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Influence of Soil Aggregate Size on Atrazine and Trifluralin Leaching

S. M. Novak,[1,2] J.-M. Portal,[1] M. Schiavon[2]

[1] Centre de Pédologie Biologique, CNRS FRE 2111, associated with H. Poincaré University, B.P. 5, 54501 Vandœuvre-lès-Nancy Cédex, France
[2] Laboratoire Sols et Environnement ENSAIA–INRA/INPL, B.P. 172, 54505 Vandœuvre-lès-Nancy Cédex, France

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Several studies have provided evidence that pesticides can be transferred rapidly at high concentrations beyond the root zone in well structured soils (e.g. Kladivko et al. 1991; Johnson et al. 1994; Brown et al. 1995). Since the maximum concentration permitted in drinking water is relatively low (0.1 μg L^{-1} as set by the directive 80/778 of the EU for a single pesticide), this leaching may threaten the quality of drinking water resources.

The main parameters affecting pesticide leaching losses are related to: (i) climatic conditions, (ii) soil properties and (iii) physicochemical characteristics of the pesticide (Nicholls 1988). Under given agro-pedo-climatic conditions, pesticide losses can be limited by choosing the suitable soil management and active ingredient. Recently, Brown et al. (1999) showed that total losses of the herbicide isoproturon were three times lower with a finer, deeper topsoil tillage of a heavy clay soil than with a standard agricultural tillage.

The main objective of the work described here was to study the influence of soil structure and sorption properties on the leaching of pesticides. Experiments were conducted using columns repacked with aggregates of different sizes and treated with two herbicides (atrazine and trifluralin), and a conservative, non-interactive tracer (bromide). In order to differentiate between the effect of structure and the effect of the physico-chemical properties of the soil, the leaching experiments were conducting using two soils with contrasting texture. An additional objective was to identify the mode of transport of the two herbicides, i.e. in the aqueous phase or sorbed on soil particles that were suspended in the leachate.

MATERIALS AND METHODS

The plough layer of a clay Vertic Cambisol and a loamy Stagnic Luvisol (Table 1) was used for the experiments. Soils were air-dried and sieved through 1-, 5-, 13- and 20-mm mesh sieves. The <1-mm fractions were rejected so that four aggregate size classes were obtained for each soil: 1-5, 5-13, 13-20 and >20 mm. Each of the aggregate size classes was used to fill three polyvinyl chloride (PVC) columns to a depth of 18 cm. The columns were made up from a 15-cm internal diameter PVC cylinder, fitted at the bottom with a concave perforated PVC plate

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Correspondence to: M. Schiavon

connected together with a 16-mm internal diameter PVC nozzle. Soil columns were then saturated with water by placing the columns in a tall container half-full of tap water. This allowed for the water to slowly diffuse upward. Once the columns were fully saturated, they were randomly mounted in stands and allowed to drain to field capacity before being treated with herbicides. The columns were kept indoors at a temperature of 10°C.

Table 1. Soil characteristics (0-20 cm).

Soil	pH (water)	Clay (%)	Silt (%)	Sand (%)	Carbon (%)	CEC[a] (cmol kg^{-1})	Bulk density (g cm^{-3})	K_{hs}[b] (m d^{-1})
Vertic Cambisol	8.2	54.2	40.5	5.3	1.90	20.7	1.17	0.100
Stagnic Luvisol	6.6	26.0	52.0	21.9	1.36	17.2	1.28	2.250

[a] Cation exchange capacity
[b] Saturated hydraulic conductivity

Table 2. Characteristics of the treatment (each triplicate of aggregate size classes received one of the three solutions). Herbicides solutions are in methanol.

Treatment	1		2		3	
	atrazine	trifluralin	atrazine	trifluralin	atrazine	trifluralin
[kg ha^{-1}]	3.04	3.00	3.03	2.98	3.00	3.01
[mg L^{-1}]	179.19	176.88	178.24	175.65	177.12	177.34
[10^3 Bq mL^{-1}]	41.52	-	-	56.13	-	-

