Raw or Incubated Olive-Mill Wastes and Its Biotransformed Products as Agricultural Soil Amendments—Effect on Sorption–Desorption of Triazine Herbicides

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Raw olive-mill waste and soil amendments obtained from their traditional composting or vermicomposting were added, at rates equivalent to 200 Mg ha^{-1}, to a calcareous silty clay loam soil in a laboratory test, in order to improve its fertility and physicochemical characteristics. In particular, the effects on the sorption−desorption processes of four triazine herbicides have been examined. We found that comparatively hydrophobic herbicides terbuthylazine and prometryn increased their retention on amended soil whereas the more polar herbicides simazine and cyanazine were less affected. Soil application of olive cake, without transformation, resulted in the highest herbicide retention. Its relatively high content in aliphatic fractions and lipids could explain the increased herbicide retention through hydrophobic bonding and herbicide diffusion favored by poorly condensed macromolecular structures. On the other hand, the condensed aromatic structure of the compost and vermicompost from olive cake could hinder diffusion processes, resulting in lower herbicide sorption. In fact, the progressive humification in soil of olive-mill solid waste led to a decrease of sorption capacity, which suggested important changes in organic matter quality and interactions during the mineralization process. When soil amended with vermicompost was incubated for different periods of time, the enhanced herbicide sorption capacity persisted for 2 months. Pesticide desorption was reduced by the addition of fresh amendments but was enhanced during the transformation process of amendments in soil. Our results indicate the potential of soil amendments based on olive-mill wastes in the controlled, selective release of triazine herbicides, which varies depending on the maturity achieved by their biological transformation.

KEYWORDS: Simazine; terbuthylazine; prometryn; cyanazine; soil; sorption−desorption; olive cake; compost; vermicompost

INTRODUCTION

The olive culture is of utmost importance for the Mediterranean countries, with the European Union and Tunisia leading in world olive oil production, which accounted for 75 and 8%, respectively, in the 1998/1999 campaign (*1*). The olive culture in Spain amounted to 11% of the national agricultural surface, representing about 2.42 × 10^6 ha (http://www.mapya.es). In Andalusia, with ca. 60% of the total national production, olive oil in the 2002−2003 campaign accounted for ca. 680000 Mg.

This culture generates important amounts of industrial wastes with high organic contents, such as olive cake, which can be used like other amendments to improve soil fertility and modify the soil physical and chemical properties of semiarid Mediterranean soils (*2−6*). It has been shown that agricultural wastes of the olive culture can be used without further treatment (*7,*

8). In particular, solid olive-mill waste applied to soil resulted in an increase of simazine and imazaquin retention, with a positive effect of reducing herbicide leaching into groundwater (*3, 9−11*). However, olive cake may have a high electrical conductivity and ammonia concentration (*12*), and it contains potentially antimicrobial compounds such as polyphenols and phytotoxic substances such as organic acids. Consequently, if applied as received, olive cake waste could have a negative environmental impact. For this reason, and depending on olive cake use and management, its biological transformation has been encouraged to stabilize its organic matter (*13*).

In fact, these wastes can be stabilized by treatments based on either bacterial transformation (anaerobic and aerobic digestion) or chemical means (irradiation, heat, chlorine, etc.) (*4*). Olive cake modification by composting or vermicomposting (*12, 14, 15*) usually results in a decrease of total organic matter content and water-soluble fractions (*4*). The addition of these stabilized byproducts to the soil increases crops yield (*16, 17*) and reduces the impact of disposal methods on environmental

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Table 1. Analytical Characteristics of Raw Substrates and Elementary Composition of the HA-like Fraction

| | | | g/100 g (ashfree basis) | | | | | atomic ratios | |
	pH	lipids (g kg^{-1})	C	H	O	N	C/N	H/C	O/C
S	7.9	5.8×10^{-2}	49.7	5.2	40.9	4.2	11.8	1.26	0.61
A	5.8	71.5	58.2	7.5	31.4	2.9	19.9	1.55	0.40
C	8.8	1.3×10^{-1}	51.3	6.4	37.7	4.6	11.0	1.49	0.54
V	7.8	1.2	52.2	5.4	38.9	3.5	14.9	1.24	0.55

Table 2. Organic Carbon and pH ($\pm$ Standard Deviation) of Nonamended and Amended Soil at Different Incubation Times (0, 1, 2, and 3 Months)[a]

| | C (g kg^{-1}) | | | | pH | |
	0	1	2	3	0	3
S	21.8	21.0	20.3	18.9	7.9 ± 0.1	7.7 ± 0.1
SA	48.9	47.2	45.6	35.4	7.1 ± 0.1	7.5 ± 0.1
SV	36.7	35.5	34.4	33.1	7.7 ± 0.2	7.6 ± 0.2
SC	37.1	35.0	33.0	32.5	7.9 ± 0.1	7.7 ± 0.1

[a] S, nonamended soil; SV, SC, and SA, soils amended with vermicompost, compost, and olive cake, respectively.

quality. In fact, vermicomposting of olive-mill solid waste has been related to a decrease of its toxicity linked to a reduction in the polyphenols concentration (18). Apart from this, in traditional agricultural practices, fresh and composted or vermicomposted olive cakes can also be transformed in the field to reach increased maturity. In this process, its organic matter content is qualitatively modified with the concomitant biodegradation of its accompanying toxic organic compounds (2).

