

Effect of solid olive-mill waste amendment on pesticide sorption and leaching in soil

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Abstract

Organic amendment addition to soil is an agricultural practice that can greatly influence pesticide sorption and movement through the soil profile. In this work, we have investigated the effects of the addition of a solid olive-mill waste (SOMW) on the sorption and leaching of the herbicide simazine in a sandy loam soil. The effect of SOMW addition on soil porosity was also assessed. The soil was amended in the laboratory with SOMW at two different rates (5% and 10% w/w). Simazine sorption isotherms showed a great increase in herbicide sorption after soil amendment with SOMW; sorption increased with the amount of SOMW added. Simazine sorption-desorption isotherms on unamended and amended soil were reversible. Breakthrough curves of simazine in unamended and amended soil columns showed that, upon SOMW addition, simazine concentrations in leachates were greatly reduced and the maximum concentration peak was shifted to larger volumes of water added, thus indicating reduced leaching of simazine in the amended soils. Total amounts of herbicide recovered from the soil columns indicated enhanced degradation and/or irreversible sorption of simazine in the amended soil. Mercury intrusion porosimetry data indicated that SOMW addition to soil gave rise to an increase in the volume of pores with radii about 10 µm. The results showed that SOMW addition may reduce the risk of ground water contamination associated with rapid leaching of simazine in soils.

1 Introduction

The study of pesticide movement throughout the soil profile is of great interest as far as biological performance and groundwater contamination are concerned [1,2]. Sorption and mobility, in general, have been shown to be inversely related [2,3]. Pore size distribution, as accounting for different pore water velocity, is also related to the transport of solute in soils [4].

Organic amendments are used in agriculture to enrich soils of low organic matter content and to improve soil structure. In addition, because organic matter is a primary sorbent for pesticides, organic amendments can also be used to promote pesticide sorption and, therefore, to reduce the risk of ground water contamination associated with pesticide leaching through soil [5].

In a recent study, Cox et al [6] reported important changes in porosity and herbicide leaching after addition of olive-mill wastewater to soil. In this work, we report the effects of the addition of a solid olive-mill waste (SOMW) on sorption-desorption and leaching of the herbicide simazine in a sandy loam soil, sampled from an olive-growing area located in North-eastern Badajoz (Spain). The effect of SOMW addition on soil porosity is also assessed.

2 Materials and Methods

2.1 Soils and herbicide

The soil used in this study came from an olive-growing area located in North-eastern Badajoz (Spain). The soil was sampled (0-25 cm), air-dried, and sieved to pass a 2 mm mesh before used. The soil was amended in the laboratory with 0, 5 and 10% (w:w) of a solid olive-mill waste (SOMW) consisting of the first subproduct ("*alperujo*") of the olive oil extraction. The solid waste was air-dried and ground to a fine powder before its addition to the soil. Some physicochemical characteristics of the unamended and amended soils are given in Table 1.

Table 1: Physicochemical properties of the soils.

Soil property	Unamended soil	Amended soil (5% SOMW)	Amended soil (10% SOMW)
% Organic carbon	0.56	2.21	4.54
pH (H ₂ O)	5.3	5.0	4.8
% Sand	54		
% Silt	35		
% Clay	11		

Simazine [2-chloro-4,6-bis(ethylamino)-1,3,5-triazine] is a non-selective herbicide commonly used in olive-growing areas of Mediterranean regions. It is a colourless solid of melting point= 226°C, vapour pressure= 810×10^{-9} Pa

(20°C), and water solubility = 5 mg L⁻¹. The herbicide simazine used in this study was the high purity compound (purity = 99%) supplied by Riedel-de Haën (Germany).

2.2 Sorption-desorption experiment

Duplicate samples of 10 g of unamended or amended soil were equilibrated (24 h) with 10 mL of simazine initial solutions with concentrations (C_{ini}) ranging from 0.5 to 20 µM prepared in 0.01 M CaCl₂. After equilibration, the suspensions were centrifuged and the equilibrium concentration (C_e) was determined in the supernatant by HPLC (UV detection at 230nm). Previously, it was checked that equilibrium was reached before 24 hours and that no significant degradation occurred during this period. Differences between C_{ini} and C_e were assumed to be sorbed. Sorption isotherms were fit to the logarithmic form of the Freundlich equation (1):

$$\log C_s = \log K_f + N_f \log C_e \quad (1)$$

where C_s (µmol g⁻¹) is the amount of herbicide sorbed at the equilibrium concentration C_e (µmol L⁻¹), and K_f and N_f are the empirical Freundlich constants.

