

SESSION 3

POSTER SESSION A

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The influence of lipophilicity and formulation on the distribution of pesticides in sediment/water systems

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ABSTRACT

The sorption of pesticide by sediment and the influence of pesticide formulation on this process have been examined in small-scale mesocosms. Eight pesticides, spanning a range of physicochemical properties, were individually applied to the water. Sorption equilibrium was reached at between 15 and 30 days, the proportion of pesticide then in the sediment ranging from 20% for the acidic and so polar triasulfuron to 97% for the lipophilic permethrin; this behaviour was not influenced by formulation. Sorption coefficients measured in batch tests over two hours gave good estimates of the equilibrium distribution. It is concluded that lipophilicity is the chief determinant of pesticide distribution in sediment/water systems, and predictions based on this were acceptable for initial appraisals.

INTRODUCTION

Pesticides reach surface waters either from point sources, such as spills or tractor washings, or from diffuse sources such as contaminated water draining from sprayed fields. If concentrations of a pesticide exceed the threshold value set for the Environmental Quality Standard, then damage will be caused to the ecology of the aquatic system. Additionally much surface water is used for drinking water and as such has to meet the EU standards.

Knowledge of the behaviour of a pesticide in sediment/water is generally a registration requirement for agricultural pesticides, this usually being studied in small-scale systems of volume about 500 ml with the overlying water gently stirred. Being done primarily for registration purposes and so on a compound-by-compound basis, little has been drawn together on the overall principles of such processes. The present study investigated the behaviour of eight pesticides spanning a wide range of physicochemical properties, and examined also the influence of formulation on the redistribution and loss processes.

MATERIALS AND METHODS

Pesticides

The pesticides used were analytical grade and the formulated materials were commercial products (Table 1). [α -benzyl- 14 C]Permethrin had a specific activity of 67 MBq mmol $^{-1}$ (2.2 GBq mmol $^{-1}$ for the sorption tests).

Sediment/water system

Sediment and water were collected from a pristine shallow pool at Great Linford, Bedfordshire, U.K. The moist sediment was sieved to 5 mm and thoroughly mixed; it comprised 64% sand (63-2000 μm), 20% silt (2-63 μm) and 16% clay (<2 μm), with 2.5% organic carbon and pH 7.32 (water).

The test vessels (Figure 1) were designed according to the guidelines for the registration studies of pesticides (BBA Guidelines, 1990; Hill *et al.*, 1994). Wide-necked glass jars (500-ml) contained wet sediment (120 g containing 51.7 g solids) and pond water (400 ml). After allowing the sediment to settle, pesticide (80 μg per jar) was introduced into the overlying water using the diluted formulated product (0.2 ml) or acetonitrile (0.2 ml) for the pure pesticide; this amount represents overspray at 180 g a.i. ha^{-1} . The water was gently stirred by a stainless-steel blade (2.5 cm diameter) rotated at 60 rpm. Eight replicate vessels were set up for each test, two of which had water analysed regularly whilst the other six were destructively sampled to obtain a mass balance, usually over a 90-day period. The vessels were kept in the dark at 10°C.

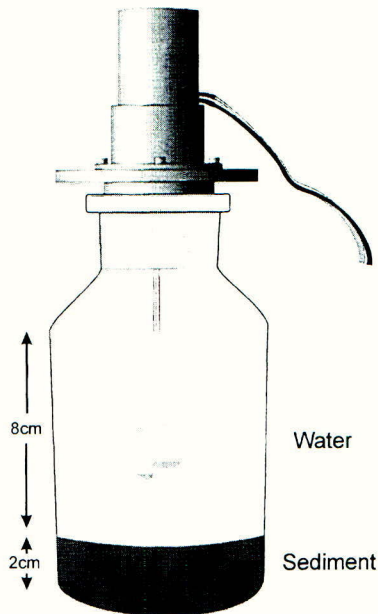


Figure 1. Sediment/water system

Sorption measurements

Air-dry sediment (0.2 to 0.5 g according to the expected K_d) was shaken for 2 hours with pesticide dissolved in 0.01M aq CaCl_2 (10 ml of *ca* 0.2 μg pesticide ml^{-1} ; 25 ml of 0.001 μg ml^{-1} for permethrin). After centrifugation, the supernatant solution was analysed.

Chromatographic analysis

The non-radiolabelled compounds in the water phase were determined by direct injection into a high-pressure liquid chromatograph (HPLC) fitted with a 50- μl loop and a C-18 reverse-phase column (20 cm x 4.6 mm ID). The running solvent was methanol/water or acetonitrile/water, with detection by UV. This procedure was insufficiently sensitive for chlorpyrifos, which was extracted from water aliquots (20 ml) with dichloromethane prior to evaporation and redissolving in HPLC running solvent (1.0 ml). To analyse the sediment, the overlying water was removed by suction, methanol (300 ml) was added to the sediment and the vessel orbitally shaken for four hours. Aliquots (25 ml, in duplicate) were evaporated and redissolved in HPLC running solvent as described above, with 20- μl loop injections. [^{14}C]Permethrin was extracted similarly, the residues being subjected to thin-layer chromatography on silica gel with hexane + ethyl acetate (65 + 35, v/v) as elution solvent. Bands containing parent [^{14}C]permethrin, R_F 0.65, were scraped off and subjected to liquid scintillation counting. All analyses were corrected for the appropriate recovery factors.

