Porosity and surface fractal dimension of soils as affecting sorption, degradation and mobility of polar herbicides

R Celis, L Cox, M C Hermosín, J Cornejo

Instituto de Recursos Naturales y Agrobiol., CSIC, PO Box 1052, 41080 Sevilla, Spain
EMail: rcelis@irnase.csic.es

ABSTRACT

Sorption, degradation and soil porosity are major factors influencing pesticide mobility in soil. In this paper, we attempt to show a link between soil porosity, as described by the soil-surface fractal dimension (D_s), and herbicide behaviour in soil. We have studied the sorption, persistence and leaching of two polar herbicides (clopyralid and thiazafluron) in one sandy and two silty clay soils and related these to the porosity characteristics of the soils. Very little sorption in batch tests or degradation of clopyralid was observed in the three soils but there was considerable sorption and degradation of thiazafluron. Despite its negligible sorption, clopyralid displayed broader breakthrough curves in the two silty clay soils than in the sandy soil, which was attributed to the presence of small-sized pores and in turn with slightly higher D_s values of the silty clay soils. For thiazafluron, the higher D_s values associated with the silty clay soils compared to the sandy soil resulted in greater degradation during leaching compared to the batch experiment. This was attributed to retention or entrapment of the herbicide in stagnant, small-sized pores, which may have increased the residence time of the herbicide in the soil column, so retarding leaching and enhancing degradation.

INTRODUCTION

Sorption, degradation and movement through the soil profile determine the fate of pesticides in soil and aquatic environments. Sorption and degradation are generally inversely related to pesticide mobility (Beck *et al.*, 1993); soil physical properties such as texture, aggregate size and pore-size distribution also affect the transport of these solutes in soil (Cox *et al.*, 1999).

Even though the importance of soil structure to many soil processes, such as solute leaching, is well recognised, the progress from qualitative appreciation to quantitative understanding of structure-process interactions remains very slow (Crawford *et al.*, 1997). The recent recognition of soil as a fragmented porous medium, appropriate for fractal representation, has resulted in an increasing interest in the development of models relating soil fractal parameters, such as the soil-surface fractal dimension, to structure-dependent soil properties such as solute movement. In this work, we have compared the leaching patterns of the polar herbicides clopyralid (3,6-dichloropicolinic acid) and thiazafluron (1,3-dimethyl-1-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl)urea) in one sandy and two silty clay soils, and related these to herbicide sorption, persistence and the porosity characteristics of the soils. Mercury intrusion porosimetry and nitrogen adsorption techniques were used to characterise soil porosity in the macro- and micropore range, respectively. Porosity data were interpreted in terms of fractal geometry, and soil-surface fractal dimensions (D_s) were used as a descriptor of soil structure.
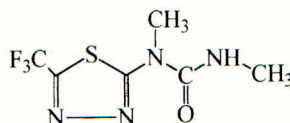
MATERIALS AND METHODS

Herbicides and soils

Analytical standards (chemical purity > 99%) of clopyralid and thiazafluron were supplied by the manufacturers.
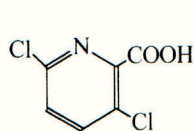
Clopyralid   Thiazafluron

The three soils were agricultural soils from Southern Spain: one sandy soil and two silty clay soils. Soil samples were air-dried, sieved to pass a 2-mm mesh and stored at 4°C. Their classification and physicochemical properties were determined by standard methods and the clay mineralogy by X-ray diffraction on orientated specimens (Table 1).

