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Influence of ageing of residues on the availability of herbicides for leaching

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"Capsule": *Ageing of herbicide residues leads to reduced losses by leaching.*

Abstract

Losses by leaching of chlorotoluron, isoproturon and triasulfuron from small intact columns of a structured clay loam and an unstructured sandy loam soil were measured in five separate field experiments. In general, losses of all three herbicides were greater from the clay loam than from the sandy loam soil and the order between herbicides was always triasulfuron ≫ isoproturon > chlorotoluron. Differences between experiments were also consistent for every soil/herbicide combination. There was no relationship between total loss and either total rainfall or cumulative leachate volume. When weighting factors were applied to the rainfall data to make early rainfall more important than later rainfall, there were significant positive relationships between cumulative weighted rainfall and total losses. Also, there were significant negative correlations between total losses and the delay to accumulation of 25 mm rainfall (equivalent to one pore volume of available water) in the different experiments. In laboratory incubations, there was a more rapid decline in aqueous (0.01 M calcium chloride) extractable residues than in total solvent extractable residues indicating increasing sorption with residence time. However, the rate of change in water extractable residues could not completely explain the decrease in leachability with ageing of residues in the field. Short-term sorption studies with aggregates of the two soils indicated slower sorption by those of the clay loam than by those of the sandy loam suggesting that diffusion into and out of aggregates may affect availability for leaching in the more structured soil. Small scale leaching studies with aggregates of the soils also demonstrated reductions in availability for leaching as residence time in soil was increased, which could not be explained by degradation. These results therefore indicate that time-dependent sorption processes are important in controlling pesticide movement in soils, although the data do not give a mechanistic explanation of the changes in leaching with ageing of residues.

Keywords: Herbicides; Soils; Adsorption; Bioavailablity; Leaching

1. Introduction

An important environmental concern with pesticides is their potential to move through soils and to contaminate surface water via drainflow, or deeper groundwater resources by percolation through subsoils and the deeper soil horizons. There is considerable variation in the extent of pesticide movement through soils as a result of variation in (i) soil properties that control water movement, (ii) pesticide/soil interactions that control availability for movement, and (iii) weather patterns, particularly rainfall, that control the timing of major leaching events. There is increasing evidence that the timing of rainfall relative to the time of pesticide application may be the major factor controlling leaching losses. In experiments over six successive winter periods at the Brimstone Farm site, Oxfordshire, UK, losses of isoproturon in drainflow were reduced by about 50% for every 10 day increase in the time between application and the first major rainfall event causing significant drainflow (Jones et al., 2001). The results also demonstrated that

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the decrease in total losses of isoproturon with increasing time from application to the first drainflow event was much greater than would be expected on the basis of degradation rates in the soil. This suggests that other ageing processes, such as increasing sorption with residence time (Walker et al., 1995, 1999), may also be involved in controlling availability for leaching. The objectives of the present experiments were to further investigate the variations in leaching losses of some soil-applied herbicides from two contrasting soil types, and to gain further information concerning the factors influencing the availability of pesticides for movement in soils.

2. Materials and methods

2.1. Soils and herbicides

The soils used were an unstructured sandy loam of the Wick series (Whitfield, 1974) and a moderately structured sandy clay loam of the Brockhurst series (Whitfield, 1974). Properties of the soils are shown in Table 1. Organic matter content was determined by loss on ignition at 450 °C, pH was measured with a glass electrode in a 1:1 (w/v) suspension of the soils in distilled water, and particle size distribution was determined by laser granulometry on organic matter free samples at the Macaulay Land Use Research Institute, Aberdeen, UK. Moisture content at a soil water potential of -10 kPa was measured on a sand tower with 100 cm pressure head of water, and at -33 kPa using a pressure membrane apparatus. The herbicides used were a water dispersible granule formulation of triasulfuron (20% active substance (a.s.), w/w) and suspension concentrate formulations of isoproturon (44.6% a.s., w/w) and chlorotoluron (46.2% a.s., w/w). Analytical grade samples of the compounds (>99% purity; British Greyhound, Birkenhead, UK) were used as reference standards in all analyses.

2.2. Field leaching studies

Field leaching experiments were prepared on five separate occasions: 23 November 2000, and 5 January, 6 March, 20 November and 18 December 2001. Each experiment involved five freshly collected replicate cores of the Wick sandy loam and five replicate cores of the Brockhurst clay loam. The cores were removed intact from the field site by gently pushing the holding tubes into the soil with a JCB. Each core was 25 cm long and 20 cm internal diameter. Following removal from the field, the cores were inverted, and the soil at the base was picked back by about 4 cm and the space produced was filled with 3-mm sieved, water washed, pea gravel. The base was then sealed with Tygan mesh (0.25 mm) held in place with waterproof tape. The columns were then fixed at their base to 20 cm diameter polypropylene filter funnels with further waterproof tape before being mounted outdoors in the lysimeter box described by Walker et al. (1996). The outlet from the filter funnels fed directly into separate 1-l Duran bottles. The columns were allowed to equilibrate for 3–4 weeks before application of the herbicides to the soil surface on the dates listed above.

The herbicides were applied evenly across the surface by pipette as a mixture of the commercial formulations in 15 ml water to give a concentration on the soil surface equivalent to 2.5, 1.5 and 0.2 kg ha^{-1} of isoproturon, chlorotoluron and triasulfuron, respectively. All columns were exposed to natural weather conditions. The Duran bottles were replaced after each significant rainfall event (minimum 200 ml drainage), or following accumulation of 200 ml drainage water. At each sampling time the volume of drainage water from each column was recorded and the leachate samples were stored at 4 °C until analysed (usually within 3 days).

Table 1
Soil properties

Soil series	Organic matter (%)	pH	Clay (%)	Silt (%)	Sand (%)	Soil moisture (%w/w)	
						−10 kPa	−33 kPa
Wick	2.38	6.9	17	8	75	15.9	12.1
Brockhurst	2.79	6.7	23	10	57	18.1	14.2

2.3. Analysis of water samples

Each water sample was acidified to pH 3–4 with orthophosphoric acid (addition of 5 ml l^{-1}) and then passed through an Enviroguard C-18 solid phase extraction cartridge (Supelco, UK). Herbicides were eluted with 2 ml acetonitrile:water:orthophosphoric acid (80:20:0.25 v/v) and quantified by HPLC using Kontron Series 300 equipment. The column used was LichroCart C-18 (Merck, Darmstadt, Germany) with an isocratic mobile phase flow rate of 1 ml min^{-1}. The mobile phase was acetonitrile:water:orthophosphoric acid (70:30:0.25 v/v), and detection was by UV absorbance at 230 nm. The retention times of triasulfuron, chlorotoluron and isoproturon were 2.89, 3.95 and 4.30 min, respectively, and the limit of detection (starting with a 500-ml sample) was about 0.5 μg l^{-1} for all of the compounds. Recoveries from 250-ml samples containing 50 μg l^{-1} were >95% for the three herbicides.

2.4. Laboratory incubation experiments

Samples of soil were taken from the 0–10 cm layer from locations close to those from which the lysimeter cores had been removed. The soils were air-dried overnight and then sieved (3-mm mesh). Triplicate subsamples of each soil (1 kg) were treated separately with