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Influence of kinetic sorption and diffusion on pesticide movement through aggregated soils

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Abstract

Laboratory studies were carried out to investigate solute leaching at different times from application in relation to temperature and initial soil moisture. Aggregates of a heavy clay soil were treated with a non-interactive solute (bromide) and the herbicides chlorotoluron, isoproturon and triasulfuron. The soil was incubated at 90% field capacity and either 5 or 15^{o}C. The influence of application to initially dry and initially wet aggregates on the behaviour of isoproturon was also investigated. At intervals, samples were either leached in small columns, centrifuged to characterise the fraction of chemical available in pore water under natural moisture conditions or extracted with organic solvents to assess total residues in soil. Bromide concentrations in leachate and in pore water extracted by centrifugation were constant with time. In contrast, availability for leaching and concentration in pore water of the herbicides decreased with increasing time from application in soil incubated at 15^{o}C. The effect of residence time was much smaller at 5 than at 15^{o}C. At the higher temperature, pesticide concentrations in leachate and pore water declined faster than would be expected from

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degradation alone, probably due to slow diffusion of the pesticides into soil aggregates where they are less available for leaching and/or slow sorption-desorption. The faster decline in availability for leaching at 15 than at 5^{o}C was attributed to faster degradation of the readily available fraction. There was no significant influence of initial soil moisture on either the leaching behaviour of isoproturon or its availability in soil water.

Keywords: Kinetic sorption, diffusion, leaching, temperature, antecedent moisture

1. Introduction

Drainflow in structured clay soils with a potential for bypass flow is an important mechanism for the movement of diffusely applied pesticides to surface waters. An understanding of the mechanisms that control pesticide behaviour in such soils is essential for the development of practices that reduce pesticide leaching. There is increasing evidence that chemicals become less available for uptake and transformation by soil organisms the longer their residence time in soil (Alexander, 1995; Scow and Johnson, 1997). The availability of chemicals for soil organisms and the potential of a chemical to leach to groundwater or surface waters often decline with time (Pignatello *et al.*, 1993, Walker *et al.*, 2003, Renaud *et al.*, 2004). Work at the field scale showed that losses of some, but not all pesticides from a cracking clay soil decreased with increasing time from application to first drainflow event (Jones *et al.*, 2000). Losses of the moderately mobile, moderately persistent herbicide isoproturon in drainflow initiated 10 days after application were four orders of magnitude larger than those in drainflow initiated 110 days after application. This decline in isoproturon losses was faster than could be explained by degradation alone. In contrast, the effect of residence time on leaching of the weakly sorbed herbicide triasulfuron was not significant.

The decline in pesticide bioavailability and its potential for leaching to depth with increasing time of contact with soil are likely to be caused by slow sorption kinetics and/or diffusion. Desorption often occurs more slowly than adsorption and may not be fully reversible (Pignatello, 2000). Diffusion may be a limiting factor during (a) movement of pesticide through bulk aqueous solution to the surfaces of sorbing materials; (b) movement in solution through micropores to areas protected from the main regions of soil water flow; and (c) movement through the three dimensional network of organic material. Diffusion in soil is slow relative to that in water due to the tortuosity and increased length of the flow path within soil particles, sorption to pore walls, steric interference from pore walls and the viscous nature of water near hydrophilic surfaces (Pignatello, 2000). Reactions between the pesticide and the sorbent may also be time-dependent. The distribution between the dissolved and sorbed state may thus require days, weeks or even months to reach equilibrium (Cox and Walker, 1999; Koskinen *et al.*, 2002). A depletion of the readily available fraction of pesticide by degradation, uptake into soil organisms and plants or leaching to depth results in a shift in pesticide distribution towards the unavailable state. Further losses may be limited by the rate of mass-transfer from the unavailable to the available state.

To date, there is no clear understanding of how slow sorption and diffusion influence mass transfer in complex, structured soils under different environmental conditions. The influence of temperature and moisture on the mass transfer of solutes is particularly complex (Delle Site, 2001). Solubility of the compound in water, transport to the binding sites via diffusion and chemical sorption reactions are enhanced at higher temperatures. In contrast, physical sorption is decreased due to its exothermic nature.

Desorption usually requires energy and may be enhanced at higher temperature. The influence of soil water content on pesticide sorption depends strongly on the properties of the pesticide (Roy *et al.*, 2000). The structure of humic substances is modified and surfaces become more hydrophobic at low soil moisture contents which favours sorption of hydrophobic pesticides. In contrast, hydrophilic compounds, are often more strongly sorbed at high soil moisture content due to their higher affinity for hydrophilic regions of humus. Water is the medium in which pesticide molecules diffuse to binding sites within the aggregates. Mass-transfer of pesticides is thus expected to be faster in wet soils. In work by Gaillardon and Dur (1995), sorption of diuron and isoproturon was only stronger in dry than wet soil up to 30 min from application. Thereafter, sorption was stronger in wet soil, probably due to faster diffusion.

Soil moisture at the time of pesticide treatment is also expected to influence pesticide availability for leaching. Application to relatively dry soil may result in advective movement of pesticide into soil aggregates where it is protected from leaching. Application to wet soil is likely to initially concentrate the pesticide in the outer regions of soil aggregates. More pesticide may thus be available for leaching after application to wet soil.

