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Adsorption and Degradation of Three Pesticides in a Vineyard Soil and in an Organic Biomix

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Abstract: A soil and an organic biomix (soil/vine branch/garden compost 20/40/40) were used in this lab experiment to evaluate adsorption and degradation parameters for three pesticides (chlorpyrifos, metalaxyl and cymoxanil) used in a vineyard. Adsorption in the biomix material was higher than in the soil for the three pesticides and chlorpyrifos was the most adsorbed pesticide. The role of the organic carbon is essential for enhancing the adsorption of the three pesticides, especially for the most apolar chlorpyrifos. Degradation was generally faster in the biomix material than in the soil although the process was slower in the case of chlorpyrifos if compared with the other two chemicals, due to a more toxic effect of this pesticide on soil microflora and a larger adsorption of this pesticide on the organic biomix that reduces its availability for dissipation. Amendment with cheap and available organic wastes or a grass-covered management of soil in the vineyard could reduce the impact of pesticides in the vineyard ecosystem and contribute to the sustainable management of chemicals in the environment.

Keywords: pesticides; adsorption; degradation; organic biomix

1. Introduction

Recent research has shown that only a small percentage of the pesticides used in vineyards reaches its target; most of the chemicals reach surface and ground water as a result of diffuse contamination from percolation, run-off, drainage and drift [1–3]. Another form of environmental contamination due to pesticides is from point sources, including tank filling, washing and waste disposal, spillages and leaks from faulty equipment [4–7].

The use of pesticides against plant pests, weeds and pathogens has been shown to affect the chemical and biological fertility of soils in several cases, and includes a number of potential adverse effects on soil microorganisms and/or non-target organisms [8]. Long-time exposure of non-target organisms for long time to high concentration of pesticide residues in soils could have several harmful effects including genotoxic and carcinogenic risks and may even lead to death in the most serious cases.

Hence, it is of fundamental importance to have a thorough knowledge of the behavior of pesticides in soils in different situations and with the influence of external and internal factors and environmental conditions so as to avoid the long persistence and high bioavailability of these chemicals. The new Registration Procedure allows only “safe” molecules to be included as active ingredients in Annex 1 of EU Regulation 1108/2009 [9]. These molecules are easily adsorbed and rapidly degraded in soils after their use against crop pests and diseases. The most important chemo-dynamic processes for

understanding the fate and behavior of pesticides in soils are adsorption and degradation, whose parameters are generally derived in laboratory experiments and under standard conditions.

The main factors influencing the fate of pesticides in soils and organic substrates are the amount and quality of organic matter, and, generally, pesticide adsorption and degradation was found more effective in organic wastes than in soils [10–12]. For this reason, together with many others, soil amendment with organic wastes coming from different sites and activities has become a widespread agricultural practice, involving a number of activities to recycle organic wastes even in the perspective of circular economy [13]. In this context, some research groups in Italy have started to conduct research in vineyards, testing the possible use of various cheap organic residues as amendments to reduce the negative impact of xenobiotics [14,15]. Further studies were pointed out to test various agricultural organic wastes as amendment in soil and/or as organic biofilters to adsorb and degrade pesticides in agricultural waters coming from washing of agricultural equipment's [12,16,17]. The present paper describes a laboratory trial to test the efficiency of a biomix composed of soil, green compost and vine branches in adsorbing and degrading three of the most widely used pesticides in vineyards in Italy, chlorpyrifos (insecticide), metalaxyl (fungicide) and cymoxanil (fungicide), chosen for their different characteristics with regards to soil adsorption and degradation processes. Adsorption and degradation parameters were derived in the laboratory both for the soil and the biomix and the influence of different organic carbon fractions on the two chemo-dynamic processes was assessed.

2. Materials and Methods

2.1. Soil, Biomix and Pesticides

The soil used was a topsoil (mixed calcic Haploxcept) supplied by the Experimental Farm of the Marche Polytechnic University, Ancona, Italy, while the biomix was based on 20% soil, 40% garden compost composted for five years and 40% vine branches. The biomix composition was chosen for the tentative to use it as biofilter for water decontamination by pesticides in vineyard. The organic wastes were thoroughly chopped (0.2–0.5 cm) before mixing them with the 2 mm soil sample. The main characteristics of the soil, the organic wastes and the biomix are reported in Table 1. All the forms of organic carbon were determined in order to evaluate their influence on adsorption and degradation of the pesticides used in the experiment.