Table 1. Pesticide properties, formulations and behaviour in the sediment/water systems

Pesticide ^a	log <i>K_{ow}</i>	Formulated product ^b			Sorption coefficient <i>K_d</i> (l kg ⁻¹)	Proportion ^c predicted in sediment (%)	DT ₅₀ (day)
		EC	SC	WG			
Triasulfuron ^d (h)	1.6	-	-	Logran	0.2	19.2	>90
Isoproturon (h)	2.48	-	Isoguard	-	2.3	36.1	>90 ^e
Chlorotoluron (h)	2.5	-	Dicurane	-	1.8	32.5	55-85
Phenmedipham (h)	3.6	Stefes Forte 2	Betanal Flo	-	20.7	77.4	2.5-4
Difenoconazole (f)	4.2	Plover	-	-	48	85.8	>90
Chlorpyrifos (i)	4.99	Dursban	-	-	83	92.1	55 ^f
Pendimethalin (h)	5.18	Stomp 330	Stomp 400	-	125	95.2	60 ^g
Permethrin (i)	6.1	Permasect 25	-	-	343	98.2	15-20

^a h, herbicide; f, fungicide; i, insecticide.

^b Emulsifiable concentrate (EC), suspension concentrate (SC) or water-soluble granule (WG).

^c Proportion predicted from the batch *K_d* to be in the sediment at equilibrium.

^d Triasulfuron is acidic, pKa 4.64; the log *K_{ow}* is given for the undissociated acid.

^e Value for the pure isoproturon; enhanced degradation started at 60 d for the suspension concentrate.

^f Extrapolated from 45 d.

^g Value for the two formulated products; enhanced degradation started at 14 d for the pure pendimethalin.

RESULTS AND DISCUSSION

Batch sorption measurements

The measured sorption coefficients (*K_d*) onto the sediment in the equilibration tests over 2 h spanned three orders of magnitude (Table 1). For the seven non-ionised pesticides, there was a straight-line relationship between log *K_d* and log *K_{ow}* :-

$$\log K_d = 0.62 \log K_{ow} - 1.12 \quad (r^2 = 0.97) \quad (1)$$

Normalising this to sorption on the sediment organic matter (4.3%) gives:-

$$\log K_{om} = 0.62 \log K_{ow} + 0.25 \quad (2)$$

This relationship is comparable to that derived by Briggs (1981) from sorption measurements over many non-ionised pesticides and soils, viz:

$$\log K_{om} = 0.53 \log K_{ow} + 0.62 \quad (3)$$

This gives confidence that Eqn. 2 can be used to predict sorption of a wide range of non-ionised pesticides on sediments with differing contents of organic matter.

Pesticide behaviour in laboratory-scale sediment/water systems

Examples of the changes in distribution pattern with time are given for four compounds spanning the observed range of behaviour (Figure 2). Sorption behaviour was not influenced by the application vehicle. Although most redistribution from the water to the sediment took place within 30 d of application, interpretation was complicated by the substantial degradation over the 90-d period for compounds such as phenmedipham and permethrin.

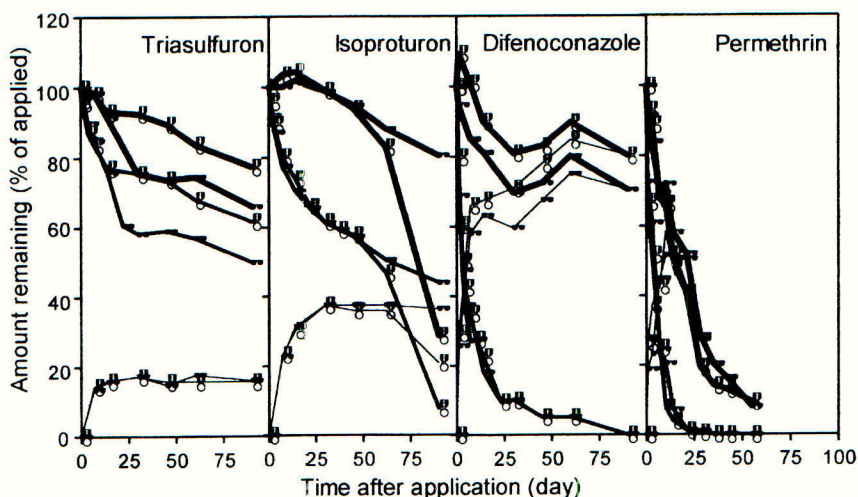


Figure 2. Redistribution and degradation of pesticide in sediment/water systems □ pure pesticide; ♦ formulated; thin lines, sediment; medium lines, water; thick lines, total (mass balance).

To eliminate the complication of degradation, the distribution patterns of the eight pesticides in the systems over time were expressed as a percentage of the amount recovered. These show that the proportion of pesticide moving into the sediment layer increased with increasing lipophilicity (Figure 3). For the most polar compound, triasulfuron, only 20% was sorbed, equilibrium being reached in about 15 d and then remaining constant. For the most lipophilic compounds, pendimethalin and permethrin, at equilibrium over 95% of the compound was sorbed by the sediment, final equilibrium being reached only after 20-30 d. It appeared that diffusion into the 2-cm deep sediment layer was complete for the weakly sorbed triasulfuron within 15 d, but the larger mass transfer required to reach equilibrium for a strongly sorbed compound required about twice that length of time to achieve by diffusive processes.

