Effect of grass cover on pesticides transport through soil: Undisturbed column studies and field experiments in the Morcille watershed (Beaujolais)

Sylvie Dousset[A], Mathieu Thévenot[B], Véronique Gouy[C] and Nadia Carluer[C]

[A]LIMOS, Nancy-Université, Vandoeuvre-les-Nancy, France, Email sylvie.dousset@limos.uhp-nancy.fr
[B]Géosystèmes, Université Lille 1, Villeneuve d'Ascq, France, Email mathieu.thevenot@univ-lille1.fr
[C]Milieux Aquatiques, Ecologie et Pollutions, Cemagref, Lyon, France, Email gouy@cemagref.fr, carluer@cemagref.fr

Abstract
The objective of this study is to elucidate the role of grass cover on the leaching of diuron, tebuconazole and procymidone through undisturbed soil columns of a bare vineyard soil and a grass-covered soil. Run-off events containing a mixture of the three pesticides were simulated. Lower quantities of the three pesticides leached through the buffer zone soil (from 6.7 to 24.3% of the initial amount in runoff) than the bare soil (from 8.0 to 55.1%), in correspondence with their adsorption coefficients, which were from 4 to 6 times higher in the buffer zone than in the bare soil. Diuron was recovered in higher amounts in leachates (from 14.6 to 32.2%) than tebuconazole (from 6.7 to 8.0%), in agreement with their adsorption coefficients. However, despite having an adsorption coefficient similar to that of diuron, more procymidone ($K_d = 4.2$-14.1 L/kg) was recovered in the leachates (from 24.3 to 55.1%). This may be due to facilitated transport of procymidone by dissolved organic matter. Thus even in this very permeable soil, higher organic matter contents associated with grass-cover reduce the amounts of pesticide leaching and limit the risk of ground water contamination by the pesticides. The results are in agreement with field observations.

Key Words
Buffer zone, vineyard soil, leaching, herbicide, fungicide, commercial formulation.

Introduction
Many recent studies have reported the presence of pesticide residues, at concentrations higher than the European Quality Standards, in surface- or ground-waters near several vineyards. Consequently, agricultural institutions advise wine producers to use alternative practices to chemical weeding, and to reduce pesticide transfer such as grass-covered inter-row vineyard or buffer zones. Several studies have shown that the amount of pesticide in the run-off from vegetated buffer zones is lower than the amount entering the zone (Patty *et al.* 1997; Watanabe and Grismer 2001) due to processes of retention and/or infiltration within the vegetated zone (Kloppel *et al.* 1997; Mersie *et al.* 2003). However, reducing the quantities of pesticides found in surface waters by promoting their infiltration in buffer strips may threaten shallow water tables or even groundwater with pesticide contamination. Very few studies have been conducted on the quantities of pesticides leached from vegetated soils. The Cemagref of Lyon established an experimental site in 2004, in order to assess the efficiency of vegetated buffer zone to reduce pesticide run-off, and the subsequent pesticide infiltration through the buffer zone (Boivin *et al.* 2007). Their results demonstrated a global reduction in pesticide concentrations leached to a 50 cm soil depth relative to the initial concentration of the incoming runoff. Their attempts to quantify the reduction, however, were hampered by the difficulty in making reliable mass balances in the field.

Thus, the objectives of this study were (i) to implement an experiment permitting the comparison of pesticide leaching in a buffer zone soil and a bare cultivated soil, that results in better mass balance control; (ii) to better assess the role of grass cover on water infiltration, and leaching or adsorption of one herbicide (diuron) and two fungicides (tebuconazole and procymidone), through a Beaujolais vineyard soil during run-off events; and (iii) to compare the possible release of pesticides from soils after subsequent run-off events. The results of our work were compared to those obtained at the experimental site in St Joseph by Boivin *et al.* (2007).

Material and methods
Chemicals
Diuron, two of its metabolites (DCPMU and DCPU), tebuconazole, and procymidone were supplied from Cluzeau (Sainte-Foy-La-Grande, France) with > 99% certified purity. Commercial pesticide formulations were used: Canyon (diuron), Folicur EW (tebuconazole) and Sumisclex (procymidone).