Table 1. pH (H₂O) and organic carbon content (%) of soil, organic wastes and biomix used in the experiment (mean of three replicates ± standard deviation).

	Soil	Compost	Vine Branches	Biomix
pH	8.2	5.1	7.9	7.9
TOC	1.1 ± 0.1	31.2 ± 1.4	32.5 ± 1.1	28.7 ± 0.9
TEC	0.8 ± 0.1	21.2 ± 1.2	4.5 ± 0.4	21.8 ± 0.9
HAC	0.6 ± 0.0	16.5 ± 0.8	1.1 ± 0.1	6.8 ± 0.3
FAC	0.2 ± 0.0	4.7 ± 0.4	3.4 ± 0.2	6.0 ± 0.4

TOC = Total Organic Carbon; TEC = Total Extractable Carbon; HAC = Humic Acid Carbon; FAC = Fulvic Acid Carbon.

The tested pesticides were supplied by Labor Dr. Ehrenstorfer-Schäfers (Augsburg, D); the chemicals had purities of 98.4% (chlorpyrifos, CH), 99.5% (metalaxyl, ME) and 96% (cymoxanil, CY). Their main characteristics are reported in Table 2.

Table 2. Main physico-chemical characteristics of the pesticides used in the experiment.

	Chlorpyrifos	Metalaxyl	Cymoxanil
Water solubility (mg/L)	1.05	8400	780
Vapour pressure (mPa)	1.43	0.75	0.15
t _{1/2} soil lab 20 °C (days)	386	36	1.5
DT50 field (days)	27.6	38.7	3.5
Koc range (L/kg)	3187–7733	29.6–283.8	15.1–87.1

Data derived from Pesticide Properties DataBase (PPDB) [18].

2.2. Determination of Organic Carbon Fractions

Substrates were thoroughly homogenized by hand kneading before analyses. Different fractions of organic carbon were determined in triplicate on air-dried samples in all the organic substrates and in soil. Total organic carbon (TOC) was determined using the Walkley–Black method without external heating and slightly modified to avoid underestimation of total organic carbon. Briefly, samples were passed through a 0.5 mm sieve, and 0.2 g of each organic substrate were used. 20 mL of potassium dichromate (K₂Cr₂O₇ 1/6M) and 40 mL of concentrated H₂SO₄ (96%) were added to the samples. After half an hour, the excess of dichromate was titrated with ammonium ferrous sulfate (NH₄)₂Fe(SO₄)·6H₂O (0.5 M) to calculate the amount of total organic carbon.

Chemical analyses of organic carbon fractions were performed by extracting total organic carbon (TEC) in an alkaline solution as reported by Schnitzer [19] with slight modifications. Briefly, 10 g of each organic substrate were treated with a sodium hydroxide and sodium pyrophosphate 0.1 M solution (10:1 liquid:solid ratio) and shaken in the dark on an orbital shaker at 160 rpm at room temperature overnight. The mixture was centrifuged at 13,000 rpm for 15 min, and the supernatant was collected. The insoluble residue of the extraction was washed three times using 50 mL of deionized water. The rinsed solution was then centrifuged (14,000 rpm for 15 min) and added to the alkaline extract. The alkaline extract was subdivided into two aliquots. One aliquot was analyzed by using the Walkley Black (WB) method to determine the total extractable organic carbon (TEC) which represents the humified fraction. The other aliquot was subjected to fractionation to obtain the humic and fulvic acid aliquots. Concentrated H₂SO₄ was added to reach pH < 2 in order to determine the precipitation of the humic acid (HA) fraction, which was allowed to coagulate for 24 h at 4 °C. The HA fraction was then separated from the soluble fulvic acid (FA) fraction by centrifugation for 15 min at 13,000 rpm. The supernatant containing only the FA fraction was then collected, and the relative organic carbon content was determined using the WB method. The organic carbon concentration relative to the HA fraction was then estimated by subtracting the thus determined amount of FA fraction from the determined amount of TEC.