The distribution of a chemical between the readily available and protected state is influenced by the rate of degradation in relation to the rate of slow sorption or diffusion. Patterns of spatial distribution of soil microorganisms suggest that degradation occurs mainly at surfaces or in outer layers of soil aggregates (Scow and Johnson, 1997). Degradation of many compounds appears to be largely restricted to the fraction available in the soil solution (Ogram *et al.*, 1985; Rijnaarts *et al.*, 1990). Pesticide which

is either sorbed or held in micropores which are inaccessible for degrading microorganisms may be protected from degradation. Faster degradation at higher temperatures and in wetter soils is thus likely to result in faster depletion of the fraction of the pesticide readily available for leaching.

The aim of the study reported here was to test the following hypotheses:

1. The concentration of solutes in readily extractable pore water and their availability for leaching decreases with increasing residence time in soil.
2. The decline is faster than can be explained by degradation alone.
3. The decline is more pronounced for sorbing compounds than for weakly or non-sorbing compounds.
4. The decline is more pronounced under conditions that favour degradation.
5. More pesticide will be available for leaching after application to wet soil compared with application to dry soil.

The laboratory study investigated leaching of solutes with contrasting degradation and sorption properties at different times from application in relation to temperature and antecedent moisture conditions. At each sampling interval, soil water was extracted from parallel samples by a centrifugation technique in order to characterise the fraction of chemical available in soil water under natural moisture conditions. The total amount of chemical remaining in the soil was also measured.

2. Material and methods

Three experiments were carried out. The behaviour of a non-degrading, non-sorbing solute (bromide) was investigated in the first study. The second experiment assessed the

behaviour of the pesticides chlorotoloron, isoproturon and triasulfuron at two temperatures. In a third experiment, initially dry and initially wet aggregates of the same soil were treated with isoproturon in order to assess the influence of soil moisture status at the time of application.

2.1. Soil

A heavy clay soil (Lawford series; 55% clay, 3.6% organic carbon, pH (H_2O) 6.4) was used for this study. The soil was taken from the upper 10 cm of an agricultural field and soil aggregates with diameters of 3-6 mm were isolated by passing through a 3-mm and a 6-mm sieve. Soil used for the three experiments was taken from the same location, but at different times within the year. Field capacity was measured prior to the experiments. Aggregates were filled into metal rings (2.0 cm in height, 5.4 cm in diameter). Four replicate samples were saturated and then equilibrated on a sand table at a tension of 50 cm generated by a hanging water column. Water contents were determined by weighing the samples before and after drying at 105^{o}C over night.

2.2. Pesticides

The herbicides chlorotoloron (CT), isoproturon (IPU) and triasulfuron (TSU) were studied (Table 1). Commercial formulations of the three herbicides were used. All pesticide concentrations reported in this paper are expressed as active substance. Sorption of the three pesticides was measured in the Lawford soil by Renaud *et al.* (2004).

2.3. Experimental methodology

Details of the three experiments are given in Table 2. For all studies, aggregates of the Lawford soil were filled into glass petri dishes. Separate sets of dishes were prepared for the leaching experiment, extraction of readily available soil water and the extraction of total residues. Each replicate sample for the leaching study consisted of 10 g dry weight soil filled into petri dishes of 80 mm diameter. Additional samples (80 mm dishes, 10 g soil) were prepared for the extraction of soil pore water. Larger amounts of soil were used for the degradation study (20 g or 25 g) and these were placed into dishes with a diameter of 12 mm A solution of KBr or commercial formulations of the pesticides in 5 mmol l^{-1} $CaSO_4$ (0.6 ml per 10 g dry soil) was dripped onto the soil. Previous experiments with a dye solution had shown that this volume of application solution was sufficient to give an even distribution over the soil, which formed a single layer of aggregates in the petri dishes. The solution was added to wet soil except for the third experiment where isoproturon was applied either 23 hours before ('initially dry') or 23 hours after ('initially wet') adjusting soil moisture. The water content was at 90% field capacity after adding the solution. The soil was transferred to incubation containers (see below) which were loosely covered and stored at either 5 or 15^{o}C in the dark. Moisture was replenished every 1-3 days. Samples were taken at intervals (Table 2).

Leaching studies

The soil was incubated in 50-ml plastic syringes with a centric outlet. Four replicate samples were taken at each sampling interval and irrigated with a target volume of 27.5 mm 5 mmol l^{-1} $CaSO_4$ solution over 6 hours (4.6 mm $hour^{-1}$) using a peristaltic multi-channel pump (Watson-Marlow 205U). The irrigation volume corresponded to

approximately three times the total volume of water held by the soil after leaching. It should be noted that the soil samples used in the leaching study were not centrifuged before or after leaching. Parallel soil samples were used for this purpose.

Extraction of soil pore water

Parallel samples were incubated in Whatman® Vectaspin 20 centrifugation devices consisting of a 50-ml outer tube and a 20-ml insert with a perforated base covered by a Whatman® GF/F 0.7 μm retention glass microfibre filter. At each sampling interval, four replicate samples were centrifuged for 20 min at a speed corresponding to a tension of 200 kPa (experiments 1 and 2) and for 30 min at a tension of *ca.* 140 kPa (experiment 3). This aimed at characterising the fraction of the soil water which is readily available for transport during leaching events. Extracted soil water was collected in the outer tube.