The distribution at equilibrium was close to that predicted on the basis of the independent K_d measurements, allowance being made for the water within the sediment layer. Predictions of the equilibrium distribution made by the database/expert system 'Physicochemical Evaluation - The Environment' (PETE) using $\log K_{ow}$ alone as the compound-specific input factor (Nicholls 1994) were reasonably accurate as exemplified for isoproturon (Figure 4). About 40% of the isoproturon was found in the sediment at equilibrium, compared to predictions of 37.1 and 41.2% made from K_d and K_{ow} respectively.

Compounds differed considerably in their rates of degradation in the sediment/water systems

(Table 1). Phenmedipham was rapidly hydrolysed. Triasulfuron and difenoconazole were the

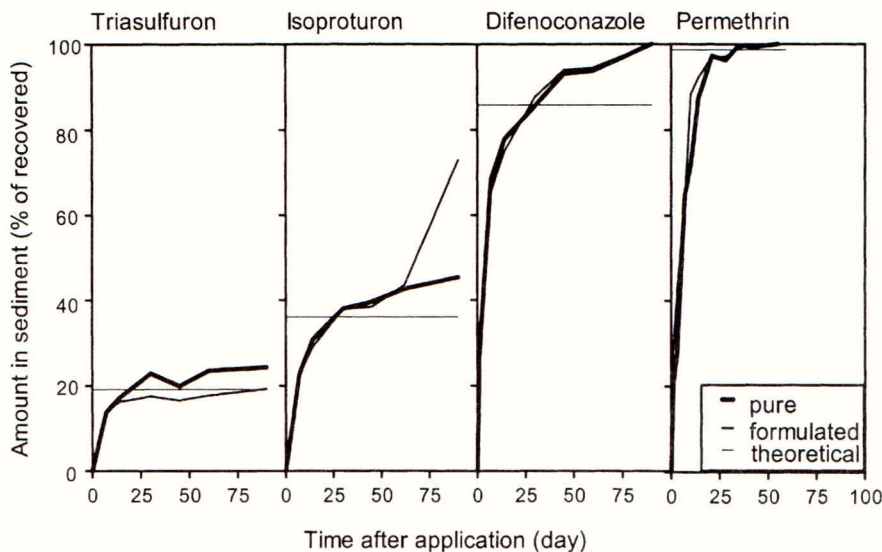


Figure 3 Proportion of recovered pesticide in sediment during equilibration of the sediment/water systems for up to 90 d. □ pure; ● EC; x SC; ▲ WG. The horizontal line represents the equilibrium position predicted from the K_d value measured in the batch tests.

most stable with about 25% loss over 90 d. Pure isoproturon also behaved similarly, but the SC formulation showed enhanced degradation after 60 d. In contrast, pendimethalin, the only other compound showing enhanced degradation, did so only for the pure compound after 14 d and not for the EC and SC formulations up to 90 d. It should be noted that the final concentration of acetonitrile in the vessels was 0.05%, less than the maximum permissible of 0.1% given by the SETAC guidelines.

CONCLUSIONS

The extent of movement of pesticides into sediment following application to the overlying water was strongly dependent on the pesticide lipophilicity though not influenced by the formulation vehicle. In these small-scale systems with a layer of sediment 2 cm deep, equilibrium was reached between 15 and 30 d, the more strongly sorbed compounds taking the longer time. A good linear free-energy relationship between $\log K_d$ and $\log K_{ow}$ was found for the seven non-ionised compounds; this allowed predictions of such behaviour for other non-ionised pesticides and organic contaminants, as examined with the PETE programme. The acidic triasulfuron, largely ionised at the sediment pH, was very weakly sorbed.

Degradation rates differed for the compounds, ranging from relatively high for phenmedipham (DT_{50} 2.5-4 d) to low for triasulfuron and difenoconazole ($DT_{50} \gg 90$ d). Differences between formulated and pure materials occurred only for isoproturon and pendimethalin; however, enhanced degradation occurred for the SC isoproturon and not the pure, but for the pure pendimethalin and not for the EC or SC.

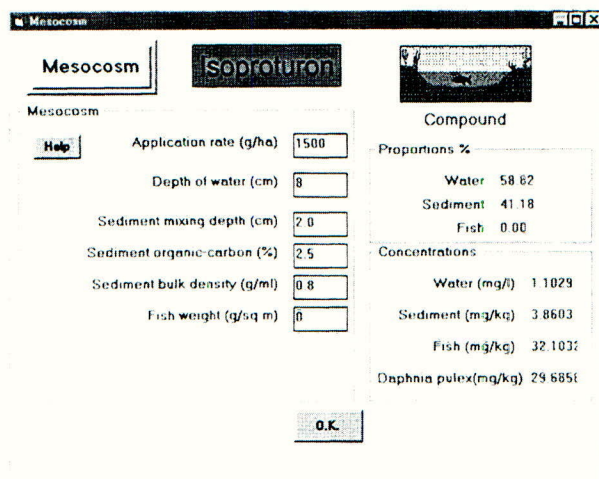


Figure 4. Prediction from log K_{ow} of the distribution of isoproturon in the sediment/water system using the PETE database/expert system.