Although several authors have reported a significant effect on pesticide retention of soil amendments rich in organic matter, such as sewage sludge, peat, or manure (19−21), less information is available about the effect of transformation in soil of composted and, especially, vermicomposted amendments (4, 16, 22−25).

The increased retention of herbicides when amendments are added to soil may result in a decrease of their efficacy in weed control, a fact that would probably lead to the increase of herbicide doses.

In the present research, we have evaluated the changes in the sorption−desorption processes of four triazine herbicides produced by the addition to a calcareous soil of raw and biotransformed olive-mill wastes, with special emphasis paid on the effect of different transformation periods of the additives in soil on the above-mentioned processes.

MATERIALS AND METHODS

Soil and Organic Amendments. Soil (S) was sampled from the upper layer (0−25 cm) of an olive orchard located near Iznalloz (Granada province, Southern Spain), air-dried, and passed through a 2 mm sieve. It was a Calcaric Regosol, with a silty clay loam texture, 340 g kg^{-1} clay, 560 g kg^{-1} loam, and 100 g kg^{-1} sand, containing 441 g kg^{-1} CaCO$_3$. The total organic carbon content determined by oxidation with K$_2$Cr$_2$O$_7$ (26) was 21.8 g kg^{-1}, and the pH (5/20 soil/water ratio) was 7.9 ± 0.1.

The amendments used, air-dried and sieved <2 mm, were prepared from olive-mill wastes and consisted of olive cake from a two-stage centrifugation process (alperujo in Spanish, A), compost from olive cake (C), and vermicompost from olive cake (V). The olive cake was obtained from an olive oil industry (Romeroliva, Deifontes, Granada, Spain). The mature compost, supplied by Sociedad Cooperativa Sierra de Génave (Jaén, Spain), was prepared from a mixture of fresh olive cake, olive leaves, and manure at a ratio of 7:4:1 (dw:dw), to form a compost pile of 40 m^3. The compost pile was mechanically turned once a month for 6 months. The material was then left undisturbed for a further 3 month maturation period. The vermicompost was produced at the Estación Experimental del Zaidín (CSIC) (Granada, Spain). The latter was prepared from a mixture of olive cake and municipal biosolids at a ratio of 8:1 (dw:dw) vermicomposted for 6 months with clitellated and nonclitellated earthworms of the species *Eisenia andrei* (15).

Lipid and Humic Acid (HA) Fractions. The total lipid content was determined by Soxhlet's extraction with 40−60 °C petroleum ether, dehydrating with anhydrous Na$_2$SO$_4$, and weighing (**Table 1**). The presumably most active macromolecular fraction, the HA-like substance, was isolated and purified for further analyses. Successive extractions of soil and amendments were carried out with 0.1 M Na$_4$P$_2$O$_7$ to isolate the HA-like fraction. After the samples were shaken for 1 h with the extractant, the suspensions were centrifuged at 3000 rpm for 10 min

(Beckman J2-21). The residue after centrifugation was subjected to four successive extractions with 0.1 M NaOH. The total humic extract obtained by mixing the alkaline supernatant solutions after centrifugation was acidified to pH 1 with HCl to precipitate the HA. The acid extract was removed by siphonation, and the residue was centrifuged at 3000 rpm for 10 min and then redissolved in 0.5 M NaOH. The solution with sodium humate was centrifuged at 20000 rpm for 10 min. The alkaline supernatant solution was reprecipitated with HCl and dialyzed in distilled water until salt-free. The resulting HA suspension was dried at 50 °C and kept for chemical analyses.

The elemental analysis of HA (C, H, O, and N, ash-free basis) was carried out with a Carlo Erba CHNS-O-EA1108 microanalyzer. The oxygen was calculated by difference. The ash content was determined after combustion at 550 °C for 8 h (**Table 1**).

Soil Incubation with Organic Amendments. Five liter polyvinylchloride containers were used for the experiments. Each container received 3 kg of soil, alone or mixed with each of the amendments indicated above. A dosage equivalent to 200 Mg ha^{-1} was applied to the soil. Incubation was carried out in a temperature-controlled camera at 28 °C for 1, 2, and 3 months, respectively. The moisture was maintained at 80% of the soil field capacity at the atmospheric pressure, by periodical addition of distilled water. After each incubation period, soil samples, alone or amended, were air-dried, passed through a 2 mm sieve, and kept in a tightly closed plastic bag until their use. **Table 2** shows the total organic carbon determined by oxidation with K$_2$Cr$_2$O$_7$ (25) and pH (5/20 soil/water ratio) of nonamended and amended soil at different incubation times.

Herbicides. The selected herbicide was terbuthylazine, 99.3% purity (Dr. Ehrenstorfer, Germany). It was a pre- or postemergence broadspectrum herbicide to control weeds in many crops (vines, fruit trees, olive trees, etc.) (27). Besides terbuthylazine, other triazine herbicides, no longer permitted, cyanazine, simazine, and prometryn, all with purity >99% (Dr. Ehrenstorfer) were also included, as reference compounds. They were all weakly basic compounds with pK_a values ranging from 0.6 to 4.1. Their water solubility and octanol/water partition coefficients as well as their chemical structures are shown in **Figure 1** (27, 28).