2.3. Adsorption Studies

Soil: 20 g of 2 mm air-dried sieved samples in centrifuge tubes were added to 100 mL of pesticide solution in CaCl₂ 0.02 M at pH 7.0 with an initial concentration of 0.1, 0.5, 1, 2 and 4 mg/L. The experiment was performed with three replicates for each concentration and separately for each pesticide. After 16 h on the shaker at 20 °C, the time necessary to reach adsorption equilibrium, tubes were centrifuged for 20 min at 6000 rotations. The solution was filtered, separated with CHCl₃ (50 mL × 3) and evaporated in a rotary evaporator at 40 °C, rinsed with 1 mL of CH₃OH and aliquots (20 mL) were injected into the HPLC.

Biomix: the procedure adopted was similar to the one used for the soil; however, the initial concentration of the three pesticides in the CaCl₂ was higher than in soil due to the greater adsorption capacity of the organic materials. Initial concentrations were: 1, 2, 4 and 8 and 16 mg/L for ME and CY and 2, 5, 10, 50 and 100 mg/L for CH.

The adsorption parameters k_F (Freundlich constant) and n (power coefficient) were derived using the Freundlich Equation:

$$C_s = k_F C_e^n \quad (1)$$

in logarithmic form:

$$\log C_s = \log k_F + n \log C_e \quad (2)$$

where C_s is the ratio of pesticide to adsorbent mass (mg/kg) and C_e is the equilibrium concentration of the adsorbate (mg/L). The Freundlich constant k_F allows to calculate k_{Foc} (organic carbon partition coefficient), which is defined by

$$k_{Foc} = (k_F / \%oc) 100 \quad (3)$$

where oc is the organic carbon content of soil or biomix.

2.4. Degradation Studies

Degradation studies were performed on the same soil and biomix used for the adsorption studies. Initial doses of the three pesticides were calculated according to the vineyard experiment carried out by Fait et al. [14], hypothesizing that with repeated treatments in vineyard, high doses of pesticide can be concentrated in a limited area on the ground. The doses were 16.6 ppm, 13.3 ppm and 14.2 ppm, respectively, for ME, CH and CY in the soil and 131.6 ppm, 26.31 ppm and 32.9 ppm in the biomix. The experiment was performed separately for each pesticide both in soil and biomix, using containers of 1 kg of air-dried sieved soil and 1 kg of homogenized biomix for each pesticide and each concentration. All the samples were at 60% of their water holding capacity and incubated at 20 °C in the dark. Samples were weighed every day in order to maintain the correct humidity. At different intervals of time after treatment, 40 g subsamples in triplicate were extracted from each container and analyzed for pesticide residues. The subsamples were collected after 0, 3, 7, 15, 30, 60, 90 and 150 days for CH and ME in the soil and in the biomix and after 0, 3, 7, 15 days for CY in the soil and 0, 3, 7, 10 days for CY in the biomix. Soil and biomix subsamples were weighed in centrifuge tubes, 80 mL methanol/water solution was added (80:20), the mixture was shaken for one hour, centrifuged at 6000 rotations for 15 min and then filtered. All extracted samples were added to 80 mL of H₂O, separated using chloroform (80 mL × 2), evaporated, dissolved in 1 mL methanol and analyzed. Adsorption samples followed the same procedure from the chloroform separation step onwards.

Degradation parameters were derived by applying the first order kinetics to degradation data, as a natural logarithm of the residual concentration versus time. From the rate constant k of the Equations, it was possible to derive the half-life value ($t_{1/2}$, days):

$$t_{1/2} = 0.693/k \quad (4)$$

2.5. Analyses

The samples coming from adsorption and degradation studies were analyzed by HPLC, using a Spectra SYSTEM P 4000 equipped with UV detector (wavelength 242 nm for CY and 230 nm for CH and ME) and Supelcosil C18 column, 25 cm × 4.6 mm i.d.; analysis conditions for CH and ME were: flow rate of 1 mL/min, mobile phase of water/CH₃CN 30/70, while for CY, the flow rate, this was 0.8 mL/min and the mobile phase consisted of water/CH₃CN 60/40. Under these conditions, retention times were 3.7 min for ME, 5.3 min for CY and 10.7 min for CH. Limit Of Detection (LOD) was 10 ng for CY and ME and 12 ng for CH. Recoveries were between 90% and 98% in soil and between 87% and 96% in biomix.