Measurement of total pesticide in soil

In experiment 2, soil samples (20 g dry weight) were incubated in duplicate in 60-ml glass bottles. At each sampling interval, 20 ml acetonitrile + water + orthophosphoric acid (90 + 9.75 + 0.25 by volume) were added to duplicate bottles and the samples were shaken on a wrist-action shaker for one hour. In experiment 3, 25 g soil was extracted with 25 ml acetonitrile + water (90 + 10 by volume) for one hour. After the soil had settled, the supernatant was transferred into HPLC vials to determine total residues of pesticide remaining in the soil at each sampling interval. Initial concentrations of the compounds in soil were derived by extracting the soil with organic solvents 1 h after adding the pesticides. No significant degradation will occur within 1 h for the pesticides used in this study and the concentration measured at this point in time can be taken as

the amount applied. The concentration measured after 1 h was compared with the theoretical amount calculated from the concentration of the application solution determined by HPLC and the volume applied. Recovery of the pesticides from the Lawford soil was between 96 and 110% of the total amount added.

2.4. Analytical methods

Bromide in leachate and soil pore water extracted by centrifugation was analysed with a Metrohm 790 Personal Ion Chromatograph (Herisau, Switzerland) equipped with Metrohm's Metrosep RP guard column, Metrosep A supp 4/5 guard column and Metrosep A Supp 4 analytical column. A 20 µl injection loop and an isocratic eluent (1.8 mM sodium carbonate / 1.7 mM sodium hydrogen carbonate) were used. The limits of quantification and detection were 0.5 mg bromide l^{-1} and 0.1 mg bromide l^{-1}, respectively.

For pesticide analysis, the solution (20 µL) was injected into a DX600 (Dionex, Sunningvale, USA) HPLC equipped with a PDA100 photodiode array detector and a Discovery C-18 column (150mm long x 4.6mm i.d. 5µm particle size, Supelco, Bellefonte, USA). The mobile phase was acetonitrile : 0.04% v/v orthophosphoric acid (40:60). The flow rate of the mobile phase was 1 ml min^{-1} with a run time of 25 min per sample and the detection wavelength for all three herbicides was 200 nm. Typical retention times were 6.6, 7.7 and 5.9 min for chlorotoluron, isoproturon and triasulfuron, respectively. Limits of quantification were 85, 70 and 25 µg l^{-1}, respectively. The limit of detection was *ca.* 10 µg l^{-1} for all three herbicides.

3. Results

3.1. Volumes of water and bromide concentrations

Average volumes of irrigation, leachate and pore water extracted are given in Table 3 for the three experiments. Water contents in the 10-g soil samples during incubation, just prior to leaching and centrifugation are also given for comparison. The soil samples were irrigated with a target volume of 27.5 mm of 5 mmol $CaSO_4$ solution which corresponds to 14.1 ml. Target volumes of irrigation were exceeded for some samples due to variability in flow generated by the peristaltic pump. Between 3 and 6% water (w/w) was extracted from the soil samples by centrifugation.

Between 78 and 96% of the applied bromide was leached from samples taken at different times from application. Concentrations of bromide in leachate ranged from 0.31 to 0.42 g l^{-1}. These concentrations were only slightly larger than those expected from complete mixing of the applied bromide throughout the soil aggregates (0.21 - 0.35 g l^{-1}). Observed concentrations in leachate were independent of the residence time in soil. The mass of bromide extracted from parallel samples by centrifugation corresponded to 12-18% of that applied. Concentrations of bromide in pore water were more variable (1.34 - 1.95 g l^{-1}) than leachate concentrations. There was no consistent influence of the time from application to sampling on bromide concentrations in pore water.

3.2. Pesticide behaviour

Concentrations of chlorotoluron and isoproturon in leachate and in pore water decreased with time for soil incubated at 5°C whereas those of triasulfuron were almost constant at this temperature (Figure 1). Leaching losses and pore water concentrations of all three herbicides decreased to a much larger extent in soil incubated at 15°C than at 5°C.

Bulk residues of isoproturon in soil declined faster than those of chlorotoluron (Figure 1) and both pesticides were degraded more rapidly at the higher temperature. Analysis of bulk soil residues for triasulfuron indicated no significant degradation within the experimental period. However, a number of measurements for this pesticide were unreliable and the results should be interpreted with care.

Times for 50% decline of concentrations of chlorotoluron and isoproturon in leachate, pore water and bulk soil (DT50 values) were calculated by fitting an exponential curve to the data. Measurements for each of the four replicates were used individually and not averaged prior to curve-fitting. The r^2 values given in Table 4 thus reflect the scatter in the data as well as deviations from first-order kinetics. It should also be noted that r^2 values are generally larger where the exponential curves are relatively flat (i.e. where degradation is slow). This explains the relatively poor r^2 values at 5°C. No DT50 values were calculated for triasulfuron because a number of measurements of total soil residues gave unreliable results (later measurements only, initial concentrations are reliable).

DT50 values for the decline in leachate and soil pore water concentrations of chlorotoluron at 5°C were shorter than those for the decline in total soil residues (Table

4). At this temperature, there was only a small difference in the DT50 values for isoproturon concentrations in leachate, pore water or bulk soil.