Sorption and Desorption Isotherms. The isotherms were determined using a batch equilibration method, with nonamended and amended soils, incubated at different times (0, 1, 2, and 3 months). Soil samples (5 g) were suspended in aliquots of 20 mL of aqueous herbicide mixture solutions, each at 2, 5, 10, 15, and 20 mg L^{-1}, prepared in Milli-Q water (Millipore, Bedford, MA) and mechanically shaken end-over-end in a thermostatic chamber at 15 ± 1 °C for 12 h. In a preliminary kinetic study, this contact time was found to be sufficient to achieve equilibrium. Soil was separated by centrifugation at 3000 rpm at 15 °C for 15 min. A 1 mL portion was taken from the supernatant solution and analyzed as described below. The amount of herbicide sorbed by the soil at equilibrium was determined as the difference between the initial and the equilibrium herbicide concentrations in solution. Desorption studies were conducted only on 20 mg L^{-1} herbicide solutions. After the sorption stage of the experiment, 10 mL of the supernatant was replaced with the same volume of Milli-Q water. Tubes were vortexed until complete dispersion, and the suspensions were shaken for 24 h at 15 ± 1 °C and centrifuged again as previously described. The desorption equilibration process was repeated four successive times. The remaining sorbed herbicide was calculated
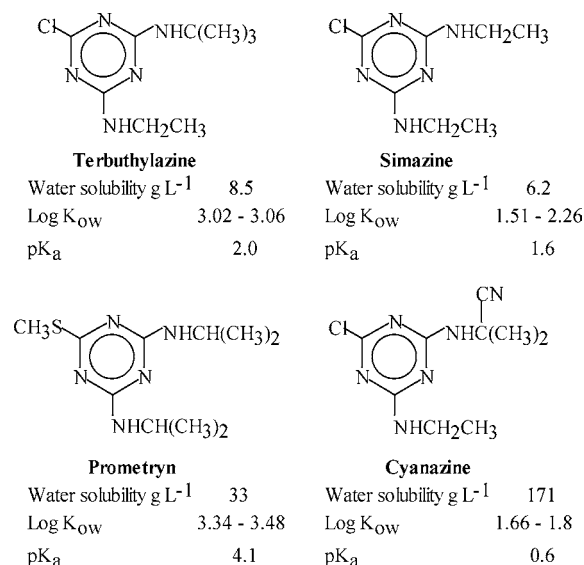
Figure 1. Chemical structure and selected physicochemical properties of the triazine herbicides.

as the difference between the initial sorbed and the desorbed concentrations. The experiments were run in duplicate with a control of the herbicides solution without soil, to account for possible herbicide degradation during the sorption and desorption processes.

The sorption−desorption experiments were fitted to the logarithmic form of the Freundlich equation

$$\log X = \log K_f + 1/n \log C_e$$

where X ($\mu g \ g^{-1}$) is the amount of herbicide sorbed at the equilibrium concentration C_e (mg L^{-1}) and K_f and $1/n$ are the Freundlich sorption−desorption constants that describe the sorption capacity of the herbicides. The constant $1/n$ depends on the sorbate, the sorbent, and the temperature properties. The sorbed herbicide amount (X_{10}) at a C_e of 10 mg L^{-1} was also calculated from the fitted equation. The organic carbon distribution coefficient (K_{oc}) was calculated from the K_d values for a C_e value of 10 mg L^{-1}. The coefficient of hysteresis was calculated according to

$$H = (1/n_{des})/(1/n_{ads})$$

where $1/n_{ads}$ and $1/n_{des}$ are the Freundlich constants corresponding to sorption and desorption processes, respectively. The coefficient of hysteresis is currently used to indicate the degree of reversibility of the desorption process (*11*). The percentage of desorption (*D*) was calculated as the ratio between the initial concentration of sorbed herbicide and the remaining sorbed concentration after the four desorption steps.

Extraction and Analytical Procedure. A 1 mL aliquot of the herbicide mixture was vortexed with 2 mL of hexane/toluene (1/1 v/v). Phase separation was achieved by sample freezing in a conventional freezer (−18 °C) for 2 h. The organic phase was transferred into a vial and analyzed. Recoveries were of 89.2% for terbuthylazine and ranged from 73.2 to 92.1% for the other triazines.

Samples were analyzed by gas chromatography in a Varian Star 3400 CX, equipped with a thermionic specific detector and an 8200 automatic injector (all from Varian, Madrid, Spain). One microliter of the sample was injected splitless, using He as the carrier gas, on a Hewlett-Packard Ultra 2 column (cross-linked 5% phenylmethylsilicone) (25 m, 0.32 mm i.d., 0.17 μm film thickness). Injector and detector temperatures were 280 and 300 °C, respectively. The oven temperature was programmed starting at 45 °C (1 min), at 25 °C min^{-1} until 160 °C, and at 7 °C min^{-1} until 210 °C (2 min). Under these experimental conditions, the retention time of terbuthylazine was 12.1 min, and the retention times were 11.6, 13.9, and 15.0 min, for simazine, prometryn, and cyanazine, respectively.