The distribution behaviour in this system, which was based on pesticide-registration guidelines, was consistent and not influenced by formulation. This last finding, presumed to be of general applicability, means that pesticide registration authorities can assess this aspect of environmental behaviour based on the properties of the pure substance without the need to consider the formulation type.

ACKNOWLEDGEMENTS

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Formulations of the anionic herbicide imazaquin based on its sorption on crystal violet-montmorillonite complexes

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ABSTRACT

Our aim was to design formulations of the anionic herbicide imazaquin to reduce its leaching and migration. Sorption of imazaquin on crystal violet (CV)-montmorillonite complexes was studied. CV-montmorillonite complexes become positively charged with adsorption of CV above the cation exchange capacity (CEC) of montmorillonite, and thus are able to adsorb organic anions. Organo-clay complexes at a CV loading of 40 and 70% above the CEC were studied. The Langmuir equation provided a good fit to the isotherms of imazaquin sorption on CV-montmorillonite complexes. However, for charged complexes an equation which combines electrostatics with specific binding was preferred. When the concentration of the CV-clay-imazaquin complex in the suspension was 5 g/L, the extent of desorption of imazaquin into water was around 5%. The presence of sulphate, acetate and phosphate in large excess over imazaquin decreased herbicide sorption according to the sequence phosphate > acetate > sulphate. Leaching of imazaquin from CV-montmorillonite formulations in soil was significantly less than that of technical imazaquin. CV-montmorillonite complexes appear to be suitable for preparation of organo-clay-imazaquin formulations that may reduce herbicide leaching in soil significantly.

INTRODUCTION

A severe problem encountered with many herbicides is their transport through the soil and contamination of underlying groundwater. Imazaquin is a pre- and post-emergence herbicide used for control of broadleaf weeds in legume crops. Imazaquin is negatively charged at the basic pHs commonly found in the calcareous soils of Mediterranean countries. Imazaquin exhibits low adsorption and high leaching in soils (Loux & Reese 1992). Our aim was to design formulations of imazaquin to reduce herbicide migration to non-target areas. Crystal violet (CV)-montmorillonite complexes become positively charged with adsorption of CV above the cation exchange capacity (CEC) of montmorillonite (Rytwo *et al.*, 1995) and thus are able to adsorb organic anions. We studied the suitability of CV-montmorillonite complexes for preparation of organo-clay-imazaquin formulations to reduce herbicide leaching.

MATERIALS AND METHODS

Imazaquin, 97% purity, was obtained from AGAN Chem. Manuf. (Ashdod, Israel). Crystal violet as the chloride salt was purchased from Fluka Chemie AG (Buchs, Switzerland). The chemical structures of imazaquin and crystal violet are shown in Fig. 1. The clay mineral used was Wyoming Na-montmorillonite SWy-1 obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). The cation exchange capacity of the clay was 0.80 mmol/g. The CV-montmorillonite complexes, containing 40% and 70% of CV above the CEC, were prepared according to Rytwo *et al.*, (1995).

Adsorption experiments were carried out as described in Polubesova *et al.*, 2000. The concentrations of the CV-clay complex suspensions were 5 g/L. Twenty four hours were sufficient to reach equilibration of imazaquin sorption. To study the effect of electrolyte concentration on the adsorption of imazaquin, the following electrolytes were added: Na₂SO₄, CH₃COONa, and Na₃PO₄.

Desorption of imazaquin was determined in water and in electrolyte solutions. We tested the possibility that loosely bound imazaquin will be desorbed in 2 hours (first step), with strongly bound herbicide being released over the next 24 hours (second step). Twenty mL of distilled water were added to the samples with pre-adsorbed herbicide. The concentrations of the CV-clay-imazaquin complex suspensions were 5 g/L. The tubes were kept at 25 ± 1°C under continuous agitation for 2 hours then centrifuged for 20 min at 15000g and imazaquin was measured in the supernatant solution. The samples were then shaken for 24 hours at the same temperature, and desorption was determined again by the same procedure. Desorption by electrolyte solutions was determined after 24 hours of agitation of samples with pre-adsorbed imazaquin by 10- and 100m-*eq*/L solutions of Na₂SO₄, CH₃COONa, and Na₃PO₄. For analysis, all supernatant solutions were filtered through Teflon filters (ISI, Israel) of 0.2 µm pore diameter. Imazaquin was analyzed by HPLC (Merck Hitachi 6200) equipped with a diode array detector at a wavelength of 242 nm. The reverse-phase column was LiChrospher^R 100 RP-18 (5 µm), and the mobile phase was a mixture of 60% methanol and 40% water with 0.65 mM trifluoroacetic acid. The flow rate was 1.0 ml/min.

Binding coefficients of sorption were calculated using the Langmuir equation and a model for ion adsorption, which combines electrostatics with specific binding (Nir *et al.*, 1994).

Leaching experiments were performed in Rehovot sandy soil (pH 7.5, organic matter content 0.2%, sand 95.5%). Plexiglass columns (25 cm in length and 5 cm i.d.), with glass fiber wicks of 25 cm length attached to the bottom, were packed with air-dry soil and 0.01M CaCl₂ was applied at the rate of 47 ml/hr using an HPLC pump to establish steady-state conditions. The flow was temporarily interrupted and solutions of technical imazaquin and suspensions of the imazaquin formulated on CV-70%-montmorillonite were applied to the surface of the columns after which application of the 0.01M CaCl₂ was resumed. Effluents were collected with an automated fraction collector and analysed by HPLC. The water content of the soil was determined at the end of experiment. Pore volumes were calculated by dividing corresponding cumulative volumes of the collected effluent by the water content of soil.