Table 1. Physicochemical properties of the soils

Soil	pH	Organic matter (%)	Fe (%)	Sand (%)	Silt (%)	Clay (%)
Soil 1 (*Typic Rhodoxeralf*)	7.9	0.99	0.98	71	9	20
Soil 2 (*Xerofluvent*)	7.7	2.24	0.82	12	44	44
Soil 3 (*Entic Pelloxererts*)	7.6	2.54	0.50	12	36	52

Porosity measurements

The distribution of pore radii of soil samples from 40 to 4×10^{-3} µm was determined using a Carlo Erba 2000 mercury depression and intrusion porosimeter. A sample of each soil (0.25 g) was heated at 90°C for 24 h, then outgassed at room temperature for 30 min prior to obtaining the mercury intrusion curve. Surface fractal dimensions corresponding to the mercury porosimetry (macropore) range were calculated according to the Pfeifer and Avnir (1983) equation:

$$\frac{-dV_p}{dr} \propto r^{2-Ds(Hg)}$$

where V_p is the volume of pore radii r and $D_s(Hg)$ is the surface fractal dimension corresponding to the mercury porosimetry range, which can be calculated from the slope of the logarithmic plot of dV_p/dr against r.

Nitrogen adsorption isotherms of soil samples were obtained using a Carlo Erba Sorptomatic 1900. Samples were outgassed at 90°C and equilibrated under vacuum for 24 h before measuring the nitrogen adsorption curve. Pore-size distributions were obtained in the range 10^{-3} to 3×10^{-2} μm using the Dollimore and Heal (1964) method assuming cylindrical pores in the calculations. Surface fractal dimensions of the soils corresponding to the nitrogen adsorption (micropore) range were calculated from nitrogen adsorption data using the Avnir and Jaroniec (1989) relationship:

$$V_{ads} \propto [\log(p_o/p)]^{Ds(N_2)-3}$$

where V_{ads} is the volume of nitrogen adsorbed at the relative pressure p/p_o and $D_s(N_2)$ is the fractal dimension of the surface accessible to nitrogen. $D_s(N_2)$ can be obtained from the slope of the plot of $\log(V_{ads})$ against $\log[\log(p_o/p)]$ in the low adsorption potential region (Avnir and Jaroniec, 1989).

Batch sorption and degradation kinetics

Duplicate slurries of soil/herbicide solution (500 g : 500 mL) were prepared in amber-glass bottles (1 L) with an initial herbicide concentration (C_{ini}) of 10 μM for thiazafluron and 2 μM for clopyralid. A blank bottle (without soil) was used as a control to account for possible abiotic degradation and volatilisation. The soil slurries were sampled at 0.25, 0.5, 1, 2, 4, 7, 10 and 14 days. The sample aliquot (approximately 20 mL suspension) was centrifuged and the herbicide concentration of the aqueous supernatant solution (C_t) determined by HPLC. The amount of herbicide removed from the aqueous solution (C_s) was calculated from the difference between the herbicide concentration in the blank bottles (C_{ini}) and C_t. For thiazafluron, the soil pellets were extracted with methanol (2:1 methanol:soil), whereas for clopyralid the soil was extracted with a 3:1 mixture of 1M NaCl : 0.1M NaOH (4:1 extractant:soil). The water content of the soil, with C_t herbicide concentration, was used to correct data from the soil extraction. The difference between the herbicide removed from the solution (C_s) and that extracted from the soil (C_r) was assumed to be degraded and/or irreversibly bound ($C_d = C_s - C_r$) (Allen and Walker, 1987).

Leaching experiments

Herbicide leaching in soils was studied using methacrylate columns, 20 cm long and 16.66 cm^2 section. After saturation of the soil columns with 0.01M $CaCl_2$, the amount of thiazafluron and clopyralid corresponding to the maximum application rate in soils (12 kg ha^{-1} and 100 g ha^{-1}, respectively) was applied. The columns were leached with 0.01M $CaCl_2$ (25 mL daily during the first 10 days of the experiment, then 50 mL daily until the end of the experiment). Leachates were collected daily, volumes measured and herbicide concentrations determined by HPLC.