RESULTS AND DISCUSSION

Chemical Properties of the Amendments. The pH and lipid content of the different amendments, as well as the elemental composition, C/N, and the H/C and O/C atomic ratios of the isolated HAs, are shown in **Table 1**. As expected, the C/N ratio of HAs decreased from fresh olive cake to vermicomposted and composted olive cake, indicating the progress of the humification process. The atomic H/C ratio showed that vermicompost HAs had an aliphacity similar to soil HAs (*29*) and lower than that for olive cake and compost HAs. In contrast, olive cake HAs presented the greatest content in aliphatic constituents (highest H/C value) and less oxygenated groups (lowest O/C value). Previous studies (*13*, *30*, *31*) on organic matter transformation during composting of olive-mill wastes or wastewaters also found a biodegradation of both aliphatic and peptide structures and an enrichment of aromatic structures during the composting progress. The pH values increased in composted and vermicomposted materials, as a consequence of the ammonia released from the mineralization of proteins, amino acids, and peptides (*32*). Moreover, the lipid content, used as an index of compost stability or maturity (*33*), reached low values in composted and vermicomposted materials (**Table 1**) whereas in olive cake it represented 10% of total organic carbon. This decrease of the concentration of lipids has been reported by other authors (*13*, *34*) and could be an effect of microbial degradation and/or the incorporation of the lipid molecules into tightly bound unextractable forms. Different studies have shown that lipids are physiologically active. Some compounds have a depressing effect on plant growth whereas others act as growth hormones (*35*). A positive effect of lipids on soil stability by promoting resistance of waterproof soil aggregates has been described in several studies (*36−38*). Additionally, the lipid fraction could influence the sorption of herbicides to soil, as it will be discussed below.

Sorption Experiments. The experimental data were fitted to the Freundlich model. **Table 3** shows the values of K_f and $1/n$ for the herbicides studied and for the different soils, amended or not, incubated for different periods of time. Values of $1/n$ showed in most instances some degree of nonlinearity attributed to heterogeneous composition and structure of the soil and amendments, as well as to the diversity of sorption mechanisms (*39−41*) or to the possible competition among herbicides for sorption sites (*42*). However, no relationship was found between isotherm nonlinearity and soil treatment (amended or nonamended), amendment type, herbicide, or incubation time.

Herbicide Sorption on Nonincubated Substrates. Herbicide sorption on nonamended soil provided the lowest Freundlich sorption coefficients (K_f). However, because the sorption parameters are affected by the slope ($1/n$), for comparison purposes, we have chosen to compare the sorbed quantity at 10 mg L^{-1} (X_{10}) (**Table 3**), as has been done previously (*21*, *43*). According to these values, in all cases, olive cake was the amendment leading to the highest herbicide sorption enhancement, followed by soil amended with C and V (**Figure 2**), which presented similar X_{10} values for each herbicide. Nonamended soil presented the lowest sorption. Thus, the fact that amendments enhanced triazines sorption to an extent depending on the levels of the organic C added (**Table 2**) clearly indicates the major role of organic matter in this process (*10*, *24*, *44*, *45*).

Sorption in amended and nonamended soil increased in the order simazine ≈ cyanazine < prometryn ≈ terbuthylazine. It was higher for the more hydrophobic herbicides terbuthylazine and prometryn than for the less hydrophobic ones, simazine and

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Table 3. Freundlich Sorption Parameters (K_f and $1/n \pm$ Standard Deviation), Organic Carbon Normalized Distribution Coefficient ($K_{oc} \pm$ Standard Deviation), and Sorbed Amount (X_{10}) for Triazine Herbicides on Nonamended and Amended Soils, Raw and Incubated[a]