DT50 values for bulk degradation at 15^{o}C were 39.2 days for chlorotoluron and 15.2 days for isoproturon. For both pesticides, leaching concentrations declined faster than total residues (DT50 values of 17.4 and 11.1 days for chlorotoluron and isoproturon, respectively). DT50 values for the concentrations in pore water (12.9 days for chlorotoluron and 10.1 days for isoproturon) were also much shorter than those for bulk degradation.

The availability for leaching and extraction in pore water was different for the three pesticides. The mass of pesticide that was initially available for leaching corresponded to 56% of the applied amount for triasulfuron (average of both incubation temperatures), 37% for isoproturon and 27% for chlorotoluron. The initial mass in pore water extracted was 4.1% of the applied mass of triasulfuron compared with 1.5% for isoproturon and 0.94% for chlorotoluron. Losses were inversely related to the strength of sorption as indicated by batch experiments with the Lawford soil (Renaud *et al.*, 2004) and were much larger for the weakly sorbed triasulfuron (Kf = 0.62 l kg^{-1}; 1/n = 0.70) than for chlorotoluron (Kf = 6.40 l kg^{-1}; 1/n = 0.78) and isoproturon (Kf = 3.60 l kg^{-1} 1/n = 0.83).

Concentrations of chlorotoluron and isoproturon which were theoretically available for leaching assuming constant sorption with time and partitioning between the total soil and water volume were calculated and compared with measured concentrations. Theoretical concentrations for each sampling time were derived from fitted bulk

concentrations in soil, total volumes of water added and the sorption isotherms derived by Renaud *et al.* (2004). The results are shown in Figure 2.

Theoretical values and measured concentrations decreased at the same rate at 5^{o}C for both pesticides. Measured concentrations at 15^{o}C matched the theoretical values soon after treatment, but observed concentrations were smaller than those calculated later in the experiment (Figure 2).

The behaviour of isoproturon was further investigated following application to dry or wet soil. Moisture during subsequent incubation at 15^{o}C was identical for both treatments. Concentrations of isoproturon in leachate, soil pore water extracted by centrifugation and residues of the pesticide in bulk soil decreased with time for both the initially dry and wet treatments (Figure 3). There was no significant influence of moisture conditions at the time of pesticide application on either measurement on most sampling dates.

Times for 50% decline of the initial mass (DT50) of isoproturon in leachate, pore water and bulk soil were again calculated by fitting an exponential curve to the data. DT50 values for bulk degradation of isoproturon in soil were 16.1 and 17.0 days for the initially dry and wet treatment, respectively. For both treatments, soil-pesticide interactions reduced isoproturon loads in leachate at rates greater than expected from degradation alone (DT50 = 10.6 and 10.3 days for the dry and wet treatment, respectively). Times for 50% decrease in the mass of isoproturon extracted in pore water (DT50 = 13.0 and 8.9 days for the dry and wet treatment, respectively) were

similar to those for leaching losses. These results are very similar to those obtained for isoproturon in experiment 2.

4. Discussion

All solutes were applied in small volumes of water in this study and would be concentrated in the outer regions of soil aggregates soon after application. As time progresses, the chemical is likely to move into the micropores via advection and/or diffusion. The longer the time from application to the first leaching event, the smaller the concentration in the outer aggregate regions. It is likely that only the solute in the larger pores and at the surface of aggregates is immediately available for leaching whereas water in small pores inside the aggregates is virtually immobile (van Genuchten and Wierenga, 1976; Addiscott, 1977). Solute in this water is only available for leaching following diffusion back into the mobile water.

Water in pores between the aggregates is displaced by infiltrating water during leaching events. Once the concentration in these pores decreases below that in the micropores, the direction of solute diffusion is reversed. This process is slow relative to the movement of mobile soil water between soil aggregates during intense leaching events in the field. The time for interaction between immobile and mobile regions may thus be too short to allow an extensive redistribution of the solute and a large proportion may be protected from leaching.

Non-sorbing solutes are redistributed between the inner and outer regions of aggregates via advection and diffusion. Advection is relatively fast and diffusion is expected to be

the main rate-limiting process. Mass-transfer of pesticides is further retarded via sorption-desorption. An increasing number of sorption sites become available as the pesticide slowly moves into the aggregate. Desorption may be a time-dependent process and often requires an activation energy (Pignatello, 2000). Movement back into mobile soil water during leaching events will thus be slower for sorbing than for non-sorbing compounds.

Observed concentrations of bromide in leachate were slightly larger than those calculated on the basis of complete mixing with the entire volume of water present in the samples. This suggests that a small proportion of the soil water may have been excluded from bromide diffusion, possibly due to anion exclusion. Concentrations of bromide in leachate and in soil pore water extracted by centrifugation were independent of the residence time in soil. Relatively small samples of disturbed Lawford soil were used in this study which resulted in short diffusion lengths and a fast distribution of bromide within the contributing soil volume. Renaud *et al.* (2004) carried out a parallel experiment with undisturbed lysimeters (23.5 x 30 cm) of the same soil. The cores were stored outdoors for 3, 9, 24, 37 and 57 days from bromide application and then irrigated with a total of 24 mm over 8 hours (2-5 mm $hour^{-1}$). Concentrations of bromide in leachate decreased from 122 mg l^{-1} three days after application to 15 mg l^{-1} 57 days after application. The Lawford soil is a structured clay which is prone to preferential flow of water and associated solute. The decline in bromide leaching from the lysimeters with time is likely to be due to slow diffusion into soil aggregates where a fraction of the solute is held away from the main regions of flow.