Soil sampling and column set-up
The experimental site monitored by Cemagref of Lyon (69, France) is located in the Beaujolais region near St Joseph (Rhône, France). It consists of an experimental plot (25.2 m^2) on a 25% slope laid out on a vegetated buffer zone (an old meadow buffer zone), located between a chemically-treated hillside vineyard and the Morcille stream. The soil is a sandy loam (luvic cambisol, FAO 1998). Undisturbed soil columns (15.5 cm Ø x 20 cm length) were carved and excavated by hand, according to the method described by Dousset *et al.* (2007), in March 2007, before the fields were treated with pesticide. Six columns were prepared: 3 from the bare soil field (B_{L1}, B_{L2}, B_{L3}) and 3 from the buffer-zone field (BZ_{L1}, BZ_{L2}, BZ_{L3}).

Water inflows and experimental set-up
Three artificial inflows (simulating vineyard runoff events) were replicated at three different times (T_0, T_{14} and T_{28} days, respectively) on the soil surface of each column. The first water inflow (T_0) contained a homogeneous mixture of 5 mg/L bromide (Br$^-$) and, 100 µg/L diuron, procymidone and tebuconazole, simulating contaminated runoff after a rainfall event. Br$^-$ was added as a water tracer. A 3.6 L volume of solution was applied onto the surface of each column (176.6 cm^2) equivalent to the 4800 L water volume applied to the experimental vegetated buffer zone (25.2 m^2) in the field experiment monitored by Boivin *et al.* (2007). This simulated runoff corresponds to a < 2-yr rain event frequency (Lacas 2005). The Br$^-$-pesticide solution was applied at a constant flow rate of 10.2 cm/h using a peristaltic pump. Two additional water inflow additions, consisting only of 3.6 L of water, were applied to the columns fourteen (T_{14}) and twenty eight days (T_{28}) after the pesticide application in order to assess potential pesticide release from the soil.

Leachate collection and analyses
Column effluent was collected at 6-min intervals in 250-mL glass bottles. Each leachate sample from the first water inflow (T_0) was kept for analysis. When collecting effluent from the second (T14) and third (T28) water inflow events, three consecutive samples were mixed; so that, column effluent was essentially collected at 18-min intervals. Pesticide residues contained in the leachates were concentrated by solid-phase extraction with an LC-18 bonded silica cartridge (12 mL, Supelclean, Supelco). Pesticide recoveries were 95.8% for diuron, 95.1% for DCPMU, 88.8% for DCPU, 82.6% for procymidone and 55.6% for tebuconazole. All sample concentrations were corrected based on these recovery values. Pesticides and bromide analyses were performed with a Waters HPLC as described by Dousset *et al.* (2007). UV detection was performed at 249 nm for diuron, DCPMU and DCPU, 220 nm for tebuconazole and 203 nm for procymidone and 200 nm for bromide. Detection limits were 1 µg/L for diuron, DCPMU, DCPU, and tebuconazole, 2 µg/L for procymidone and, 0.25 mg/L for Br$^-$.

Soil characterization
The mean porosities were 0.41 ± 0.04 cm^3/cm^3 for the bare soil and 0.49 ± 0.02 cm^3/cm^3 for the grass-covered soil. At the end of the monitoring period, the columns were sectioned into 5 layers, air-dried, weighed, and sieved to 2 mm. All analyses (Table 1) were carried out at INRA-Arras, France.

Table 1. Main characteristics of the soils.

Depth (cm)	> 2 mm fraction	Sand	Silt	Clay	OC	pH$_{H_2O}$	CEC (cmol/kg)
		(------------------------(%)-----------------------)					
			Bare Vineyard soil				
0-2.5	4.5 ± 1.8	85.2 ± 6.6	9.5 ± 4.1	5.3 ± 2.5	0.8 ± 0.2	5.3 ± 0.3	4.1 ± 1.2
2.5-5	4.1 ± 0.7	79.2 ± 6.9	13.2 ± 4.3	7.7 ± 2.6	0.8 ± 0.2	5.0 ± 0.2	5.1 ± 1.9
5-10	9.0 ± 1.4	75.8 ± 3.5	15.2 ± 2.1	9.0 ± 1.5	0.8 ± 0.1	4.7 ± 0.4	6.2 ± 0.9
10-15	8.2 ± 1.4	74.5 ± 2.1	15.8 ± 1.3	9.7 ± 1.0	0.7 ± 0.1	4.8 ± 0.7	6.0 ± 1.4
15-20	4.6 ± 3.2	76.1 ± 4.4	14.6± 2.8	9.2 ± 1.7	0.7 ± 0.2	4.6 ± 0.4	6.5 ± 1.3
			Buffer zone				
0-2.5	1.3 ± 0.7	63.5 ± 10.2	20.4 ± 5.6	14.5 ± 4.0	4.0 ± 2.1	5.7 ± 0.3	10.0 ± 1.3
2.5-5	2.6 ± 1.0	63.2 ± 4.0	21.7 ± 2.9	14.8 ± 1.7	3.5 ± 1.1	5.5 ± 0.4	11.5 ± 2.5
5-10	5.5 ± 4.1	68.1 ± 6.8	18.1 ± 3.1	12.2 ± 1.6	2.2 ± 0.5	5.2 ± 0.1	15.6 ± 8.8
10-15	9.5 ± 1.2	69.9 ± 3.5	18.6 ± 2.3	11.6 ± 1.5	1.4 ± 0.4	5.2 ± 0.3	10.3 ± 4.6
15-20	5.3 ± 4.8	70.9 ± 8.8	17.7 ± 5.9	11.4 ± 2.9	1.3 ± 0.3	5.2 ± 0.1	8.8 ± 1.3