	K_f	$1/n$	R^2	K_{oc}	X_{10}
		terbuthylazine			
S-0	1.8 ± 0.2	0.97 ± 0.05	0.95	85 ± 6	17.0
S-1	0.6 ± 0.1	1.33 ± 0.08	0.94	76 ± 6	12.9
S-2	1.3 ± 0.1	1.14 ± 0.06	0.95	72 ± 1	17.4
S-3	1.3 ± 0.1	1.07 ± 0.05	0.96	74 ± 6	15.0
SV-0	6.0 ± 0.3	0.76 ± 0.03	0.98	116 ± 5	34.5
SV-1	1.1 ± 0.2	1.49 ± 0.11	0.92	95 ± 3	33.0
SV-2	2.1 ± 0.1	1.13 ± 0.03	0.99	83 ± 7	27.7
SV-3	2.4 ± 0.1	1.10 ± 0.03	0.98	82 ± 5	29.9
SC-0	5.2 ± 0.3	0.80 ± 0.04	0.96	125 ± 6	32.7
SC-1	0.6 ± 0.1	1.74 ± 0.09	0.96	78 ± 7	33.3
SC-2	2.2 ± 0.1	1.04 ± 0.03	0.99	73 ± 6	23.6
SC-3	1.9 ± 0.1	1.17 ± 0.05	0.96	60 ± 14	28.1
SA-0	11.5 ± 0.8	0.93 ± 0.05	0.95	233 ± 4	98.6
SA-1	1.2 ± 0.2	1.46 ± 0.09	0.94	135 ± 8	34.5
SA-2	2.5 ± 0.1	1.20 ± 0.02	0.99	84 ± 6	40.4
SA-3	1.6 ± 0.2	1.15 ± 0.07	0.93	53 ± 1	22.9
		prometryn			
S-0	3.2 ± 0.3	0.66 ± 0.04	0.94	72 ± 7	14.5
S-1	1.6 ± 0.2	0.88 ± 0.07	0.92	82 ± 1	12.2
S-2	3.7 ± 0.3	0.64 ± 0.03	0.91	83 ± 7	16.1
S-3	2.4 ± 0.2	0.73 ± 0.04	0.95	70 ± 6	12.9
SV-0	6.3 ± 0.3	0.63 ± 0.03	0.97	104 ± 8	27.3
SV-1	3.1 ± 0.5	1.00 ± 0.07	0.91	104 ± 4	30.3
SV-2	5.0 ± 0.3	0.7 ± 0.04	0.97	106 ± 5	28.6
SV-3	4.3 ± 0.4	0.77 ± 0.06	0.91	68 ± 9	25.5
SC-0	6.3 ± 0.4	0.62 ± 0.04	0.93	109 ± 9	26.4
SC-1	2.3 ± 0.3	1.04 ± 0.08	0.91	91 ± 2	25.2
SC-2	4.6 ± 0.3	0.79 ± 0.03	0.95	93 ± 1	23.2
SC-3	3.7 ± 0.3	0.82 ± 0.04	0.96	63 ± 4	24.0
SA-0	17.5 ± 0.4	0.64 ± 0.04	0.97	296 ± 49	76.4
SA-1	4.8 ± 0.5	0.80 ± 0.05	0.93	182 ± 7	30.7
SA-2	6.4 ± 0.3	0.70 ± 0.04	0.97	106 ± 3	40.0
SA-3	3.8 ± 0.4	0.69 ± 0.05	0.91	44 ± 3	19.6
		simazine			
S-0	0.7 ± 0.1	0.86 ± 0.07	0.92	22 ± 2	5.2
S-1	0.3 ± 0.1	1.17 ± 0.11	0.91	26 ± 4	4.9
S-2	1.0 ± 0.1	0.82 ± 0.05	0.94	27 ± 1	6.7
S-3	0.8 ± 0.1	0.73 ± 0.07	0.88	25 ± 4	4.4
SV-0	3.0 ± 0.2	0.59 ± 0.03	0.97	36 ± 3	11.7
SV-1	0.3 ± 0.1	1.43 ± 0.09	0.94	27 ± 6	9.5
SV-2	0.3 ± 0.1	1.61 ± 0.09	0.96	31 ± 3	12.8
SV-3	1.2 ± 0.1	0.87 ± 0.06	0.94	20 ± 2	8.8
SC-0	1.8 ± 0.2	0.77 ± 0.06	0.91	40 ± 3	10.6
SC-1	0.2 ± 0.1	1.44 ± 0.12	0.90	25 ± 1	6.4
SC-2	0.9 ± 0.1	1.13 ± 0.08	0.92	27 ± 1	11.7
SC-3	0.8 ± 0.1	0.95 ± 0.07	0.91	15 ± 1	7.0
SA-0	1.8 ± 0.1	0.90 ± 0.04	0.97	30 ± 2	14.4
SA-1	0.4 ± 0.1	1.49 ± 0.09	0.94	31 ± 5	11.5
SA-2	3.9 ± 0.2	0.51 ± 0.02	0.96	27 ± 2	12.6
SA-3	1.1 ± 0.1	0.77 ± 0.07	0.91	14 ± 1	6.7
		cyanazine			
S-0	0.7 ± 0.1	1.00 ± 0.07	0.94	28 ± 5	7.3
S-1	0.2 ± 0.1	1.55 ± 0.14	0.92	30 ± 11	6.7
S-2	0.4 ± 0.1	1.32 ± 0.10	0.91	26 ± 5	8.0
S-3	0.4 ± 0.1	1.10 ± 0.11	0.89	27 ± 8	5.6
SV-0	1.7 ± 0.2	0.82 ± 0.07	0.91	33 ± 2	11.3
SV-1	0.4 ± 0.1	1.37 ± 0.13	0.92	36 ± 5	10.4
SV-2	1.3 ± 0.1	1.01 ± 0.04	0.97	37 ± 3	13.1
SV-3	0.8 ± 0.1	1.08 ± 0.08	0.91	32 ± 1	10.0
SC-0	1.6 ± 0.2	0.85 ± 0.06	0.93	42 ± 2	11.1
SC-1	0.5 ± 0.1	1.22 ± 0.09	0.92	27 ± 1	8.7
SC-2	1.5 ± 0.2	0.86 ± 0.07	0.91	24 ± 3	11.0
SC-3	0.7 ± 0.1	1.09 ± 0.08	0.93	25 ± 2	8.2
SA-0	1.3 ± 0.1	1.05 ± 0.05	0.98	40 ± 1	14.0
SA-1	2.6 ± 0.3	0.75 ± 0.06	0.92	29 ± 2	14.7
SA-2	0.9 ± 0.1	1.21 ± 0.06	0.96	35 ± 6	14.2
SA-3	0.8 ± 0.1	0.88 ± 0.06	0.93	15 ± 1	6.3

[a] S, nonamended soil; SV, SC, and SA, soils amended with vermicompost, compost, and olive cake. Suffixes correspond to incubation time (months).

cyanazine, according to their K_{ow} values (**Figure 1**), demonstrating the role of hydrophobic sorbate−sorbent interaction (*4*, *46*). In accordance with ref *24*, differences in sorption between amended and nonamended soils were found to be nonsignificant for the most polar compounds with K_{oc} values lower than 50 L kg^{-1} C, such as simazine and cyanazine (**Table 3**). For compounds of intermediate polarity, such as terbuthylazine and prometryn, K_{oc} was higher when the soil was amended, especially with olive cake (SA).