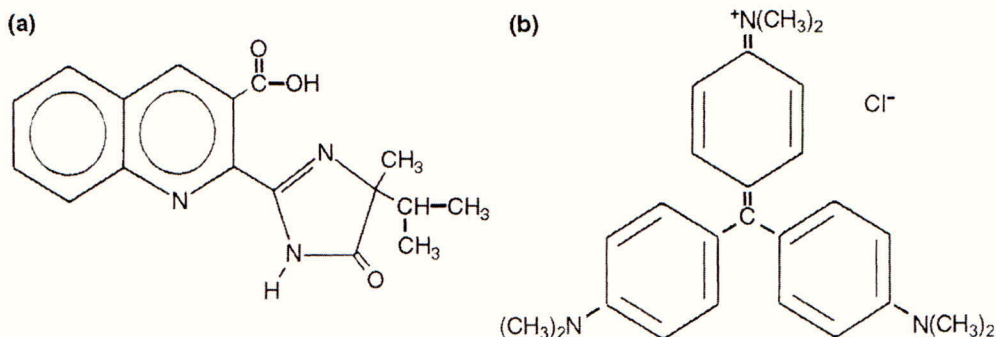


Fig. 1. The chemical structure of imazaquin (a) and crystal violet (b).

RESULTS AND DISCUSSION

The imazaquin sorbed on the positively charged CV-montmorillonite complexes reached 93-95% of the amount added for CV-40% and CV-70% complexes (40% indicates that sorption of CV exceeds the CEC by 40%). Pure montmorillonite sorbed only 2% of the amount added. CV release in sorption experiments was 3.5% and 2.4% for the CV-70% and CV-40% complexes, respectively. The Langmuir equation provided a good fit to the isotherms of imazaquin sorption on CV-montmorillonite complexes with $R^2=1$.

Binding coefficients calculated using the Langmuir equation were 3800 and 4000 M^{-1} for CV-40%- and CV-70%-montmorillonite complexes, respectively. The binding coefficients calculated using the model for ion adsorption were 40 M^{-1} for CV-40%- and 20 M^{-1} for CV-70% - montmorillonite complexes with $R^2=1$. At higher CV loadings, a significant fraction of the CV molecules interacted between themselves and were less available for interactions with imazaquin. Similar results were obtained for the interaction of benzyltrimethylammonium- and benzyltriphenylammonium-montmorillonite complexes with alachlor, metolachlor and norflurazon (Nir *et al.*, 2000) and for the interaction of a rhodamine B-montmorillonite complex with atrazine (Borisover *et al.*, 2001).

The proposed model for imazaquin sorption on CV-clays is a combination of electrostatic adsorption and hydrophobic interaction. Calculations of the binding coefficients using the ion-adsorption model were preferred because they encompass both mechanisms of imazaquin sorption.

Imazaquin sorption onto CV-clay was not affected by small amounts of sulphate and acetate, but was decreased in the presence of the same amounts of phosphate (Table 1). When these anions were added in amounts which exceeded those of imazaquin by 100 and 1000 times, they competed with imazaquin for the surface sites of the CV-clay complex and significantly reduced herbicide sorption according to the sequence phosphate > acetate > sulphate.

Table 1. Effect of sulphate, acetate and phosphate on the adsorption of imazaquin on CV-70%-montmorillonite

Imazaquin/anion ratio ¹	Imazaquin adsorbed, ($\mu\text{mol/g}$)	Reduction in adsorption (%)
-	17.68	-
	<u>Sulphate</u>	
1:1	17.55	0.7
1:10	17.20	2.7
1:100	16.37	7.4
1:1000	15.71	11.1
	<u>Acetate</u>	
1:1	17.67	0
1:10	17.63	<0.5
1:100	15.81	10.6
1:1000	14.77	16.5
	<u>Phosphate</u>	
1:1	17.40	7.2
1:10	13.17	29.8
1:100	5.37	71.4

¹ Imazaquin added at 18.76 $\mu\text{mol/g}$

The degree of desorption of imazaquin from CV-clay complexes in water was small (Table 2). The desorbed amount, in the first and second step combined (loosely and strongly sorbed imazaquin), was only 3.8-5.5 % of that sorbed for both complexes at the concentration of the CV-clay-imazaquin complex suspensions 5 g/L.

Table 2. Desorption of imazaquin from CV- montmorillonite complexes

Imazaquin added, ($\mu\text{mol/g}$)	Imazaquin adsorbed ($\mu\text{mol/g}$)	Imazaquin desorbed (% of adsorbed)	
		Step 1	Step 2
		<u>CV-70%-montmorillonite</u>	
4.75	4.53	4.2	5.3
23.75	22.20	4.1	5.5
		<u>CV-40%-montmorillonite</u>	
4.75	4.43	3.8	4.7
23.75	21.50	4.2	4.9

Desorbed amounts of imazaquin from the CV-clay complex by sulphate, acetate and phosphate for 10 and 100 meq/L of electrolyte solutions are presented in Table 3. Imazaquin was strongly bound to the surface and was not fully desorbed even by anions added at 100 meq/L, which was 1000-4000 times higher than the concentrations of the sorbed herbicide. Phosphate was the most effective anion in desorbing imazaquin.