Desorption was measured immediately after sorption by successive dilution from the 5, 10, and 20 µM initial concentration points. After the samples were shaken and centrifuged, 5 mL of supernatant was removed and analysed and 5 mL of 0.01 M CaCl₂ added to the centrifuge tubes. The samples were resuspended, shaken for another 24 hours, centrifuged, and the equilibrium concentration in the supernatant was determined. This desorption procedure was conducted three times.

2.3 Leaching experiment

Leaching was studied in 30 × 5 cm methacrylate columns made up of six 5 cm-long sections sealed with silicon. The top ring was filled with sea sand and the bottom ring with sea sand plus glass wool, to minimise losses of soil and contamination of leachates with soil particles. The other four rings were hand-packed with 600 g of unamended or amended soil. The soil columns were saturated with 0.01 M CaCl₂, allowed to dry for 24 h, and then the amount of simazine corresponding to its maximum application rate in soils (2.3 kg ha⁻¹) was applied to the top of the columns dissolved in 2.25 mL of methanol. The columns were leached with 0.01 M CaCl₂ at a rate of 50 mL day⁻¹ until no herbicide was detected by HPLC in the leachates. Leachates containing the herbicides were collected daily, filtered and analysed by HPLC. At the end of the leaching experiment, soil samples (20 g) from the different rings were extracted once with 30 mL of methanol by shaking mechanically at 20 ± 2°C for 24 h. The suspensions were centrifuged, filtered, and analysed by HPLC in

order to determine the residual amount of simazine at the different depths of the soil column. Preliminary experiments showed that this extraction procedure recovered > 95% of the herbicide freshly applied to the soil. The leaching experiment was conducted in triplicate.

2.4 Porosity measurement

At the end of the leaching experiment, aliquots of soil (1 g) were sampled from the bottom ring of the columns and their pore size distribution from $4 \cdot 10^4$ to 3.7 nm was determined using a Carlo Erba 2000 mercury intrusion porosimeter. A value for the surface tension of mercury of $\gamma = 0.48 \text{ N m}^{-1}$ and a mercury solid contact angle of $\theta = 171.3^\circ$ were assumed to use the Washburn [7] equation for the calculation of the pore size distributions.

3 Results and Discussion

3.1 Sorption-desorption isotherms

Simazine sorption on soil greatly increased upon SOMW addition (Figure 1, Table 2). Sorption increased with the amount of SOMW added, clearly indicating the role of the organic amendment in simazine sorption. Simazine sorption isotherm on unamended soil was L-type ($N_f < 1$) according to the Giles et al. [8] classification, whereas a higher degree of linearity was observed for the sorption isotherms on amended soil, in particular for the soil amended with 10% SOMW. Linear isotherms have previously been reported for triazine sorption and may reflect the principal role of organic matter in the retention mechanism [9,10]. The fact that variability between K_f values was greatly reduced after normalisation to the organic carbon content (K_{f-oc} values in Table 2) supports organic matter played a fundamental role in simazine retention [11].

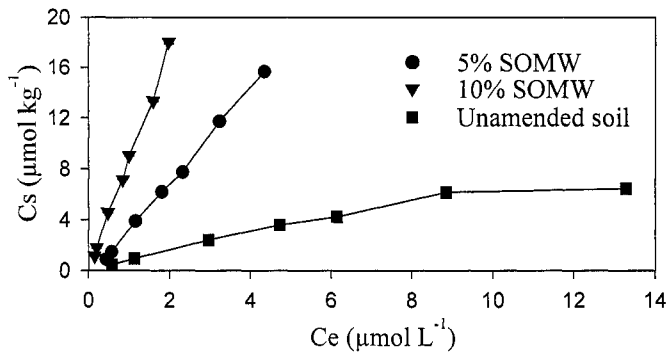


Figure 1: Simazine sorption isotherms on unamended and amended soil.

Table 2: Freundlich coefficients for simazine sorption on unamended and amended soil.