If the sorption of the triazine herbicides studied would depend only on the amount of organic matter, the K_{oc} values should be similar for each compound irrespective of the soil treatment. Nevertheless, this was not the case for terbuthylazine and prometryn, the most hydrophobic herbicides (**Table 3**), where K_{oc} values increased with the same trend of X_{10}, i.e., SA > SV = SC > S. Therefore, the variation of K_{oc} values can only be explained in terms of the soil organic matter quality (*47*). Hydrophobic bonding has been proposed as a mechanism for retention of nonpolar organic compounds by soil organic matter. Structures contributing to active surfaces for hydrophobic bonding include fats, waxes, and resins as well as aliphatic side chains on humic and fulvic acids (*35*). The study of the interactions between atrazine and soil humic substances of different molecular structure concluded that the order of atrazine sorption paralleled the concentration of aliphatic-C content in humic fractions (*48*). In fact, strong affinity of atrazine to aliphatic domains of soil organic matter was also described (*46*). This could explain the highest K_{oc} values of terbuthylazine and prometryn, which showed large affinity to soils amended with olive cake (*13*) containing HAs rich in aliphatic groups and with high content in lipids consisting of mixtures of *n*-alkanes, *n*-alkanols, and fatty acids (*34*, *35*, *49*). These molecular constituents of the soil matrix would favor the retention of triazines through hydrophobic bonding.

Apart from the effect of hydrophobic bonding, it is also worth mentioning that macromolecular surfaces based on aliphatic structures are in general more flexible, with a lower degree of intrastructural cross-linking, which will favor the diffusion of small organic molecules, such as triazine herbicides. This contrasts with the case of sorbents based on aromatic structures, which tend to form condensed structures, in several cases associated to insurmountable steric hindrances. This fact was pointed out by Piccolo et al. (*50*), who reported that the interactions between glyphosate and humic substances were controlled by the dimension and conformation of the different humic molecular structures. In the case of atrazine, its sorption was explained through significant retention by aliphatic C of the humic materials (*48*) that confers a high degree of stereochemical flexibility to the humic structure and allows for the inner sorption of herbicide through molecular sieve effect within a threedimensional macromolecular matrix.

Herbicide Sorption on Incubated Substrates. The progressive transformation in soil of the biotransformed products, vermicompost, and compost of olive-mill solid waste, for 1, 2, and 3 months did not affect the final quantity of total soil organic carbon (**Table 2**). However, a significant depletion of organic matter with incubation time was observed when soil was amended with olive cake.

As incubation time increased, the amounts of sorbed herbicide (X_{10}) diminished for soils amended with olive cake (**Table 3**). A high decrease was recorded in the first month of incubation for terbuthylazine and prometryn. On the contrary, for simazine and cyanazine, changes in X_{10} were not observed during the 2 initial months of incubation. In all cases, however, X_{10} values
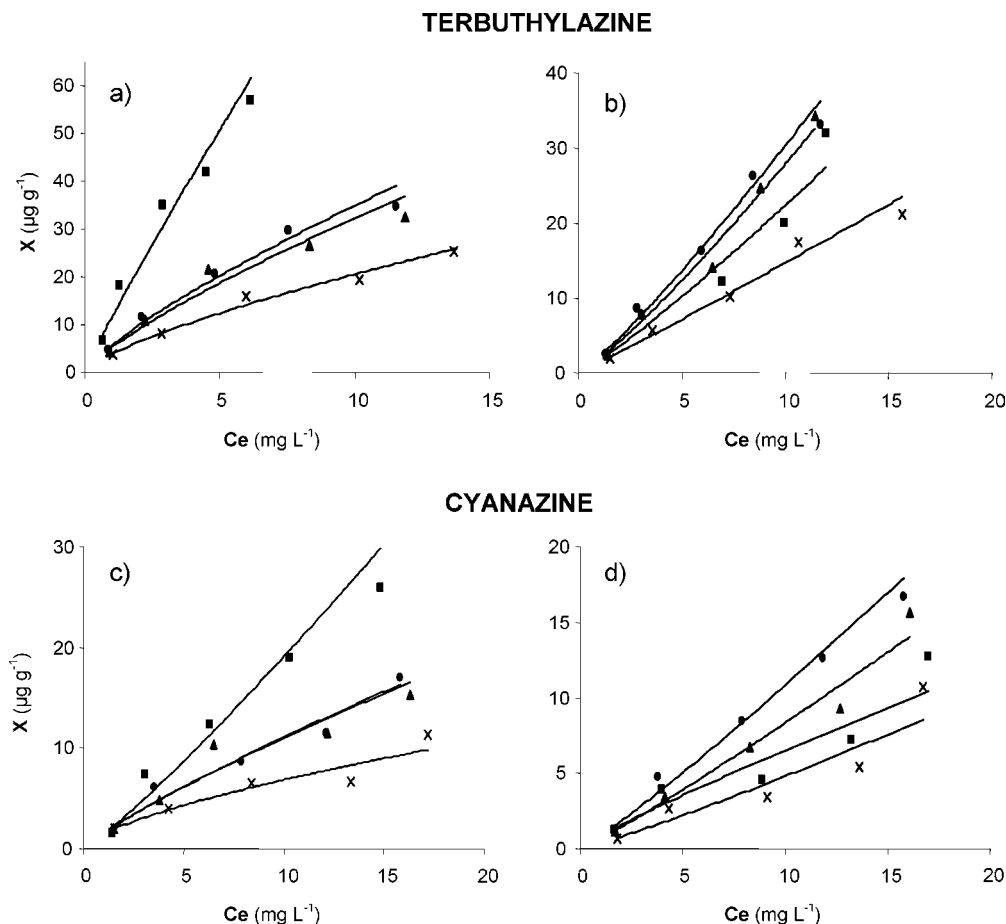
TERBUTHYLAZINE