Table 3. Desorption of imazaquin from CV-70%-montmorillonite complex in the presence of electrolytes

Electrolyte added	Imazaquin desorbed (% of adsorbed)			
	10 meq/L	100 meq/L	10 meq/L	100 meq/L
	(Imaz. adsorbed 4.71 $\mu\text{mol/g}$)	(Imaz. adsorbed 4.54 $\mu\text{mol/g}$)	(Imaz. adsorbed 23.7 $\mu\text{mol/g}$)	(Imaz. adsorbed 22.2 $\mu\text{mol/g}$)
Na ₂ SO ₄	17.5	33.0	23.2	37.9
NaCH ₃ COO	9.6	28.7	11.2	32.6
Na ₃ PO ₄	55.0	63.2	57.9	68.9

Results of leaching experiments are shown in Table 4, in which the amount of water added is presented as equivalent rain. Leaching of imazaquin from CV-montmorillonite formulations was significantly less than that of technical imazaquin for the whole range of pore volumes. Only 25% of imazaquin from the organo-clay formulation was released at 1.56 pore volumes versus 93% of technical imazaquin. Thus the results of leaching and batch experiments are consistent, indicating strong sorption and relatively small (and slow) release of imazaquin from CV-montmorillonite complexes. CV-montmorillonite complexes appear to be suitable for preparation of organo-clay-imazaquin formulations, which may significantly reduce imazaquin leaching.

Table 4. Leaching of imazaquin through soil columns (25 cm long, 5 cm i.d.)

Pore volume	Equivalent rain (mm)	Fraction of imazaquin leached through column	
		Technical imazaquin	Imaz.-CV-70%-mont. formulation
0.17	12	0	0
0.35	24	0	0
0.52	35	0	0
0.69	47	0	0
0.86	59	0.05	0.02
1.03	70	0.59	0.11
1.21	82	0.89	0.17
1.38	94	0.92	0.22
1.56	106	0.93	0.25

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Effect of sewage-sludge amendment on simazine and 2,4-D behaviour in soil: laboratory and field studies

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ABSTRACT

Laboratory and field studies have been designed to assess the influence of sewage-sludge amendment on the fate of simazine and 2,4-D in soil. A soil from IRNAS experimental farm was treated in the laboratory with a composted sewage sludge at the rate of 10 % (w/w). Herbicide sorption behaviour on amended and unamended soils was studied:- sorption by batch technique, degradation by soil incubation at 20°C and leaching in handpacked soil columns under saturated/unsaturated flow conditions. For the field study, the sewage sludge was applied at a rate of 10 kg m⁻² to experimental plots, and herbicides were applied at 2.5 kg ha⁻¹ to these and to unamended plots. Triplicate soil samples from the plots (0-10, 10-20 and 20-30 cm depth) were collected periodically and extracted for herbicide content. Sorption coefficients measured in the laboratory for both herbicides increased upon amendment, whereas simazine half-life remained unaffected and 2,4-D half-life was decreased. Simazine breakthrough curves in amended soil columns were broader and showed slower breakthrough when compared to unamended soil. No 2,4-D was leached from amended soil or unamended soil columns. The field study revealed higher amounts of simazine and 2,4-D in the upper 10 cm of amended soils than unamended soils. Only very small amounts of simazine were detected below 20 cm, without significant differences between amended and unamended soils. 2,4-D was not detected below 20 cm.

INTRODUCTION

Organic amendments, commonly used to enrich soils of low organic matter content, can modify surfaces of soils and subsurface materials so increasing sorption potential and reducing pesticide contamination of groundwater (Barriuso *et al.*, 1996; Cox *et al.*, 1997, 2000). The subsequent increase in soil organic matter is also known to stimulate soil microbial activity, which could potentially lead to accelerated degradation, reducing both the total amount of chemical available for leaching and the potential for herbicides to injure crops planted in rotation (Felsot and Shelton 1993; Topp *et al.*, 1996; Cox *et al.*, 1997, 2000). Accordingly, the study of the influence of organic amendments on pesticide behaviour in soil is of great interest when making decisions to fertilize soil or to dispose of organic wastes such as sewage sludge.

The aim of this study was to assess the influence of sewage-sludge amendment on sorption, degradation and movement of pesticides in soil. For this purpose, we selected two herbicides widely used in agriculture, simazine and 2,4-D, and performed laboratory and field studies with a soil amended with sewage sludge.

MATERIALS AND METHODS

Herbicides and soil

High-purity (>98 %) simazine (Riedel-de Haën, Germany) and 2,4-D (Sigma, St. Louis, MO) were used for laboratory studies. For the field study, commercial simazine (Gesatop, 90 WG) and 2,4-D (Primma Din, 70 % w/v) products were used.

The soil used in laboratory experiments was taken from 0-10 cm depth, air dried and treated with sewage sludge at a rate of 10 % w/w. Physicochemical properties of the original unamended soil and sewage-sludge amended soil were determined and are given in Table 1.