In contrast to bromide, concentrations of chlorotoluron and isoproturon in leachate here decreased with increasing time from application at both incubation temperatures. There are a number of possible reasons for this decrease. A decline in the total amount of pesticide in soil due to degradation is likely to have contributed to the effect. For compounds with non-linear sorption isotherms (i.e. Freundlich exponents < 1), the ratio of sorbed to dissolved pesticide is shifted towards the sorbed state at lower concentrations. As a result, concentrations in soil solution may decline faster with time than the total amount of the pesticide in soil. Additional possible reasons for the decline in leachate concentrations with time include time-dependent sorption and slow diffusion into regions where the pesticide is less available for leaching.

For incubation at 5^{o}C, the decline in leachate concentrations could mainly be attributed to a decline in the total mass of the pesticides in soil due to degradation and to the non-linearity of the Freundlich isotherm. At 15^{o}C, however, concentrations in leachate decreased faster than expected from total residues. Initially, measured pesticide concentrations in leachate matched those expected from equilibrium Freundlich sorption and contribution of the complete soil and water volume to leaching. Later in the experiment, observed concentrations were smaller than the theoretical values. This suggest that factors other than degradation and non-linear sorption have contributed to the observed decline in the availability for leaching. The results for bromide suggest that diffusion of free solute in pore water is not a rate-limiting factor in the relatively small aggregates used in this study. However, pesticides are sorbed onto the pore walls and only a small proportion is available for diffusion. This results in smaller concentration gradients and, thus, slower diffusion compared to non-sorbing compounds. In this situation, diffusion may become a rate-limiting factor. Time-dependent sorption-

desorption of the pesticides may also be of importance. Concentrations of triasulfuron in leachate decreased to a lesser extent than for chlorotoluron and isoproturon. Triasulfuron is sorbed much more weakly than chlorotoluron and isoproturon and the decline in availability for leaching was thus expected to be much less pronounced. A rapid decline in leaching losses of chlorotoluron, isoproturon and triasulfuron from undisturbed lysimeters of the Lawford soil was observed by Renaud *et al.* (2004). Losses of the herbicides declined faster than total residues in soil. In three additional soils tested, triasulfuron loads were relatively constant with time whereas leaching of chlorotoluron and isoproturon decreased. Jones *et al.* (2000) found a strong decrease in losses via drainflow with increasing time from application for isoproturon but not for triasulfuron in a field study on a soil similar to the Lawford soil.

Concentrations in leachate declined faster than expected from constant Freundlich sorption at 15^{o}C but not at 5^{o}C for both chlorotoluron and isoproturon. Pesticides are likely to be concentrated in the outer regions of soil aggregates soon after application and slowly move into the aggregates. Degradation by soil microrganisms occurs mainly in soil solution at the surface and in outer layers of soil aggregates (Scow and Johnson, 1997). The faster decline in availability for leaching at 15^{o}C than at 5^{o}C is thus probably due to a faster degradation of the readily available fraction at higher temperatures. This is in line with results from Cox and Walker (1999) who observed a stronger increase in sorption of linuron and isoproturon at 20^{o}C than at 5^{o}C. Similar effects were found by Walker and Jurado-Exposito (1998) for metsulfuron-methyl, but the increase in sorption was independent of temperature for isoproturon and diuron.

Pesticides are expected to penetrate into the aggregates through advection following application to dry soil, thereby resulting in lower availability for leaching than in initially wet soil. However, no significant effect of soil moisture at the time of application on leaching of isoproturon was observed. Johnson *et al.* (1999) also found no effect of antecedent moisture conditions on the release of isoproturon from soil aggregates into a bathing solution. It was hypothesised that the pesticide is prevented from moving rapidly into the aggregates due to its sorption. The pesticide will remain close to the surface of soil aggregates and transport into the inner regions by advection is limited. Brown *et al.* (2001) found no significant effect of the variation in soil moisture content prior to and after application upon subsequent losses of three herbicides to drains in a lysimeter experiment. In the current study, initially dry and wet aggregates were adjusted to identical moisture conditions one day after application to the dry soil. Results suggest that the subsequent diffusion of the pesticide to less accessible sorption sites inside the aggregates was independent of antecedent moisture conditions.

The centrifugation technique used in this study was suitable to extract water from the heavy clay soil. A tension of 200 kPa was applied in experiments 1 and 2. This corresponds to the empirical boundary between mobile and immobile soil water selected by Addiscott (1977). Concentrations of the three pesticides in soil pore water declined at a rate similar to that for concentrations in leachate. The proportion of applied substance that was present in pore water was larger for the weakly sorbed triasulfuron than for chlorotoluron and isoproturon. Results suggests that the centrifugation technique may be useful to characterise the fraction of a pesticide that is available for leaching.