2.6. Statistical Analysis

Student's t Least Significant Differences (LSD) tests were performed at significance level $p < 0.05$ for the mean separation between soil and biomix samples.

3. Results and Discussion

3.1. Adsorption

The adsorption isotherms for the three pesticides in the soil and in the biomix are reported in Figure 1, while Table 3 reports the derived values of the adsorption parameters based on the Freundlich model.

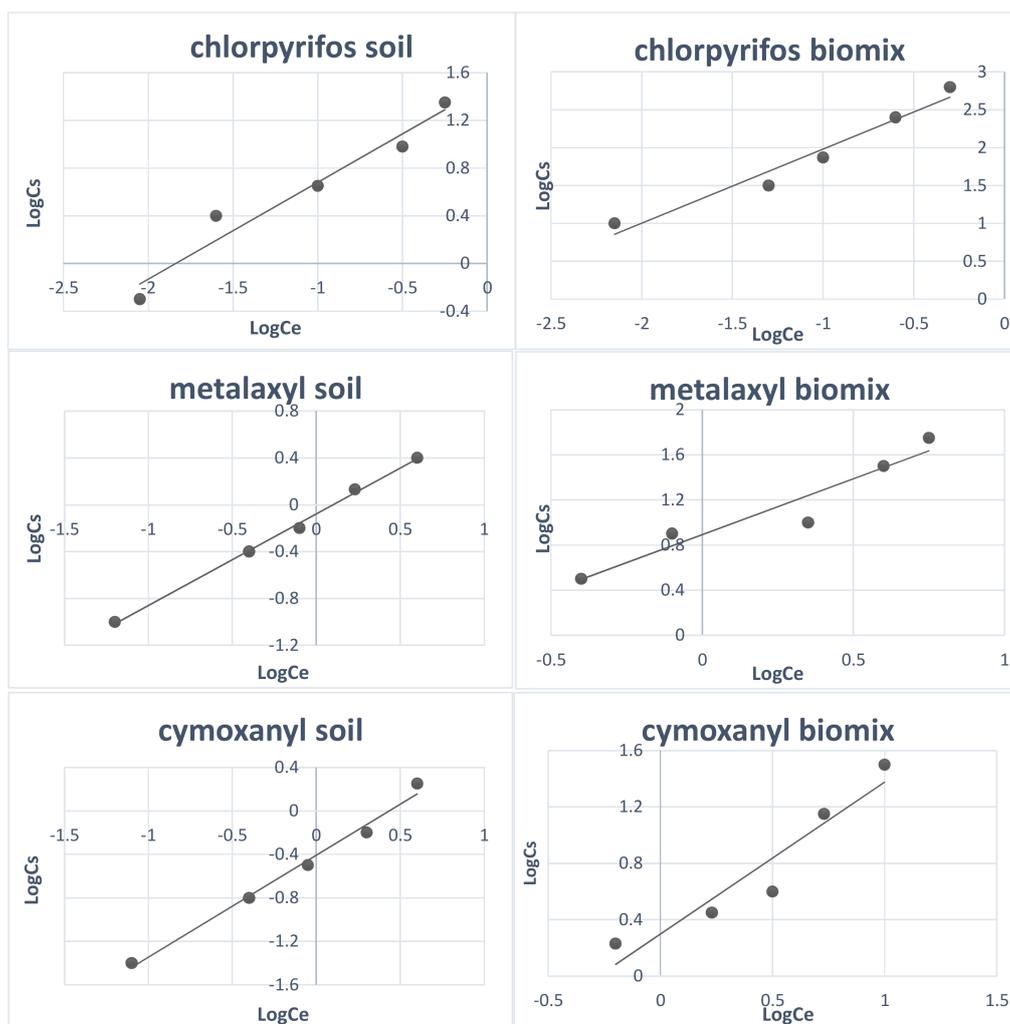


Figure 1. Adsorption isotherms for the three pesticides derived from the batch equilibrium experiment (data are the means of three replicates; standard error even <1.8% in soil samples and <3.1% in biomix samples). R^2 values always significant at $p < 0.001$ level.