Table 1. Physicochemical properties of original and sewage-sludge amended soils

Soil/depth (cm)	pH	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)
Original soil					
0-10	7.6	0.90	64	19	17
10-20	7.8	0.51	61	22	17
Amended soil					
0-10	7.4	1.24	63	18	19
10-20	7.9	0.72	58	23	19

Batch sorption and degradation kinetics

Sorption studies were performed by batch equilibration procedure. Duplicate samples (5 g) of unamended and amended soils were treated with 0.01M aq. CaCl_2 herbicide solutions (10 mL) of initial concentration (C_i) of simazine ranging from 0.5 to 10 μM or 2,4-D from 5 to 100 μM . The suspensions were shaken at $20 \pm 2^\circ\text{C}$ for 24 h and then centrifuged at 31000g. Equilibrium concentrations (C_e) in the supernatant solutions were determined by HPLC under the following conditions: Nova-Pack column, 150 mm length x 3.9 mm i.d.; column packing, C18; flow rate, 1 mL min^{-1} ; eluent system, 70:30 water-acetonitrile for simazine and 55:45 diluted H_3PO_4 (pH = 2.0):methanol for 2,4-D; UV detection was at 230 nm. Detection limits were 0.01 and 0.02 mg L^{-1} for simazine and 2,4-D, respectively. Differences between C_i and C_e were assumed to be the amounts sorbed (C_s). Sorption isotherms were fitted to the Freundlich equation, and sorption coefficients K_f and $1/n_f$ calculated.

Duplicate samples (500 g) of each soil were treated with a 100 mg L^{-1} ethanol solution of simazine or a 100 mg L^{-1} aqueous solution of 2,4-D to give a concentration of 5 mg kg^{-1} and 2.3 mg kg^{-1} of dry soil, respectively. Maximum application rates of simazine and 2,4-D were 5 and 2.3 kg ha^{-1} , respectively. The moisture content was adjusted to 40% of the water-holding capacity and soil samples were thoroughly mixed by passing them through a sieve at least 4 times. Herbicide-treated soil samples were transferred to Kilner jars where they were incubated at 20°C for 50 d (simazine) or 15 d (2,4-D). Moisture contents were maintained constant throughout the experiment by adding distilled water as necessary. Soils were sampled

periodically and frozen till analyzed. Herbicide residues were extracted by shaking soil (10 g) with methanol (20 mL, simazine) or 55:45 diluted H_3PO_4 (pH = 2.0):methanol (20 mL, 2,4-D) for 24 h and extracts were analyzed by HPLC. Recoveries were greater than 90% for both herbicides. In order to calculate half-lives from dissipation curves, we assumed that the differences between the amount of simazine or 2,4-D applied and those extracted were due to degradation in the soil.

Leaching experiments

Herbicide leaching in soils was studied using methacrylate columns, 20 cm long and 16.66 cm^2 section, handpacked with unamended and amended soils from 0-10 cm depth. After saturation of the soil columns with 0.01M $CaCl_2$, simazine and 2,4-D corresponding to application rates of 5 $kg\ ha^{-1}$ and 2.3 $kg\ ha^{-1}$ respectively were applied to the top of the soil columns. The columns were leached with 0.01M $CaCl_2$ (50 mL) daily and leachates collected, volumes measured and herbicide concentrations determined by HPLC.

Field study

Field experiments were performed on a 4 x 16 m experimental plot located at IRNAS experimental farm (SW Spain). The plot was divided into four subplots (4 x 4 m): two for simazine treatment and two for 2,4-D (each with and without sewage-sludge application). The sewage sludge was applied in February 2000 at a rate of 10 $kg\ m^{-2}$ and application was followed by chisel to 5 to 10 cm depth. One day after the sewage-sludge amendment, the herbicides were applied at a rate of 2.5 $kg\ ha^{-1}$. Triplicate soil samples from 0-10, 10-20 and 20-30 cm depth were collected periodically from the plots over 75 d with a total water input (rain plus irrigation) of 172 mm. Soil samples were air-dried and extracted for simazine or 2,4-D as described earlier.

RESULTS AND DISCUSSION

Batch sorption and degradation kinetics

Sorption coefficients (K_f) increased for both herbicides upon amendment (Table 2), although for 2,4-D the differences were not significant. The increase in sorption capacity of the amended soils is attributed to the increase in organic matter content, since both herbicides have been shown to be sorbed to this soil component (Celis *et al.*, 1999; Cox *et al.*, 2000). The coefficients $1/n_f$, which indicate sorption intensity, were much lower for 2,4-D than for simazine. Low $1/n_f$ coefficients indicate that there is a limit in sorption capacity as solution concentration increases (Giles *et al.*, 1960).

There were no significant differences in simazine half-life upon amendment, though amendment reduced the half-life of 2,4-D to less than half (Table 2). The increase in organic carbon content upon amendment has been shown to promote biodegradation (Felsot and Shelton 1993; Topp *et al.*, 1996; Cox *et al.*, 1997), which is the main process affecting the fate of 2,4-D in soils (Veeh *et al.*, 1996). Conversely, 2,4-D dissipation rates have been reported to be lowest on the soil on which sorption was greatest (Johnson *et al.*, 1995).

Leaching experiment

Simazine breakthrough in the soil columns took place later in amended soil than in unamended soil (Figure 1). Also, the simazine BTC in amended soil was broader, with a much lower maximum concentration detected in leachates than in those from the unamended soil. Total recovered simazine in this soil was greater than 60% compared to 30% in the amended soil, which difference in behaviour can be attributed to the increase in sorption upon amendment.

