inner core and a hydrophilic external part. The strong adsorbing power of the hydrophobic core for diazinon causes that the pesticide is leached very strongly.

The results of the present work are consistent with those obtained in a previous study by the authors (14) concerning the adsorption by soils of selected pesticides from aqueous solutions in the presence of SDS concentrations lower equal to and higher than the CMC. The Freundlich K constant for diazinon adsorption was found to decrease with the rise in the concentration of surfactant in solution, K reaching a value of zero for a SDS concentration equal to 20 times the CMC of the compound.

These results, indicating the possibility of increasing the leaching of hydrophobic pesticides in a controlled fashion by the addition to the soil of anionic surfactants at selected doses, are of great interest in terms of the use of such compounds in physicochemical methods for recovering soils and sediments polluted by hydrophobic pesticides.

Finally, with a view to determining the effects of SDS on the leaching of diazinon in the presence of a high content of organic matter, we studied the mobility of the pesticide in soil amended simultaneously with the high doses of CRC and SDS. The percolation curve obtained (Fig. 3) has a single maximum with a corresponding diazinon concentration of 29.4% and appears at the same leachate volume (0.54 PV) as that

corresponding to the maximum of the percolation curve of the pesticide in the column amended with the high SDS dose.
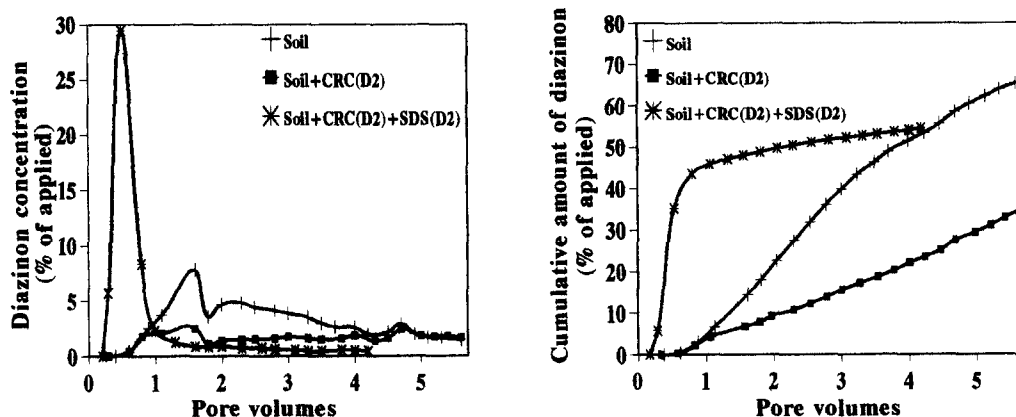

Figure 3. Breakthrough and cumulative curves for diazinon leaching in unamended soil, in soil amended with 15t ha^{-1} (D2) of city refuse compost and in soil amended simultaneously with 15t ha^{-1} (D2) of city refuse compost and of sodium dodecyl sulphate.

The value of the retardation factor R (Table 1) is 3.83 times lower than that of the soil amended with the high dose of CRC and the amount of diazinon retained in the column (Table 2) is 2.21 times lower than that retained in the column amended with CRC In the column amended with the high dose of CRC, 50% of the diazinon applied was retained in the first segment. However, in the presence of SDS diazinon retention in that segment decreased to 13%. The strong leaching capacity of SDS for diazinon causes an important amount of the pesticide is leached even in the presence of high concentrations of organic matter.

ACKNOWLEDGEMENTS

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