RESULTS AND DISCUSSION

Porosity measurements

The values of pore volumes (V_p) for the macro- and micropore range, measured by mercury intrusion porosimetry and nitrogen adsorption respectively, and the D_s values for the three

soils are given in Table 2. Although there was no clear correlation between $V_p(Hg)$ and the clay or organic matter content of the soils, the increase in $D_s(Hg)$ values from soil 1 to soil 3, reflecting increasing surface tortuosity as a result of predominance of small-size pores (Celis et al., 1996), was clearly related ($r^2 > 0.87$) to the clay and organic matter content of the soils (soil 1 < soil 2 < soil 3, Table 1). Filling of coarse pores by clay and organic matter has been shown to result in high soil D_s values as a result of a predominance of fine-sized pores which increase soil tortuosity (Bartoli et al., 1991).

Nitrogen adsorption isotherms were used to calculate the volumes of pore radii < 0.025 μm, $V_p(N_2)$ and the surface fractal dimensions, $D_s(N_2)$, corresponding to the micropore range (Avnir and Jaroniec 1989). These values, summarised in Table 2 for the three soils, show an increase in both $V_p(N_2)$ and $D_s(N_2)$ from soil 1 to soil 3, suggesting increasing numbers of micropores in the order soil 1 < soil 2 < soil 3. The similar pattern of D_s values obtained by mercury intrusion porosimetry and nitrogen adsorption techniques seems to indicate that these two pore-size measurements are related, the increase in surface fractal dimension being associated primarily with the clay and organic matter contents.

Table 2. Mercury intrusion and nitrogen adsorption pore volumes (V_p) and derived surface fractal dimensions (D_s) for the three soils.

Soil	V_p (Hg) 40 μm > r > 0.025 μm ($mm^3\,g^{-1}$)	V_p (N_2) r < 0.025 μm ($mm^3\,g^{-1}$)	V_p (total) r < 40 μm ($mm^3\,g^{-1}$)	$D_s(Hg)$	$D_s(N_2)$
Soil 1	122	24	146	2.76 ± 0.05[†]	2.71 ± 0.01
Soil 2	164	34	198	2.93 ± 0.04	2.79 ± 0.01
Soil 3	59	45	104	3.11 ± 0.06	2.81 ± 0.01

[†] standard error about the mean

Batch sorption and degradation kinetics

Sorption coefficients, K_d ($= C_s/C_t$), on the different soils were calculated from the amount of herbicide sorbed at 24 h in the batch kinetic experiment. K_d values are shown in Table 3, along with the percentage of herbicide degraded after 14 d of incubation ($\%D_{14d}$) and the half-life values ($T_{1/2}$) obtained by extrapolation of the C_d vs t curves.

Table 3. Distribution coefficients, K_d (L kg^{-1}), degradation percentage, $\%D_{14d}$, and half-life, $T_{1/2}$ (days) of herbicides in soils calculated from the batch kinetic experiments.

Soil	Clopyralid			Thiazafluron		
	K_d	$\%D_{14d}$	$T_{1/2}$	K_d	$\%D_{14d}$	$T_{1/2}$
Soil 1	0.01 ± 0.01[†]	0	-	0.7 ± 0.1	45 ± 3	15
Soil 2	0.05 ± 0.03	0	-	1.8 ± 0.1	20 ± 1	45
Soil 3	0.05 ± 0.03	0	-	2.0 ± 0.1	22 ± 1	40

[†] standard error about the mean

There was very little sorption and degradation of clopyralid in the three soils and considerable sorption and degradation of thiazafluron. The pK_a of clopyralid ($pK_a = 2.3$) indicates that at the pH of the soils the compound would be very largely in its anionic form and therefore would be repelled by negatively charged soil colloids. For thiazafluron (log $K_{ow} = 1.8$), soils 2 and 3 (with higher clay and organic matter contents and higher D_s values) displayed the highest sorption and the lowest degradation rates, indicating that sorption protected the herbicide from degradation (Table 3).