CYANAZINE

Figure 2. Sorption isotherms of terbuthylazine and cyanazine in soil (×) and soil amended with A (■), C (▲), and V (●) without incubation (**a** and **c**) and incubated for 3 months (**b** and **d**). X (μg g^{-1}) is the amount of herbicide sorbed at the equilibrium concentration C_e (mg L^{-1}).

for the third month were halved with respect to the values at the second month. This corresponds to the stage in which the highest organic carbon decrease occurred (**Table 2**). In soil amended with C and V, no differences in X_{10} values were observed for each triazine herbicide along the incubation time (**Table 3**).

In all cases, K_{oc} values (**Table 3**) for soil amended with A decreased with incubation time. After 3 months, K_{oc} was significantly ($P < 0.05$) lower than that of nonamended soil, which suggests important differences in organic matter quality during the transformation process of olive cake in soil (*7*). The K_{oc} values for soil amended with C and V were similar for each herbicide (**Table 3**). This situation could be attributed to a similar maturation of both amendments and the consequent stabilization of their organic matter content. During composting, microorganisms degrade labile organic compounds such as carbohydrate, proteins, amino acids, and peptides to carbon dioxide, water, mineral salts, and a stable organic material containing humiclike substances (*32, 51*). In addition, the processes of composting and, especially, vermicomposting of olive cake induce the formation of a highly stabilized product (*15, 18*).

For soil amended with C and V, a reduction in K_{oc} with incubation time especially pronounced for compost occurred after the first month of incubation, which would agree with a greater stability of vermicompost than compost as indicated above. These changes in K_{oc} values with incubation time indicate that even for compost and vermicompost the transformation process was not completely achieved but continued in the soil after their application. Therefore, after 3 months, the amend-

ment-derived organic matter does not have a significantly ($P < 0.05$) different sorption capacity with regard to the original soil, despite different organic carbon contents (**Table 2**). These results are in agreement with previous research about several triazines (*4*), linuron and diazinon (*52*) and imazaquin (*11*), on the use of stabilized additives to soil, which indicated no significant differences with respect to nonamended soil.

Desorption Experiments. The data for the triazine herbicides desorption are presented in **Table 4**. In the nonamended soil, the desorption process was hysteretical for all herbicides studied, since $1/n_{ads}$ was greater than $1/n_{des}$, which is an indication that desorption was not a reversible process, as can be seen in the percentage of herbicide desorbed (*D*) after four desorption steps (**Table 4**) and in the coefficient of hysteresis (*H*). Simazine and cyanazine reached desorption percentages of more than 50% of their initial concentration, but for prometryn and terbuthylazine, only 44−46% was desorbed.

The addition of fresh amendments, with no transformation in soil, increased the retention of terbuthylazine and prometryn in soil since the final desorbed quantity was even lower for these herbicides. Therefore, their leaching and consequently their ability to reach groundwater were greatly diminished. For simazine and cyanazine, no significant ($P < 0.05$) differences were found in desorbed quantity of amended and nonamended soil. This fact contrasts with other results (*9*) showing negative hysteresis of simazine in unamended soils as well as in soils amended with olive cake, which pointed to high reversibility of the sorption−desorption process. Nevertheless, Benoit and Preston (*53*) reported an increase in bound residues of atrazine in soil amended with fresh and composted straw.