The experiments confirm several previous findings reported in the literature where pesticide availability for leaching decreased with increasing residence time in soil. The decline is often faster than can be expected from degradation alone. The shift towards the non-available state is due to slow mass-transfer into and out of soil aggregates and/or slow desorption. The extent of the decline in availability depends on the rate of depletion of the readily available fraction by degradation and leaching events in relation to the rate of slow mass-transfer. It is thus influenced by pesticide properties and environmental conditions and may be greater at higher temperatures.

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Figure 1: Concentrations of chlorotoluron, isoproturon and triasulfuron in leachate (triangles; means and standard deviations of four replicates), extracted soil pore water (squares; means and standard deviations of four replicates) and bulk soil (circles; means of two replicates) at 5^{o}C and 15^{o}C

Figure 2: Measured concentrations of chlorotoluron and isoproturon in leachate at 5^{o}C and 15^{o}C and those calculated on the basis of constant Freundlich sorption

Figure 3: Concentrations of isoproturon in leachate and soil pore water extracted by centrifugation (means and standard deviations of four replicates) and bulk soil residues (means of two replicates)

Table 1: Pesticide properties (Tomlin, 1997) and formulations used

	IUPAC name	Molecular weight ($g\ mol^{-1}$)	Solubility in water ($mg\ l^{-1}$)	Octanol-water partition coefficient (log P)	Commercial formulation used in this study
CT	3-(3-chloro-p-tolyl)-1,1-dimethylurea	212.7	74 (at 25°C)	2.5 (at 25°C)	Alpha Chlorotoluron 500 (43.9% w/w suspension concentrate)
IPU	3-(4-isopropylphenyl) -1,1-dimethylurea	206.3	65 (at 22°C)	2.5 (at 20°C)	Steffes IPU (44% w/w suspension concentrate)
TSU	1-[2-(2-chloroethoxy)phenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea	401.8	815 (at pH 7)	-0.59 (at pH 6.9)	Teal A (20% w/w water dispersible granule)

Table 2: Experimental conditions

	Substance applied	Applied concentration ($mg\ kg^{-1}$)	Soil moisture content before application (% w/w)	Soil moisture content during incubation (% w/w)[a]	Incubation temperature (^oC)	Sampling intervals
Experiment 1	Bromide	602.3	35.8	41.8	15	1 h, 6 h, 14 h, 1 d, 3 d, 7 d, 15 d
Experiment 2[b]	CT	19.2	40.5	46.5	5	1 h, 6 h, 1 d, 3 d, 10 d, 21 d, 35 d
	IPU	19.5	40.5	46.5	5	1 h, 6 h, 1 d, 3 d, 10 d, 21 d, 35 d
	TSU	1.6	40.5	46.5	5	1 h, 6 h, 1 d, 3 d, 10 d, 21 d, 35 d
	CT	19.2	40.5	46.5	15	1 h, 6 h, 1 d, 3 d, 7 d, 14 d, 28 d
	IPU	19.5	40.5	46.5	15	1 h, 6 h, 1 d, 3 d, 7 d, 14 d, 28 d
	TSU	1.6	40.5	46.5	15	1 h, 6 h, 1 d, 3 d, 7 d, 14 d, 28 d
Experiment 3	IPU	19.8	16.2	35.2	15	1 d, 4 d, 7 d, 15 d, 28 d
	IPU	19.8	29.2	35.2	15	1 h, 25 h, 3 d, 7 d, 15 d, 28 d

[a] Soil used for the three experiments was taken from the field at different times and the aggregates differed somewhat in size and shape. This may explain the differences in absolute water contents at 90% field capacity.

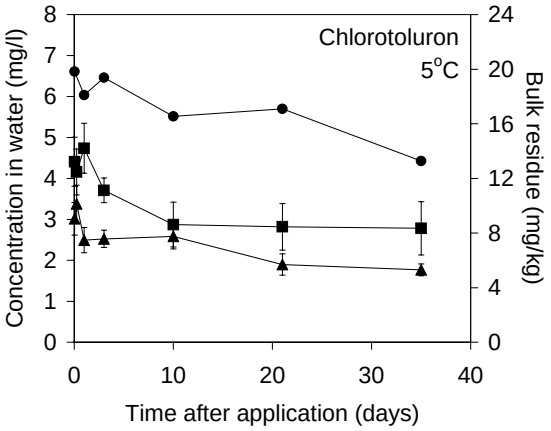
[b] Samples taken at 6 hours after application were not analysed for total soil residues

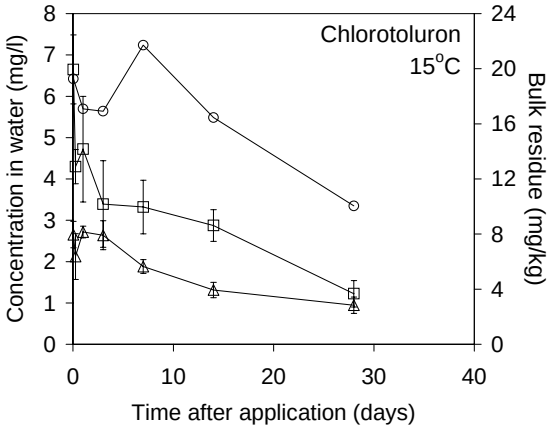
Table 3: Volumes of water added to 10 g soil and average volumes collected during leaching and centrifugation