Leaching experiment

The position of the maximum concentration peak (close to one pore volume), the symmetry of the breakthrough curves, and the total amounts of herbicide recovered (> 90%) for clopyralid in all three soils indicate little retention and degradation in the soil columns (Fig. 1), in agreement with the batch slurry results. However, despite its negligible sorption and degradation in all three soils, clopyralid displayed slightly broader breakthrough curves in the two silty clay soils than in the sandy soil (as can be clearly seen in the expanded clopyralid figure). This can be attributed to retardation of the herbicide molecules by diffusion and hydrodynamic dispersion into the small pores of soils 2 and 3 and indicated that high D_s values, as an indicator of abundance of small size pores or great tortuosity in the pore system, can be related to flattening and widening of the breakthrough curves for low-sorbing and persistent chemicals such as clopyralid. A similar feature was found by Ping et al., (1975) for the acidic, non-sorbing herbicide picloram in a silty soil.
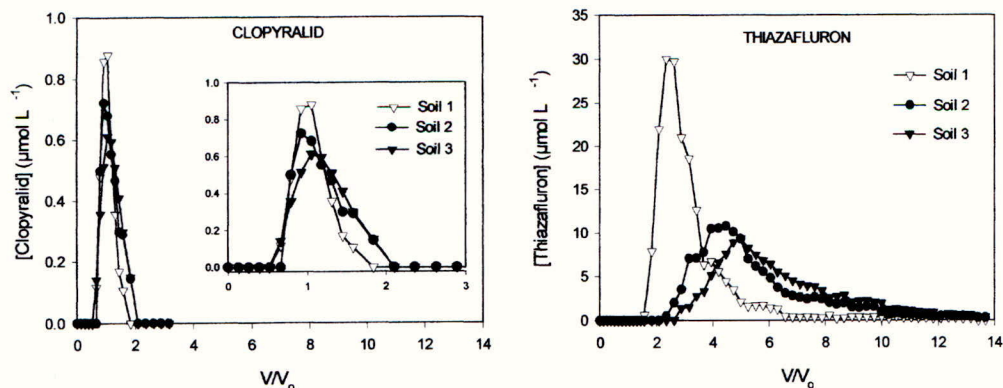

Figure 1. Breakthrough curves of clopyralid and thiazafluron in the three soils.

The pore volumes required to reach the maximum concentrations in the breakthrough curves for thiazafluron directly correlated with the K_d values given in Table 3 ($r^2 = 0.998$), indicating that the position of the maximum concentration peak was mainly determined by the extent of sorption (Beck et al., 1993). Total amounts of thiazafluron recovered after the leaching experiment (soil 1 = 90% soil 2 = 74%, soil 3 = 72%) showed greater degradation in the silty clay soils 2 and 3 than that in soil 1. This was in contrast to the batch slurry results, where the greatest degradation occurred in the less sorptive sandy soil 1. Again, the abundance of small-sized pores in soils 2 and 3, reflected by their high D_s values, may have reduced the hydrodynamic dispersion and diffusion processes of the herbicide molecules to and from stagnant micropores, enhancing the residence time of the herbicide in those pores and in turn

the likelihood for degradation. In the batch experiment, the lower soil/solution ratio, as compared to the soil column, and the effective shaking facilitated diffusion and favoured degradation in soil 1 because of the lower sorption.

CONCLUSIONS

This interpretation of herbicide leaching on the basis of soil fractal structure supported the usefulness of the fractal approach to describe soil structure by a single numerical value (i.e., D_s) and to address the relation between soil structure and solute movement. Greater herbicide retention and degradation in soil columns was strongly related to the presence of small-size pores and in turn with high D_s values in soil. These findings may, therefore, help progress from qualitative appreciation to quantitative understanding of structure-process interaction, which is one of the most important and beneficial features of soil fractal theory.

ACKNOWLEDGEMENTS

REFERENCES

Allen R; Walker A (1987). The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. *Pesticide Science* **18**, 95-111.

Avnir D; Jaroniec M (1989). An isotherm equation for adsorption on fractal surfaces of heterogeneous porous materials. *Langmuir* **5**, 1431-1433.