Two herbicides viz. atrazine (6-chloro-*N*^{2}-ethyl-*N*^{4}-isopropyl-1,3,5-triazine-2,4-diamine) and trifluralin (α,α,α–trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) were chosen because of their contrasting physico-chemical properties. Atrazine and trifluralin have aqueous solubilities of 33 and 0.221 mg L^{-1} (at 20°C and pH=7) and mean organic carbon/water partition coefficients (K_{oc}) of 100 and 15000 mL g^{-1} respectively (Dabène et al. 1995). Atrazine and trifluralin dissolved in methanol (30 mL) were applied by pipet in a cross-hatch pattern to the surface of each column. Three herbicide solutions were prepared: the first contained analytical grade atrazine and trifluralin plus [U-ring-^{14}C]-atrazine (purity 97%, specific activity = 0.56 GBq mmol^{-1}), the second contained analytical grade atrazine and trifluralin plus [U-ring-^{14}C]-trifluralin (purity 99%, specific activity =2.96 GBq mmol^{-1}) and the third contained analytical grade atrazine and trifluralin (Table 2). Each solution was used to treat one of the triplicate columns of each soil aggregate size class. Concentration of the treatment solutions was similar for both herbicides and the resulting equivalent application rate (3 kg ha^{-1}) was slightly greater, but in the same order of magnitude, as the recommended application rate (1.0 kg ha^{-1} for atrazine and 1.2 kg ha^{-1} for trifluralin). In addition a conservative tracer (bromide) was applied uniformly to the surface of each soil column with water (30 mL) at 655 mg L^{-1} Br^{-}, to give an equivalent application rate of 16.6 kg KBr ha^{-1}. Bromide was assumed to have a K_{oc} close to zero. Both photolysis (Crosby and Leitis 1973) and volatilization (Bardsley et al. 1968) greatly affect trifluralin dissipation, so a 2-cm depth bed of air-dried soil aggregates was added immediately after chemicals application and then moistened to 60% of field capacity.

The columns were irrigated once (51.0 mm during 83 min) outdoors with an automatic sprinkler three days after the herbicide application, at a mean air temperature of 8°C. The maximum irrigation intensity was 37 mm h^{-1}, which represented the intensity of a heavy rainfall. The coefficient of variation of the amount applied to the area of the columns was 6.5%. Leachate from each column was collected in brown glass bottles.

The total porosity was calculated using an experimentally determined particle density of 2.65 in the clay soil and of 2.77 in the loamy soil (Cros and Jacquin 1972). Sediment loss was determined by evaporating the water from a sample (100 mL oven-dried at 105°C for 48 h).

After filtration (0.2 µm) of the water samples, bromide was analyzed with an electrophoresis capillary ion analyzer. Conditions were the following: capillary: 60 cm x 75 µm fused silica; wavelength: 254 nm; injection mode: hydrostatic (10 cm height for 30 s); applied voltage: 20 kV. Determination limit was 0.1 mg L^{-1}.

Radioactivity of the leachates containing radiolabelled molecules was determined by counting the supernatant solution (2 x 1 mL) in 10 mL of scintillation fluid (Ultima Gold, Packard Instrument Co.) using a Packard Tri-Carb 2100 TR liquid scintillation counter. These samples were also extracted as follows. For all triplicates, leachates (250 mL) were extracted with dichloromethane (2 x 50 mL). Because of emulsions, the combined extract was frozen. Thereafter the dichloromethane phase was recovered and evaporated to dryness under reduced pressure and redissolved in acetonitrile (2 mL). Recovery rates were 98.0 ± 6.8% (n=3) for atrazine and 88.0 ± 3.7% (n=3) for trifluralin for a fortification concentration of 20 µg L^{-1}. Correction for recovery values was made. The herbicides were determined by reverse-phase high performance liquid chromatography (HPLC) with a diode-array detector. Conditions were the following: Kromasil column C18 (porosity: 5 µm; 250 x 3.9 mm), injection volume: 20 µL. Peak areas were evaluated at 220 nm for atrazine and at 205 nm for trifluralin. The samples were eluted by a gradient of acetonitrile + water (0-5 min, 2 + 3 by volume; 15 min, 4 + 1 by volume; 25 min, 9 + 1 by volume;

35 min, 19 + 1 by volume) at a flow rate of 0.8 mL min^{-1}. Determination limits were 0.1 and 0.5 µg L^{-1} respectively for atrazine and trifluralin.

To distinguish the fraction of herbicides dissolved from the fraction sorbed on soil particles, leachates (210 mL) were centrifuged at 48400 x g at 4°C for 20 min. The fraction of herbicide sorbed on sediments was calculated as the difference between the concentration of the whole leachate and the concentration of the supernatant solution (determined by liquid scintillation or by HPLC after extraction).

Table 3. Physical properties and leachate volume of the two soils columns. Values in brackets are standard deviations.