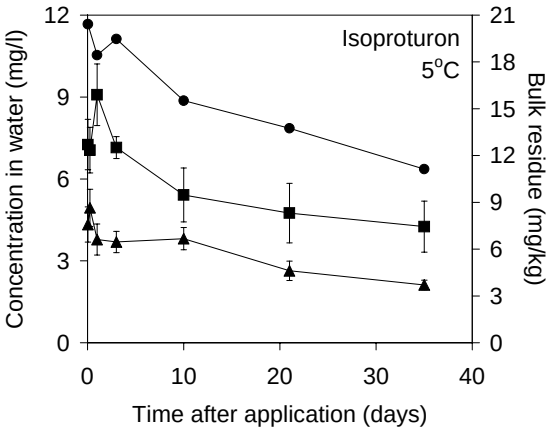
	Soil moisture content during incubation (ml)	Irrigation (ml)	Leachate (ml)	Pore water extracted (ml)	Pore water extracted (% of initial)
Experiment 1	4.18	14.9	14.0	0.59	14.1
Experiment 2	4.65	16.0	15.1	0.28	6.1
Experiment 3	3.52	13.7	13.0	0.30	8.4

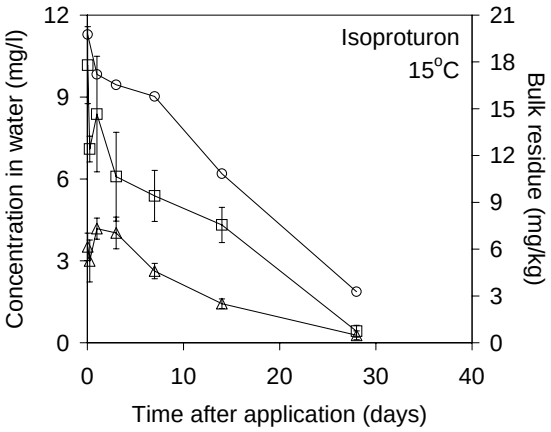
Table 4: Times for 50% decrease of the initial mass of chlorotoluron and isoproturon (DT50) in leachate, soil pore water and bulk soil at 5°C and 15°C

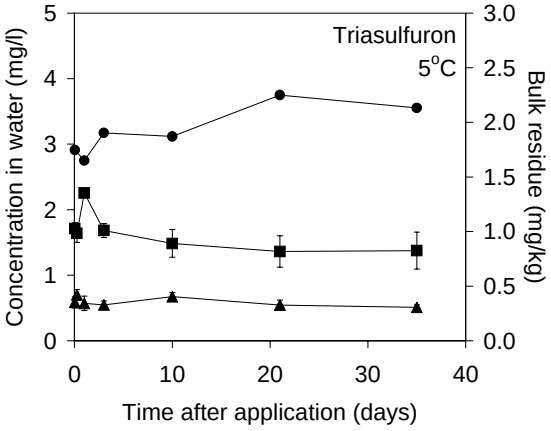
		5°C		15°C	
		DT50 (days)	r^2	DT50 (days)	r^2
CT	Leachate	42.0	0.59	17.4	0.74
	Soil pore water	41.6	0.51	12.9	0.64
	Total soil residues	73.5	0.79	39.2	0.74
IPU	Leachate	32.8	0.69	11.1	0.77
	Soil pore water	34.0	0.61	10.1	0.77
	Total soil residues	40.4	0.93	15.1	0.88

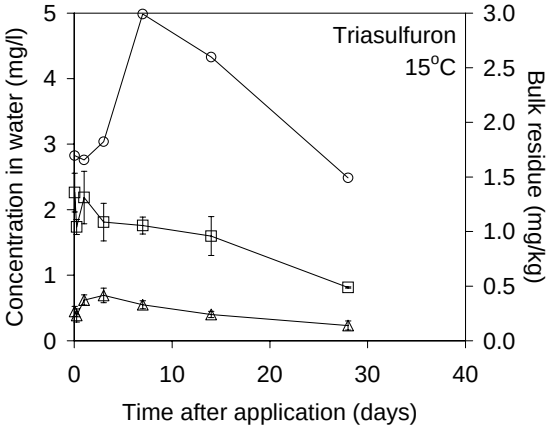

Chlorotoluron
5°C
Concentration in water (mg/l)
Bulk residue (mg/kg)
Time after application (days)