Bartoli F; Philippy R; Doirisse M; Niquet S; Dubuit M (1991). Structure and self-similarity in silty and sandy soils: the fractal approach. *Journal of Soil Science* **42**, 167-185.

Beck A J; Johnston A E J; Jones K C (1993). Movement of nonionic organic chemicals in agricultural soils. *Critical Reviews in Environmental Science and Technology* **23**, 219-248.

Celis R; Cornejo J; Hermosín M C (1996). Surface fractal dimensions of synthetic clay-hydrous iron oxide associations from nitrogen adsorption isotherms and mercury porosimetry. *Clay Minerals* **31**, 355-363.

Cox L; Calderón M J; Hermosín M C; Cornejo J (1999). Leaching of clopyralid and metamitron under conventional and reduced tillage systems. *Journal of Environmental Quality* **28**, 605-610.

Crawford J W; Verrall S; Young I M (1997). The origin and loss of fractal scaling in simulated soil aggregates. *European Journal of Soil Science* **48**, 643-650.

Dollimore D; Heal G R (1964). An improved method for the calculation of pore size distribution from adsorption data. *Journal of Applied Chemistry* **14**, 109-114.

Pfeifer P; Avnir D (1983). Chemistry of noninteger dimensions between two and three. *Journal of Chemical Physics* **79**, 3558-3565.

Ping C L; Cheng H H; McNeal B L (1975). Variation in picloram leaching patterns for several soils. *Soil Science Society of America Journal* **39**, 470-474.

Herbicide partitioning to hard surfaces

C T Ramwell

Cranfield Centre for EcoChemistry, Cranfield University, Shardlow Hall, Shardlow, Derby, DE72 2GN, UK
Email: c.ramwell@cranfield.ac.uk

ABSTRACT

The herbicide atrazine, despite having a low K_{oc}, partitioned to asphalt and concrete, but not to granite ballast. Partitioning accounted for 36 and 16% loss of formulated product when applied to asphalt and concrete respectively. Partitioning was enhanced for formulated atrazine compared to technical grade.

INTRODUCTION

The current UK approach to regulating herbicides applied to hard surfaces is highly precautionary and assumes that 100% of the applied compound is removed within 25 mm of rainfall. An improved Tier 1 risk-assessment model has been developed (Hollis *et al.*, 2000) but its use remains limited due to a lack of knowledge on processes affecting the loss of herbicides following application.

The K_{oc} (organic carbon/water partition coefficient) of a pesticide is fundamental to predicting its behaviour in soils. The natures of soils and hard surfaces (*e.g.* concrete) are intrinsically different and the K_{oc} value does not necessarily reflect the behaviour of the compound on hard surfaces. Furthermore, in the field, pesticides are in contact with a 3-dimensional 'volume' of soil whereas on a hard surface they are in contact with a 2-dimensional 'area' of material. Consequently, existing methods for determining the adsorption/desorption of pesticides to soil may not be suitable for representing processes occurring on hard surfaces, but quantification of a partition coefficient (K_p) for herbicides and hard surfaces could assist in understanding their fate and behaviour.

The aim of this study was to develop a method for determining herbicide partitioning to hard surfaces and to explore relationships between physico-chemical properties and sorption. Furthermore, the development of laboratory-scale methodology to investigate pesticide behaviour on hard surfaces will enable more accurate comparisons between compounds, and could provide a basis for further, process-based research in this area.

Compounds (*e.g.* triazines, ureas) were chosen to span a range of hydrophobicity; this should enable more accurate prediction of the behaviour of a wide range of amenity pesticides. Surfaces used in the experiment – concrete, hot-rolled asphalt and granite ballast – represent materials commonly treated with herbicides in the UK. The study is ongoing and only atrazine results are presented here.

METHODS AND MATERIALS

The principle of determining a partition coefficient between a herbicide and a hard-surface material followed OECD guidelines for quantifying adsorption, in that the wearing surface of the material was exposed to a test compound whose concentration was measured over time.