Aggregate size (mm)	Bulk density (g cm^{-3})	Total porosity (%)	Leachate volume (mL)
	clay Vertic Cambisol		
1-5	0.96 (± 0.01)	63.8 (± 0.2)	760 (± 89)
5-13	0.93 (± 0.01)	64.8 (± 0.3)	970 (± 123)
13-20	0.94 (± 0.02)	64.4 (± 0.6)	735 (± 146)
>20	0.99 (± 0.03)	62.6 (± 1.0)	817 (± 104)
	loamy Stagnic Luvisol		
1-5	1.01 (± 0.01)	63.8 (± 0.2)	949 (± 35)
5-13	0.99 (± 0.00)	64.2 (± 0.1)	927 (± 88)
13-20	0.98 (± 0.01)	64.7 (± 0.3)	983 (± 265)[a]
>20	0.98 (± 0.01)	64.4 (± 0.5)	918 (± 88)

[a] Mean with n=2, due to accidental loss of leachate of the column treated with solution 3.

RESULTS AND DISCUSSION

The resulting bulk densities of the repacked columns (Table 3) were slightly lower than bulk densities measured in the field (Table 1). Therefore the soil columns had a higher inter-aggregate porosity than the plough layer for both soils. Total porosity was approximately the same for each aggregate size of both soils.

There was no difference (P=0.05) in the total volume of leachate collected from the different aggregate sizes of each soil (Table 3). But leachate volumes of the finest aggregates of the clay soil columns were slightly lower than that of the loamy soil. The greater water holding capacity of the finest aggregates of the clay soil was certainly due to a larger microporosity volume, induced by the higher clay content of this soil and the lower inter-aggregate porosity of these aggregate size columns.

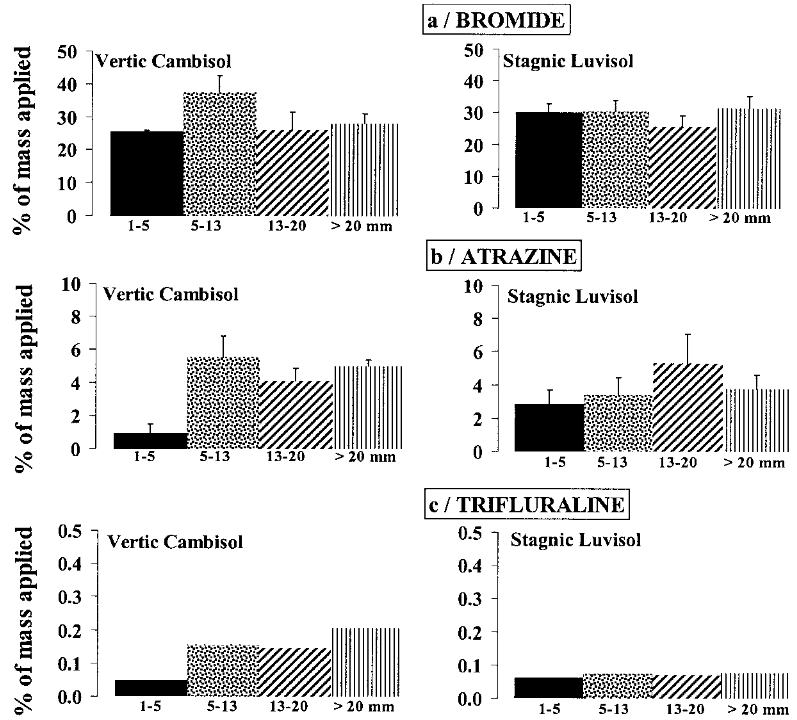

Figure 1. Relative losses of bromide (a), atrazine (b) and trifluralin (c) in the leachates of the clay Vertic Cambisol and the loamy Stagnic Luvisol columns for the 1-5, 5-13, 13-20 and >20 mm aggregate sizes.

Figure 1 gives the amount of bromide and herbicides (% of applied) in the leachates of the triplicate columns. Trifluralin losses were 19-79 times less than those of atrazine, which again were 5-30 times less than bromide losses. These results are in accordance with the K_{oc} and the water solubility of the chemicals, which suggest a mobility increasing in the order: trifluralin< atrazine< bromide. The dissipation of the herbicides by degradation and volatilization can be neglected as the soil columns were watered only 3 days after the treatment and the air temperature was not exceeding 12°C. It should be noted that relative trifluralin losses in leachate are only given for the columns treated with the radiolabelled molecule (treatment 2 in Table 2), because most unlabelled trifluralin concentrations were below the detection limit of the HPLC.

Relative bromide losses showed little differences between the aggregate sizes and between the two soils (Fig. 1). Atrazine and trifluralin losses were also similar for all aggregate size columns of the loamy soil (P=0.05). But the loss patterns of the two herbicides were different for the clay soil. Relative losses of atrazine and trifluralin were indeed the lowest for the finest aggregates, and similar for >5-mm aggregates. The small pore size of the <5-mm columns and its resulting larger aggregate surface area and narrower pore-water velocity distribution may have contributed to increased sorption during herbicides transport. These results show that soil aggregate size has much greater effects on the herbicide transport in clay than in loamy soils.