Soil	K_f	N_f	R^2	K_{f-oc}
Unamended	0.94 ± 0.10	0.82 ± 0.06	0.975	167 ± 17
Amended (5% SOMW)	2.99 ± 0.11	1.16 ± 0.04	0.995	135 ± 5
Amended (10% SOMW)	8.80 ± 0.20	0.99 ± 0.03	0.996	193 ± 4

Simazine desorption branches from three different concentrations showed in general low or even negative hysteresis for both unamended and amended soils (Figure 2), which indicates a high reversibility of the sorption-desorption process. Cases of negative hysteresis (i.e., the desorption branch lies below the sorption isotherm) have previously been found in sorption-desorption studies with triazine herbicides and related to highly reversible sorption mechanisms [12,13]. Reversibility from high concentration points was even greater than that from low concentration points, probably as a result of sorption site heterogeneity [14]. The soil amended with 10% SOMW displayed ill-defined desorption isotherms, because the very high simazine sorption by this soil made the desorption analysis complicated [12].

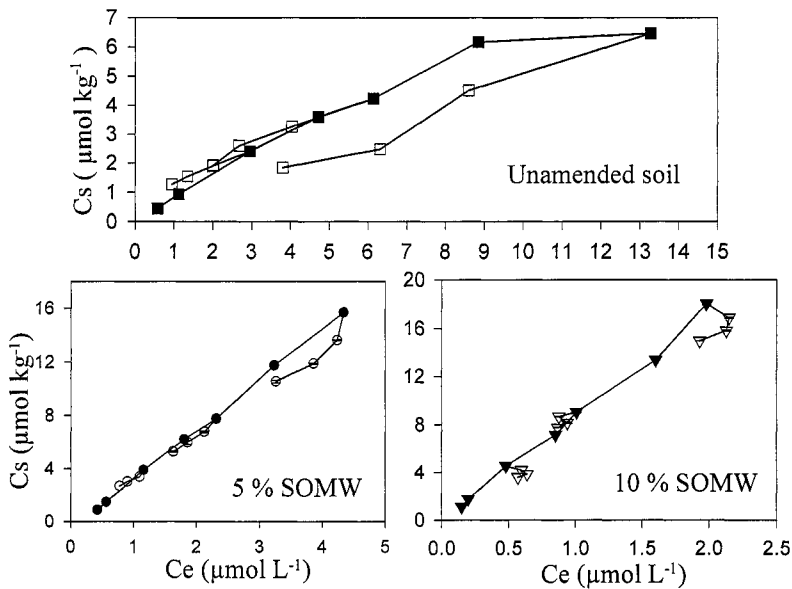


Figure 2: Simazine sorption-desorption isotherms on unamended and amended soil. Solid symbols are sorption points, whereas open symbols are desorption points.

3.2 Leaching study

Figure 3 shows relative and cumulative breakthrough curves of simazine in unamended and amended soil columns. The maximum concentration of simazine in leachates decreased from 4 μM in the unamended soil to 2 μM and 1 μM in the soil amended with 5% and 10% SOMW, respectively. In addition, retardation of simazine breakthrough as a result of SOMW addition to soil is evident in Figure 3a. Thus, the maximum concentration peak was shifted from 550 mL of water added in the unamended soil to 1400 and 2500 mL in the amended soils (Figure 3a). Pore size distributions of the soils, showing an increase in the volume of pores with radii about 10 μm upon SOMW addition (Figure 4), could not account for the slower breakthrough of simazine in the amended soil. This suggests that the sorptive properties provided by the organic matter of SOMW more than a change in soil porosity was responsible for the reduced leaching of simazine observed in the amended soils. This is supported by the good correlation ($R^2= 0.96$) found between simazine retardation in soil columns (position of the maximum concentration peak) and the Freundlich K_f values obtained in batch experiments for the different soils [2].

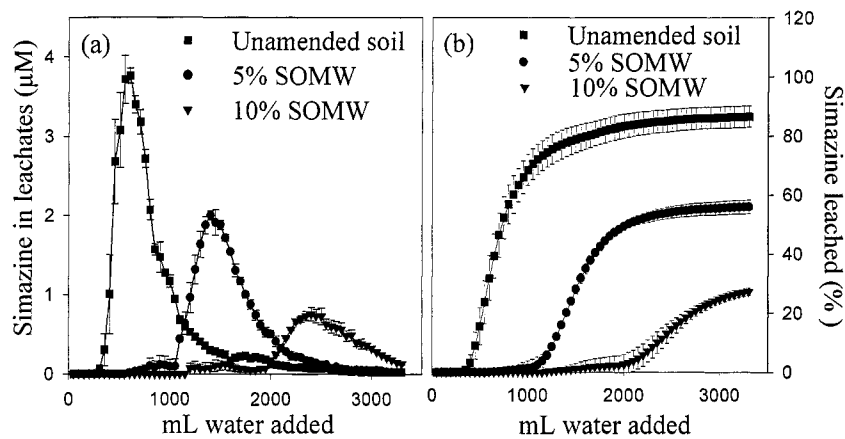


Figure 3: Simazine breakthrough curves in unamended and amended soil:
a) relative BTCs, b) cumulative BTCs.