The hard-surface materials comprised commercially available concrete paving slabs cut to 0.1 m x 0.15 m blocks. Asphalt slabs were made to the same size using 30/14 hot-rolled wearing-course asphalt. Granite ballast was measured by weight (0.5 kg) rather than area as this is the unit commonly associated with this material. All surfaces were new and were washed with water prior to use.

Pyrex glass dishes were used to hold the test solution. The volume of solution used (250 ml) was determined such that, when in position, approximately 3 mm depth of the slab was exposed to the solution ensuring that the wearing course was the main adsorption site. Slabs were raised at each corner on a small, glass bead. Both technical grade atrazine and formulation (MSS Atrazine 50 FL, a suspension concentrate containing 500 g a.i. l^{-1}) were investigated. The required concentration of the solution was calculated by dividing the mass of active that would be applied to a 0.015 m^2 area at label application rate by the nominal volume of 250 ml. The solution was made up in a ten-litre aspirator and divided between the dishes to minimise variation between replicates. Distilled water was the solvent for both the technical grade and formulated atrazine.

The experiment was conducted in the dark at room temperature (18°C) and the solution was stirred throughout. Each test was conducted in triplicate. Dishes containing the test solution but no slab served as a control. An asphalt slab placed in distilled water served as a control to ensure no interference during analysis. Ballast was placed in stainless steel containers and all the surfaces of the ballast were exposed to the solution. A control of the solution containing no ballast was run in parallel. These containers were agitated using a shaker. Samples (1.0 ml) were taken prior to the slabs being placed in the solution (t = 0), and after 2, 6, 24 and 144 hours. Samples were stored in glass vials at 4°C prior to analysis.

After 144 hours (T_{144}), the slabs were removed from solution and air dried for 24 hours. After a 10 second rinse in distilled water (250 ml), the slabs were transferred into clean water (250 ml) and desorption studied by taking samples (1.0 ml) after 1, 24 and 144 hours. Samples were analysed by HPLC fitted with a Genesis C18 reverse phase TMS end-capped ODS column (150 x 4.6 mm) with 4 μ packing and using a mobile phase of 65% methanol to 35% water.

Total losses of atrazine to the hard-surface materials were calculated by subtracting the mass of atrazine desorbed following exposure to clean water over 144 h from the mass present after 144 h of sorption in the first phase. Partitioning to the hard surface was determined in relation to the control and was calculated by dividing the mean total loss of atrazine to the hard surface by the mean concentration of the control at 144 h. Mass rather than concentration was used in the data analysis to account for the successive one millilitre decrease in water volume due to sampling. Students t-test was used for data analysis. The

partition coefficient was calculated as a ratio of the mean mass of atrazine partitioned to the hard-surface area (mg m^{-2}) after 144 hours to the mean atrazine concentration of the solution after 144 hours.

RESULTS

There was no interference in analysis by leachates from asphalt. On the whole, variability at each time point for the different treatments was good (standard deviation < 0.1); for the few exceptions, the maximum standard deviation was 0.32. All samples contained less than 23 mg L^{-1} of atrazine hence the solubility limit (33 mg L^{-1}) was not exceeded.