Batch adsorption coefficient measurement
Adsorption of the three commercial pesticide formulations (Canyon, Sumisclex and Folicur EW) to the soils was measured using a batch equilibrium method. Each sample consisted of 2 g of dried soil (0-5 cm depth) mixed with 10 mL pesticide solution, in concentrations ranging from 1 to 10 mg/L, in a 50-ml Teflon centrifuge tube. Sorption isotherms were obtained following the procedure outlined by Dousset *et al.* (2007) and were described using linear isotherms (K_d).

Results
Adsorption isotherms of diuron, tebuconazole and procymidone
The adsorption coefficients of the three soils are higher in the buffer zone soil (K_d = 12.0-42.2 L/kg) than in the bare soil (K_d = 2.2-10.5 L/kg) (Table 2), in relation with their organic carbon contents at the 0-5 cm depth (buffer zone: 3.8%, and bare soil: 0.8%) (Table 1). For the grass-cover and the bare soils, tebuconazole is adsorbed in greater amounts (K_d = 10.5-42.2 L/kg) than procymidone (K_d = 4.2-14.1 L/kg) and diuron (K_d = 2.2-12.0 L/kg). Similar diuron adsorption values were obtained by Lacas (2005) with bare soil from the 0-20 cm depth (K_d = 4.6 L/kg) and buffer zone soil from the 0-5 cm depth (K_d = 14.2 L/kg).

Table 2. Distribution coefficients (K_d) of the 3 pesticides on the bare (B) and the buffer zone (BZ) soils.

Pesticide	Soil	K_d (L/kg)	r^2
Diuron	B	2.20	0.982
	BZ	12.0	0.979
Tebuconazole	B	10.5	0.979
	BZ	42.2	0.983
Procymidone	B	4.2	0.996
	BZ	14.1	0.995

Water infiltration and bromide recovered
The water flow was relatively homogeneous between the triplicates of each soil treatment; the eluted water flow rates were quite similar and constant for both the bare (83 ± 3 mm/h) and the buffer zone (80 ± 0.3 mm/h) soils throughout the three flow events. The buffer zone flow rate is slightly lower than the saturation hydraulic conductivity of 125 mm/h at 15 cm depth reported by Lacas (2005). After the three water inflows, bromide was eluted in greater amounts in the percolates of the bare soil (74.0 ± 1.0%) than in those of the buffer zone soil (59.9 ± 1.2 %) (Table 3). At the St Joseph experimental site, Boivin *et al.* (2007) estimated a bromide leaching rate of 90% of the total amount added in the inflow, at the 50 cm soil depth, which is relatively similar to our results, especially when considering the uncertainty linked to their results (extrapolation of the results from 4 x 2 lysimeters (0.125 m² each) to the total buffer strip (25 m²)).

Table 3. Recovery percentages of initial amounts of bromide and pesticides for the 3 water inflows.

	Eluted water volume (L)	Bromide	Diuron	DCPMU	DCPU	Tebuconazole	Procymidone
B_{L1}	9.7	73.1	31.5	8.9	0.1	3.9	90.1
B_{L2}	9.6	75.1	22.7	7.0	0.1	1.3	24.3
B_{L3}	9.4	73.9	42.5	7.1	2.9	18.7	50.8
Mean ± SD	9.6 ± 0.2	74.0 ± 1.0	32.2 ± 9.9	7.6 ± 1.1	1.0 ± 1.6	8.0 ± 9.4	55.1 ± 33.1
BZ_{L1}	10.2	60.7	12.2	0.2	0.1	4.6	18.2
BZ_{L2}	10.3	58.5	10.3	0.1	0.0	3.7	17.5
BZ_{L3}	10.2	60.5	21.5	0.2	0.2	11.9	37.2
Mean ± SD	10.2 ± 0.1	59.9 ± 1.2	14.6 ± 6.0	0.2 ± 0.1	0.1 ± 0.1	6.7 ± 4.5	24.3 ± 11.1