Table 2. Sorption coefficients (K_f , $1/n_f$) and half-lives ($t_{1/2}$) for simazine and 2,4-D in original unamended and sewage-sludge amended soil

Herbicide/ Soil	Sorption			Degradation	
	K_f	$1/n_f$	R^2	$t_{1/2}$ (day)	R^2
Simazine					
Unamended	0.63 (0.60-0.67) [†]	0.89(±0.05)	0.99	26.0 (23.1-33.5)	0.98
Amended	1.03 (0.99-1.08)	0.87(±0.04)	1.00	31.2 (27.1-35.6)	0.92
2,4-D					
Unamended	1.04 (0.84-1.30)	0.51(±0.14)	0.96	3.24 (2.88-3.78)	0.97
Amended	1.40 (1.14-2.70)	0.55(±0.14)	0.89	1.10 (1.08-1.11)	1.00

[†] Numbers in parentheses are standard error about the mean

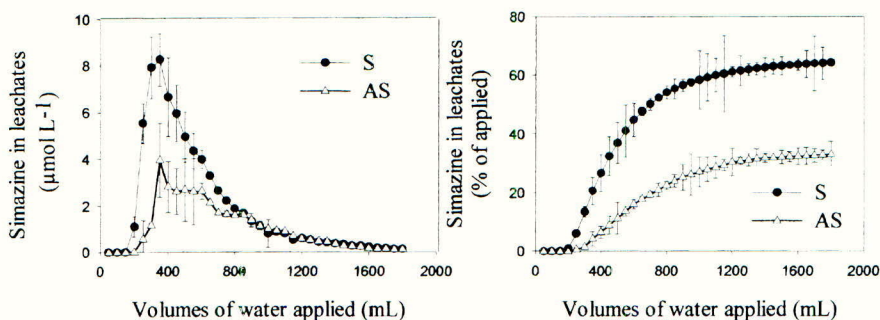


Figure 1. Simazine breakthrough curves in unamended (S) and amended (AS) soils

Sorption gives rise to retardation in movement and later breakthrough (Beck *et al.*, 1993), which also favours degradation due to longer residence of pesticide molecules in the soil columns. 2,4-D was not leached from soil columns, which can be attributed to the rapid degradation of 2,4-D observed in both soils.

Field Study

Larger amounts of simazine in the top 10 cm were recovered from the amended soil than unamended soil (Table 3). This can be attributed to the increase in sorption, as revealed in

sorption studies. It should also be noticed that simazine was moved further in the unamended soil, as indicated by the higher amounts detected below 10 cm than in the amended soil, which also agreed with the earlier breakthrough in the soil column studies. However, only very small amounts of simazine were detected below 20 cm, there being no significant differences here between the two soils.

As with simazine, larger amounts of 2,4-D were detected in the first 10 cm of sewage-sludge amended soil and smaller amounts below 10 cm when compared with the unamended soil (Table 4). No 2,4-D was detected below 20 cm. This small movement of 2,4-D in soil, despite its anionic character, is due to its rapid degradation in soil, as shown in the laboratory studies.

Table 3. Simazine concentrations in the field trial of non-amended (S) and sewage-sludge amended (AS) soils

Soil depth (cm)	Simazine concentration (mg g ⁻¹ dry soil)					
	Time after herbicide application (day)					
	1	5	13	20	29	75
S						
0-10	1.56(±0.12) [†]	1.53(±1.01)	1.41(±0.39)	1.61(±1.12)	1.07(±0.09)	0.32(±0.21)
10-20	0.23(±0.04)	0.20(±0.11)	0.46(±0.15)	0.46(±0.15)	0.51(±0.33)	0.12(±0.11)
20-30	0	0	0	0.05(±0.03)	0.14(±0.12)	0.07(±0.01)
AS						
0-10	2.34(±0.28)	2.13(±0.67)	2.05(±0.45)	2.12(±0.66)	1.45(±0.18)	0.74(±0.20)
10-20	0.01(±0.01)	0.02(±0.01)	0.12(±0.02)	0.14(±0.01)	0.43(±0.10)	0.12(±0.02)
20-30	0	0	0	0.08(±0.09)	0.25(±0.05)	0.06(±0.05)

[†] Numbers in parentheses are standard error about the mean

Table 4. 2,4-D concentrations in the field trial of non-amended (S) and sewage-sludge amended (AS) soils

Soil depth (cm)	2,4-D concentration (mg g ⁻¹ dry soil)					
	Time after herbicide application (day)					
	1	5	13	20	29	75
S						
0-10	0.92(±0.02) [†]	0.57(±0.08)	0.69(±0.06)	0.45(±0.11)	0	0
10-20	0.03(±0.01)	0.03(±0.01)	0.10(±0.05)	0.30(±0.11)	0	0
20-30	0	0	0	0	0	0
AS						
0-10	1.31(±0.18)	0.68(±0.10)	1.03(±0.51)	0.57(±0.13)	0	0
10-20	0	0	0	0.15(±0.10)	0	0
20-30	0	0	0	0	0	0

[†] Numbers in parentheses are standard error about the mean

CONCLUSIONS

The addition of sewage sludge to soil gave rise to an increased sorption of the herbicides in the laboratory studies, which caused more retention of pesticide in the top 10 cm of the soil profile in a field study with the amended soil. This increase in sorption will reduce pesticide movement in soil and, consequently, the risk of groundwater contamination if heavy rain takes place shortly after herbicide application.

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