Atrazine partitioning to the hard surfaces was calculated as a percentage of the control. Within six hours of the concrete and asphalt slabs being exposed to the formulated atrazine, 7% of the active ingredient had been removed regardless of material type (Figure 1).
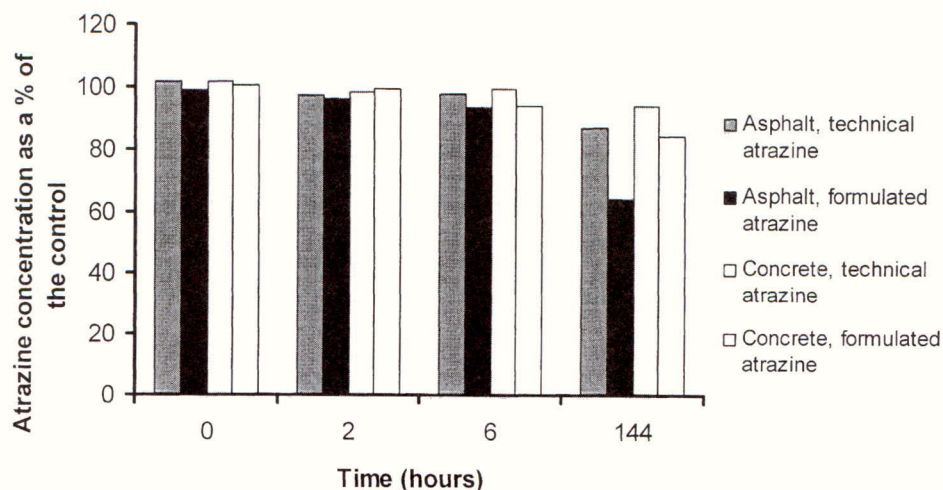

Figure 1. The percentage of atrazine remaining in solution when exposed to asphalt and concrete surfaces.

This compares to a loss of 2-3% of the technical grade during the same time period. After 144 hours, atrazine partitioning to asphalt was significantly ($P < 0.01$) greater than to concrete, and atrazine losses were enhanced when present as formulation rather than technical grade.

There was no partitioning of atrazine to granite ballast either as the formulated product or technical grade (Figure 2).
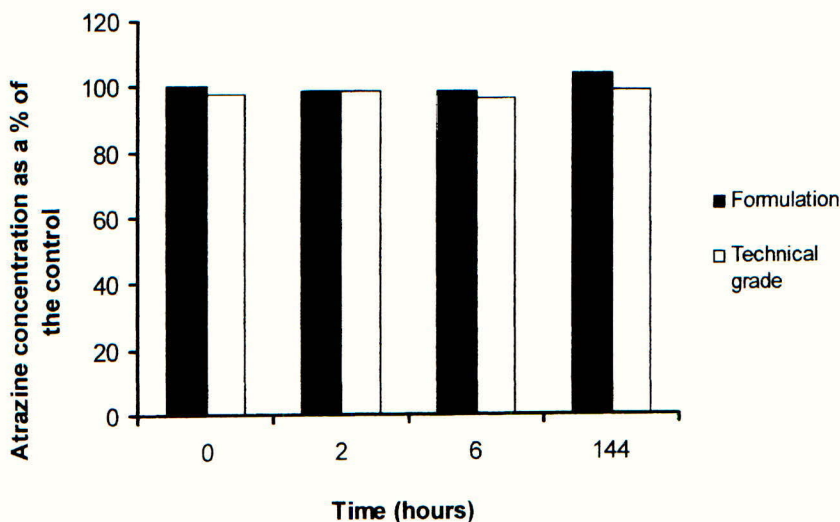
Figure 2. The percentage of atrazine remaining in solution when exposed to ballast.

Partition coefficients (measured at T_{144}) for technical grade atrazine were less than for the formulated product (Table 1). The K_ps also reflect the greater partitioning to asphalt than to concrete.

Table 1. K_p values for atrazine : asphalt and concrete at T_{144}.

Surface Type	K_p (L m^{-2})	
	Technical grade	Formulation
Asphalt	2.44	9.17
Concrete	1.09	3.09

DISCUSSION

Greater partitioning of atrazine to asphalt rather than to concrete may be explained by both the physical and chemical characteristics of asphalt. An asphalt surface is more pitted than a concrete surface and hence the larger surface area will create more potential sorption sites. Furthermore, solution may be physically retained in the fissures by capillary forces. The presence of organic carbon in asphalt would also enhance its sorption capacity.