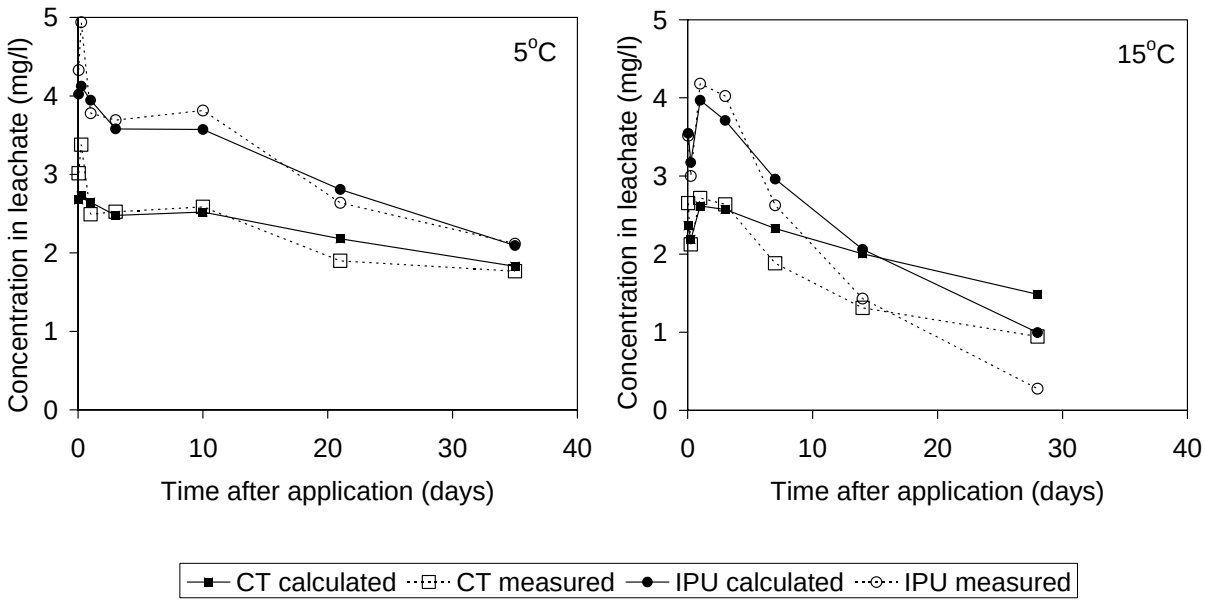

Chlorotoluron
15°C
Concentration in water (mg/l)
Bulk residue (mg/kg)
Time after application (days)

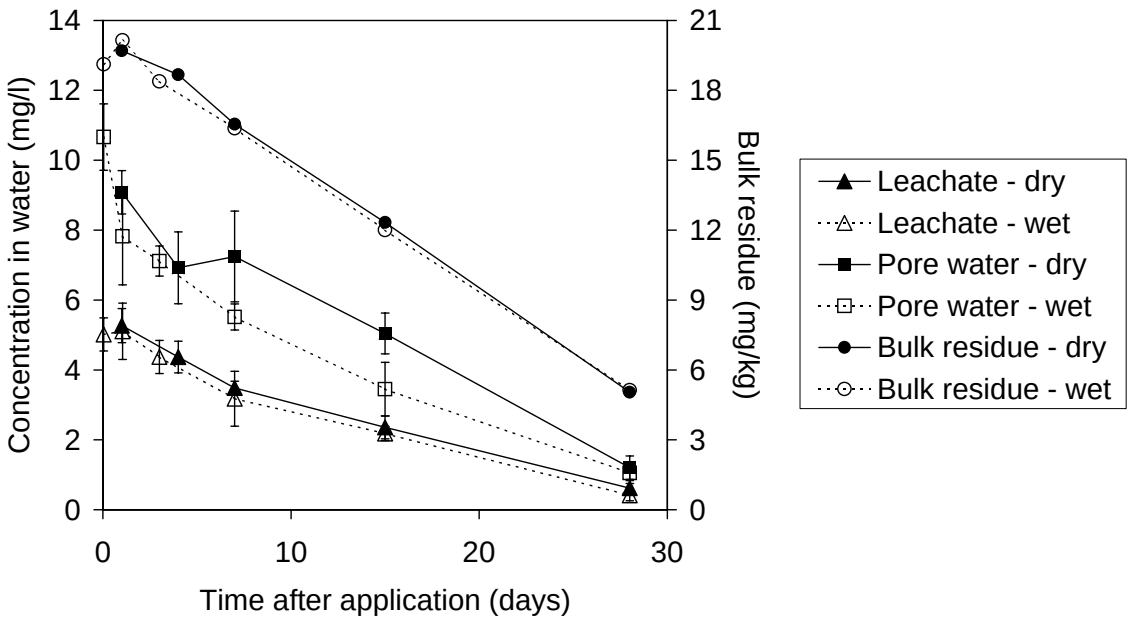

Isoproturon
5°C
Concentration in water (mg/l)
Bulk residue (mg/kg)
Time after application (days)


Isoproturon
15°C
Concentration in water (mg/l)
Bulk residue (mg/kg)
Time after application (days)


Triasulfuron
5°C
Concentration in water (mg/l)
Bulk residue (mg/kg)
Time after application (days)


Triasulfuron
15°C
Concentration in water (mg/l)
Bulk residue (mg/kg)
Time after application (days)


5°C
15°C
Concentration in leachate (mg/l)
Time after application (days)
0
1
2
3
4
5
0
10
20
30
40
CT calculated
CT measured
IPU calculated
IPU measured


Concentration in water (mg/l)
Bulk residue (mg/kg)
Time after application (days)
0
2
4
6
8
10
12
14
0
3
6
9
12
15
18
21
0
10
20
30
Leachate - dry
Leachate - wet
Pore water - dry
Pore water - wet
Bulk residue - dry
Bulk residue - wet



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Influence of kinetic sorption and diffusion on pesticide movement through aggregated soils

Beulke, Sabine; Brown, Colin D.; Fryer, Christopher J.; van Beinum, Wendy

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