Relative atrazine losses of <5-mm aggregates columns were lower in the leachates of the clay than of the loamy soil. As atrazine concentrations were lower in the leachates of the <5-mm aggregates columns of the clay (31-100 μg L^{-1}) than in those of the loamy soil (118-198 μg L^{-1}), it is likely that the decreased leachate volumes of the clay soil columns explain only partially the reduced leaching of atrazine. The lower concentration suggests a greater sorption of atrazine on the clay soil, which is consistent with the higher distribution coefficient (K_d) determined by Schiavon et al. (1990) for this soil (K_d=1.76) than for the loamy soil (K_d=1.17). Additionally the inter-aggregate porosity may have been narrower for the clay than for the loamy soil due to swelling of clay, thus increasing the atrazine sorption.
On the other hand, when aggregate size increased (>5 mm), relative herbicides losses were similar for the two soils, whereas atrazine adsorption is greater on the clay soil. Thus, increasing the aggregate size to >5 mm, sharply decreased the amount of herbicides sorbed on the clay soil. This suggests that there were less opportunities for re-sorption of herbicides during the transport through >5-mm aggregates of the clay soil, compared with the loamy soil. This difference may result from the lower saturated hydraulic conductivity of the clay soil (Table 1). The permeability of the surrounding matrix was probably so low that the water mainly flowed through the inter-aggregate macropores, thus decreasing the interactions between herbicides and the soil aggregates. It can also be hypothesized that, during irrigation, the erosion of fine particles of the loamy soil partly sealed its macroporosity, which would increase the sorption surface area. At the field scale, this soil is characterized by a slaking crust, indicating its weak structure stability.

Trifluralin K_d values were not evaluated in either soil, but several authors have reported increased trifluralin sorption with increasing organic matter content and, to a lesser degree, with increasing clay content (Hollist and Foy 1971; Francioso et al. 1992). Our results did however not show any increased sorption on the clay soil, which has the highest organic carbon and clay contents. As trifluralin is a highly sorbed and little soluble molecule, it could also have been transported sorbed onto soil particles. Alternatively, the enhanced transport of trifluralin through the > 5-mm aggregates of the clay soil may have resulted from the larger water flow through the inter-aggregate macroporosity of this soil compared to the loamy soil.

One objective of this study was to determine whether the herbicides were transported in the aqueous phase or bound to soil particles. Since concentrations were similar in the supernatant solutions (after centrifugation) and in the whole leachate (prior to centrifugation), no transport on soil particles seems to have occurred for the two herbicides. Regarding atrazine, this result agrees well with

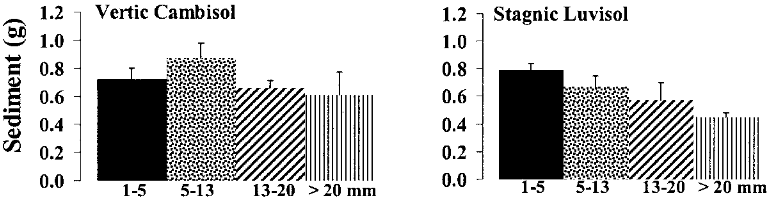

Figure 2. Total sediment losses in the leachates of the clay Vertic Cambisol and the loamy Stagnic Luvisol for the 1-5, 5-13, 13-20 and >20 mm aggregate sizes.

those of Zhang et al. (1997) who found 10- to 20-fold less atrazine in the sediment phase than in the water phase of runoff. Regarding trifluralin, our results are inconsistent with the statement of Wauchope (1978) that pesticides with solubilities ≤ 1 mg L^{-1} are transported partly in the sediment phase of runoff. Additionally, Brown et al. (1995) found that trifluralin losses to drainage water were larger in the sediment phase than in the aqueous phase. However in our study, sediment losses were <1 g (Fig. 2) and trifluralin concentrations were low (<10 μg L^{-1}), so that trifluralin bound to soil particles may not have been detected. The low trifluralin concentration in the leachates, below its water solubility limit, may also have favored its desorption from soils particles to the aqueous phase, all the more so since the leachates were centrifuged only 24 h after being collected. Additionally, the centrifugation may not have separated the dissolved organic matter or fine colloids on which trifluralin may have been bound, from the supernatant solution.

Practically, this study suggests that if a heavy rainfall occurs soon after herbicide application, preparation of a finer tilth would reduce the transport of moderately to strongly sorbed pesticides beyond the plough layer of clay soils, but it would have no effect on pesticide losses from a loamy soil. In any case, even if the soil structure affects the pesticide leaching, the physico-chemical properties of the chemicals are the major determinants for their leaching losses.

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