Minimal retention of atrazine by concrete surfaces was also observed by Shepherd & Heather (1999). However, concentrations of atrazine in runoff water for their study were such that there was an 'unexplained' loss from the system of 80% of the active (MSS Atrazine 50 FL) applied to asphalt and 65% when applied to concrete. The current study indicates that less than half this loss may be explained by partitioning to the surface. Nevertheless, Parsons *et al.*, (1998) accounted for *ca.* 85% of the applied atrazine to a concrete surface in runoff; thus only *ca.* 15% was unaccounted for which is comparable to the quantity partitioned in the current study.

Shepherd and Heather (1999) also demonstrated an increase in atrazine loss from ballast with increasing rainfall and the rate of loss did not decrease significantly after 25 mm of rainfall. This finding indicates that the removal of atrazine was not limited by its availability which is in accordance with the current study where no significant partitioning occurred. Other studies examining herbicide losses from railway formations have demonstrated the ability of herbicides to be leached (Heather & Shepherd 1999; Torstensson 1994) but these results contrast to a study by Ramwell (unpublished data) where herbicides were not detected above $0.1 \ \mu g \ L^{-1}$ in surface or groundwaters following herbicide application to a railway. It is probable that lower rainfall and greater distances between the treated area and sampling sites in the latter study militated against detection of the herbicides. If herbicides do not partition to granite ballast or if such partitioning is very limited, then knowledge of the composition of the ballast formation would be required to enable the more accurate prediction of herbicide leaching in this medium.

This study indicates that the formulation may enhance partitioning of atrazine to asphalt and concrete, possibly due to the presence of 'stickers'. (Although the working concentrations of the technical grade and formulated atrazine differed, a study by Shepherd (2000) suggested that atrazine partitioning was not affected by concentration). Other research has demonstrated differences between the active ingredient and formulated atrazine when studying degradation and it was proposed that the ratio of surfactant to active may influence the rate of reactions (Texier *et al.*, 1999). The influence of formulation on the ability of a compound to adhere to a hard surface may therefore be specific to the active substance, and research involving further compounds would be required to substantiate the findings of this study.

CONCLUSIONS

Atrazine, despite having a low K_{oc} partitioned to asphalt and concrete, but not to ballast. Preferential partitioning to asphalt may be both a physical and chemical process. The surfactants used in the formulated product appeared to enhance the ability of atrazine to partition to both asphalt and concrete, but this effect was not observed for ballast.

The study provides a relatively simple method for quantifying partitioning in a controlled environment, such that comparisons between compounds can be made with confidence. Further quantification of partitioning of herbicides with a range of K_{oc} values is to be conducted and this will enable investigation into the possibility that K_{oc} may be used as a predictor of herbicide sorption to hard surfaces. Comparison of results generated in the

laboratory to field studies will indicate the importance of partitioning in describing herbicide removal from hard surfaces.

ACKNOWLEDGEMENTS

REFERENCES

Hollis J M; Syed B; Shepherd A J; Ramwell C T; Heather A I J (2000). Development and evaluation of a regulatory first tier model for predicting surface water exposure resulting from herbicides applied to land not intended to bear vegetation. *Soil Survey & Land Research Centre report to MAFF*, 40 pp.

Parsons R G; Brockelsby C D; Newby S E (1998). Adherence of herbicides to hard surfaces. *Book of Abstracts - 9th International Congress, Pesticide Chemistry: The food-environment challenge*, pp.6C-012.

Shepherd A J; Heather A I J (1999). Factors affecting the loss of six herbicides from hard surfaces. *Proceedings of the XI Symposium Pesticide Chemistry – Human and Environmental Exposure to Xenobiotics 1999*, pp. 777-784.

Shepherd A J (2000). Herbicide losses from engineered surfaces: Management practices and impacts, Cranfield University, unpublished PhD thesis.

Texier I; Giannotti C; Malato S; Richter C; Delaire J (1999). Solar photodegradation of pesticides in water by sodium decatungstate. *Catalysis Today*, **54**: 297-307.

Torstensson L (1994). Mobility and transformation of diuron in railway embankments. *Proceedings of the 5th International Workshop Environmental Behaviour of Pesticides and Regulatory Aspects*, pp. 366 – 371.