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Table 4. Freundlich Desorption Parameters (K_{des}, $1/n_{des} \pm$ Standard Deviation), Hysteresis Coefficient (*H*), and Percentage of Desorption (*D*) for Triazine Herbicides from Nonamended and Amended Soils, Raw and Incubated[a]

	K_{des}	$1/n_{des}$	R^2	H	D
		terbuthylazine			
S-0	13.4 ± 0.4	0.28 ± 0.02	0.92	0.29	40 ± 1
S-3	7.8 ± 0.4	0.41 ± 0.07	0.90	0.38	44 ± 1
SV-0	23.7 ±0.4	0.17 ± 0.01	0.92	0.22	26 ± 1
SV-3	3.2 ± 0.4	0.99 ± 0.07	0.92	0.90	73 ± 1
SC-0	21.2 ±0.4	0.21 ± 0.01	0.95	0.27	30 ± 1
SC-3	1.6 ± 0.3	1.33 ± 0.11	0.91	1.14	81 ± 1
SA-0	40.6 ±0.3	0.19 ± 0.01	0.98	0.20	22 ± 1
SA-3	2.1 ± 0.3	1.13 ± 0.07	0.94	0.98	78 ± 1
		prometryn			
S-0	13.4 ±0.4	0.28 ± 0.02	0.92	0.29	43 ± 1
S-3	7.8 ± 0.4	0.41 ± 0.07	0.90	0.38	46 ± 3
SV-0	23.7 ±0.4	0.17 ± 0.01	0.92	0.22	28 ± 1
SV-3	3.2 ± 0.4	0.99 ± 0.07	0.92	0.90	33 ± 2
SC-0	21.2 ±0.4	0.21 ± 0.01	0.95	0.27	26 ± 3
SC-3	1.6 ± 0.3	1.33 ± 0.11	0.91	1.14	43 ± 1
SA-0	40.6 ±0.3	0.19 ± 0.01	0.98	0.20	20 ± 9
SA-3	2.1 ± 0.3	1.13 ± 0.07	0.94	0.98	47 ± 1
		simazine			
S-0	13.4 ±0.4	0.28 ± 0.02	0.92	0.29	52 ± 2
S-3	7.8 ± 0.4	0.41 ± 0.07	0.90	0.38	47 ± 5
SV-0	23.7 ±0.4	0.17 ± 0.01	0.92	0.22	61 ± 2
SV-3	3.2 ± 0.4	0.99 ± 0.07	0.92	0.90	115 ±9
SC-0	21.2 ±0.4	0.21 ± 0.01	0.95	0.27	51 ± 2
SC-3	1.6 ± 0.3	1.33 ± 0.11	0.91	1.14	110±21
SA-0	40.6 ±0.3	0.19 ± 0.01	0.98	0.20	57 ± 4
SA-3	2.1 ± 0.3	1.13 ± 0.07	0.94	0.98	105 ± 2
		cyanazine			
S-0	13.4 ±0.4	0.28 ± 0.02	0.92	0.29	57 ± 1
S-3	7.8 ± 0.4	0.41 ± 0.07	0.90	0.38	45 ± 1
SV-0	23.7 ±0.4	0.17 ± 0.01	0.92	0.22	57 ± 1
SV-3	3.2 ± 0.4	0.99 ± 0.07	0.92	0.90	102 ±2
SC-0	21.2 ±0.4	0.21 ± 0.01	0.95	0.27	54 ± 2
SC-3	1.6 ± 0.3	1.33 ± 0.11	0.91	1.14	108 ±2
SA-0	40.6 ±0.3	0.19 ± 0.01	0.98	0.20	56 ± 1
SA-3	2.1 ± 0.3	1.13 ± 0.07	0.94	0.98	116 ±3

[a] S, nonamended soil; SV, SC, and SA, soils amended with vermicompost, compost, and olive cake. Suffixes correspond to incubation time (months).

However, the transformation in soil of the amendments for 3 months turned out in an increase of the amounts of herbicide desorbed resulting in almost a complete reversible process for simazine and cyanazine. In the case of prometryn, an *s*-triazine containing a methylthio group in its structure (**Figure 1**), the desorption was less affected. The *s*-triazines may form hydrogen bonds of high energy with the phenols present in the organic matter (*46*), preventing extensive prometryn desorption.

The increase in the percentage of pesticide desorbed after 3 months of transformation in the soil could be explained because the humification and maturity processes affect the physico-chemical properties of the organic matter of the amendments. Moreover, the interactions with soil components would block the most energetic sites, so that triazines sorption would be restricted to sites where the retention forces were weaker and from which the desorption was easier. This assumption is in accordance with the decrease observed in sorbed quantities and K_{oc} values along the incubation time for all of the pesticides studied. In fact, González-Vila et al. (*34*) found significant differences in the qualitative composition of soil lipid fraction

in a soil amended with compost from urban waste. Numerous studies have reported competition for sorption sites on soil between pesticides and exogenous dissolved organic matter (*24, 45, 54*), but little is known about how the aging process of exogenous organic matter in soil and its interaction with soil constituents could affect pesticides desorption. This point should be substantiated by further studies.

In conclusion, when used as soil amendments, raw olive-mill solid waste and its compost and vermicompost enhanced the retention and decreased the desorption of triazine herbicides. However, the effect on triazine sorption capacity, after amendments transformation in soil for 3 months, almost disappeared for compost and vermicompost and decreased for olive cake, with respect to the nonamended soil. Moreover, in the course of its progressive transformation in soil, triazine desorption increased. This indicated that the extent of the sorption–desorption process in soil could be controlled or forecasted in terms of the characteristics and maturation of the olive cake, in a way depending on the physicochemical properties of the pesticides.

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