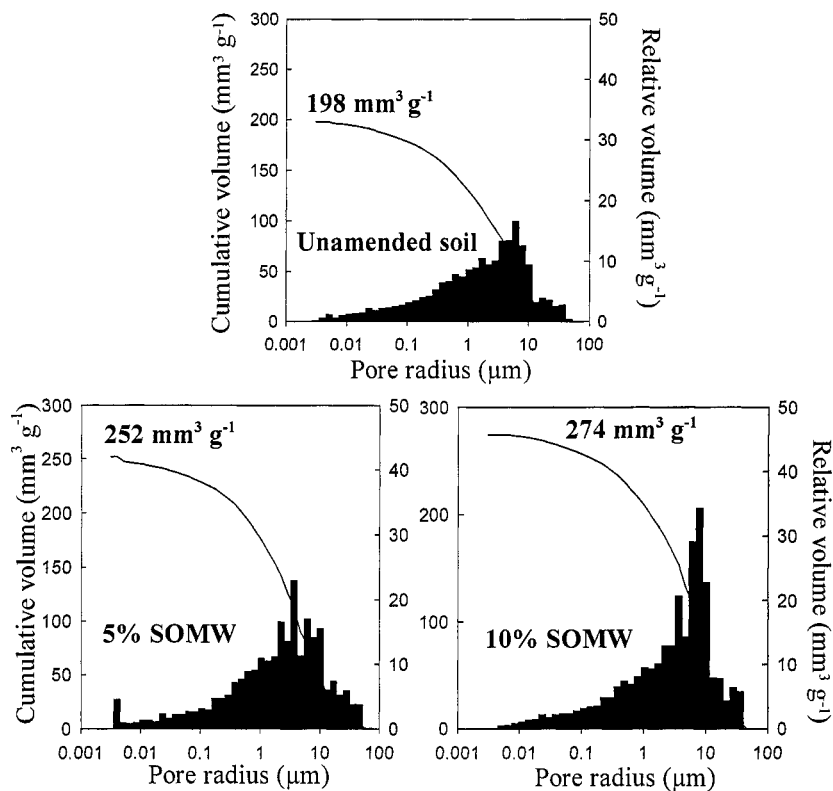


Figure 4: Relative and cumulative mercury pore volume of unamended and amended soil.

Cumulative breakthrough curves of simazine (Figure 3b) showed that total amounts of simazine leached from the soil columns were significantly lower for the amended soil (56% and 27%) compared to the original soil (87%). Although some of the herbicide not leached in the amended soil was found to be extractable from the soil columns after the leaching experiment (Table 3), a significant amount of the simazine applied to the soil columns was not recovered either in leachates or by extraction of the soil after the leaching experiment. This amount may represent herbicide degraded or irreversibly bound to the soil particles. In any case, SOMW addition led to slower breakthrough and reduced leaching of simazine, suggesting that the use of this organic amendment may be helpful in decreasing the risk of ground water contamination associated with rapid leaching of simazine in soils.

Table 3: Simazine leached, extracted from the soil column, and not recovered during the leaching experiment.

	Unamended soil	5% SOMW	10% SOMW
Leached (%)	87 \pm 2	56 \pm 1	27 \pm 4
Extracted (%)	0	10 \pm 5	21 \pm 9
Not recovered (%)	13	34	52

4 Conclusions

The results of this study indicate that solid olive-mill waste addition to soil can significantly influence the fate of other compounds used in agriculture, such as pesticides. In particular, solid-mill waste addition to soil slightly increased soil porosity and greatly enhanced sorption of the herbicide simazine, thus reducing the vertical movement of the herbicide through the soil. Organic wastes, such as SOMW, can therefore be used to attenuate pesticide leaching in soil, preventing movement of the pesticide from the surface horizon and decreasing the risk of ground water contamination.

5 Acknowledgement

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