Pesticides recovered
The quantities of pesticide leached at the end of the three simulations were greater in the bare soil leachates (8.0% to 55.1% of applied) than in those of the buffer zone soil (6.7% to 24.3%) (Table 3). For both soils, the amounts of the pesticides recovered in the leachates varied somewhat between triplicates of a given soil treatment despite having similar pore volumes, coarse fraction contents, and Br⁻ recoveries. Diuron metabolites (DCPMU and DCPU) were recovered in greater amounts in the bare soil leachates (7.6 and 1.0% of the initial amount of parent molecules, respectively) than in those of the buffer zone (0.2 and 0.1%).
Of the total amounts of pesticide leached in the three simulations, diuron was recovered in greater amounts (32.2% and 14.6% of the applied amount)) than tebuconazole (8.0% and 6.7%) in the percolates of bare and buffer zone soils (Table 3), in correspondence with their respective adsorption coefficients (K_d = 2.2-12.0 L/kg and 10.5-42.2 L/kg). However, procymidone was measured in greater amounts in the leachates (24.3 to

55.1%) than either diuron or tebuconazole, contrary to what would be expected based on its adsorption coefficient ((K_d = 4.2-14.1 L/kg) (Tables 2, 3). After the second and third runoff events (14 and 28 days after the first inflow event), low to significant amounts of pesticide were released to the soil solution (11.3-50.4% of the total leached amounts, or, 1.5 to 26.4% of the applied pesticide). The buffer zone soil released less pesticide to the soil solution (0.9 to 12% of the applied amounts) than the bare soil (1.5 to 26.4%) (Table 4) in agreement with their adsorption coefficients. Furthermore, diuron was detected in greater amounts (4.4 to 11.5% of applied) than tebuconazole (0.9 to 1.5%) in the leachates, also in agreement with their respective adsorption coefficients (Table 2) and similar half-lives (Footprint, 2007-2008). Again, procymidone was released in greater amounts (12.0 to 26.4%) than either diuron or tebuconazole (Table 4).

Boivin *et al.* (2007) also found that more diuron (34%) than tebuconazole (31%) leached through the buffer zone at the St Joseph experimental site. Although their values are far higher than ours (8.5% for diuron and 0.8% for tebuconazole), the uncertainty associated with their results must be considered, as suggested for Br⁻.

Table 4. Recovery percentages of initial amounts bromide and pesticides for the (2ⁿᵈ+3ʳᵈ) water inflows.

	Eluted water volume (l)	Bromide	Diuron	DCPMU	DCPU	Tebuconazole	Procymidone
B_{L1}	6.6	7.0	11.9	5.4	0.1	0.7	51.4
B_{L2}	6.5	8.5	12.9	4.6	0.1	0.6	11.1
B_{L3}	6.3	2.1	9.8	4.8	2.9	3.1	16.7
Mean ± SD	6.5 ± 0.1	5.9 ± 3.4	11.5 ± 1.6	4.9 ± 0.4	1.0 ± 1.6	1.5 ± 1.4	26.4 ± 21.8
BZ_{L1}	6.8	0.5	4.0	0.2	0.1	0.2	9.2
BZ_{L2}	6.8	3.6	3.2	0.1	0.0	0.5	9.4
BZ_{L3}	6.8	2.0	5.9	0.2	0.2	1.9	17.5
Mean ± SD	6.8 ± 0.0	2.0 ± 1.6	4.4 ± 1.4	0.2 ± 0.1	0.1 ± 0.1	0.9 ± 0.9	12.0 ± 4.7

Conclusion

More diuron than tebuconazole is recovered in the leachates in agreement with their adsorption coefficients. However, more procymidone than diuron was recovered in the leachates, despite their similar adsorption coefficients. This may be due to the facilitated transport of procymidone by dissolved organic matter. All three pesticides used in this study were eluted in lower amounts through the buffer zone than through the bare soil, in correspondence with their adsorption coefficients, which were from 4 to 6 times higher in the buffer zone than in the bare soil. Consequently, buffer zones not only reduce the risk of contamination of surface waters, but also do not appear to increase the risk of groundwater contamination by pesticides.

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