Table 3. Adsorption parameters for the three pesticides in soil and biomix (data are the mean of three replicates; standard error even <1.8% in soil samples and <3.1% in biomix samples; low case letters represent Least Significant Differences at $p < 0.05$ in soil and biomix, separately for each pesticides).

	k_F		n		R^2		k_{Foc}	
	Soil	Biomix	Soil	Biomix	Soil	Biomix	Soil	Biomix
chlorpyrifos	31.2 ^b	909 ^a	0.81	0.98	0.952	0.957	2836 ^a	3168 ^a
metalaxyl	0.84 ^b	7.81 ^a	0.78	0.99	0.997	0.917	76.6 ^a	28.2 ^b
cymoxanil	0.33 ^b	1.99 ^a	0.94	1.1	0.988	0.903	30.0 ^a	6.9 ^b

The Freundlich model fitted the adsorption data with values of R^2 always being significant at $p < 0.001$ level.

The k_F values obtained for the soil showed that CH ($k_F = 31.2$) was better adsorbed than ME (0.84) and CY (0.33). The K_{Foc} value of 2836.6 was close to the lower limit of the range of PPDB [18] and was somewhat lower than those found by Huang and Lee [20], who reported results from 3900 to 6100 for two soil types containing 1.3% organic carbon.

The k_F value found in soil for ME is in the same order as the ones found by Andrades et al. [21] who reported k_F values between 0.01 and 0.64 in sixteen Spanish vineyard soils with an organic matter content between 0.31% and 1.37%; the same authors reported k_F values between 1.05 and 2.83 for natural soils with an organic matter percentage between 3.3% and 8.2%. The k_F value of 0.33 found for CY in soil is in agreement with EPA values [22], which ranged between 0.29 and 0.79 in soil with 1.3% of organic matter. ME and CY are much more soluble in water than CH and much more polar, according to the octanol–water partition (k_{ow}) values. In fact, the adsorption values, k_F , are ranged according k_{ow} , rather than according their solubility values, and the k_{oc} values in soil reported in the PPDB [18] were considerably lower than the results for CH. The k_{oc} values found in soil were 76.6 for ME and 30.0 for CY, falling just in the range of the PPDB report and that of CH was very close to the lower value reported by PPDB.

The biomix showed a good adsorption efficiency for the three pesticides, increasing the values of the adsorption parameters in all cases respect to the soil, albeit to a different extent: k_F for CH was about 29-fold higher in the biomix than in the soil, for ME about 9-fold and for CY about 6-fold higher, indicating that the most apolar compound CH is adsorbed much better in a substrate, which is rich in organic matter compared with ME and CY which are more polar and water soluble pesticides (Table 2), even if the k_F values of the last two pesticides increased in any case, indicating the positive effect of organic matter also in the adsorption of soluble pesticides.

The Freundlich exponent n increased in all cases from soil to biomix, indicating a higher affinity of the three pesticides for the substrate with a high organic carbon content.

Several authors [12,17,23] studied the adsorption of some pesticides in different organic substrates and soils, with the main aim to find a substrate suitable to be used in organic biofilters, especially for southern European conditions, due to the unavailability of organic natural substrates such as peat. The values of adsorption parameters found in the present experiment are in agreement with those found by the above authors, which showed increasing in k_F values in the same order of those of the present experiment and positively correlated to the organic carbon content of the adsorbing substrate.

CH maintained a value of k_{Foc} in the biomix similar to that in soil, while ME and CY showed a k_{Foc} value in the biomix which was lower than in soil, indicating a decrease in the adsorption power of the unit of the organic carbon in the biomix, probably due to the different fraction of organic carbon reported in Table 1; the humified fraction is mainly responsible for pesticide adsorption in the organic matter of soils and humic acids are more effective than fulvic acids in adsorbing apolar compounds. The humified fraction of biomix is about 76% of total organic carbon (21.8%, with respect to a total of 28.7%) with a slight prevalence of humic acids and this is reflected in a preferential adsorption of CH compared with ME and CY. In a previous paper, Vischetti et al. [23] reported a similar behavior for ME in different organic substrates and soils with an increase in organic substrates with respect to soils, especially in more humified substrates which are rich in humic acids. However, the relative ability (relative to OC units) was lower for the more polar ME and CY. This would mean that the biomix was relatively less efficient in retaining those polar pesticides.

3.2. Degradation

The degradation trends of the three pesticides in soil and biomix are reported in Figure 2, while Table 4 reports the degradation parameters derived by applying the first order kinetics to the degradation data.

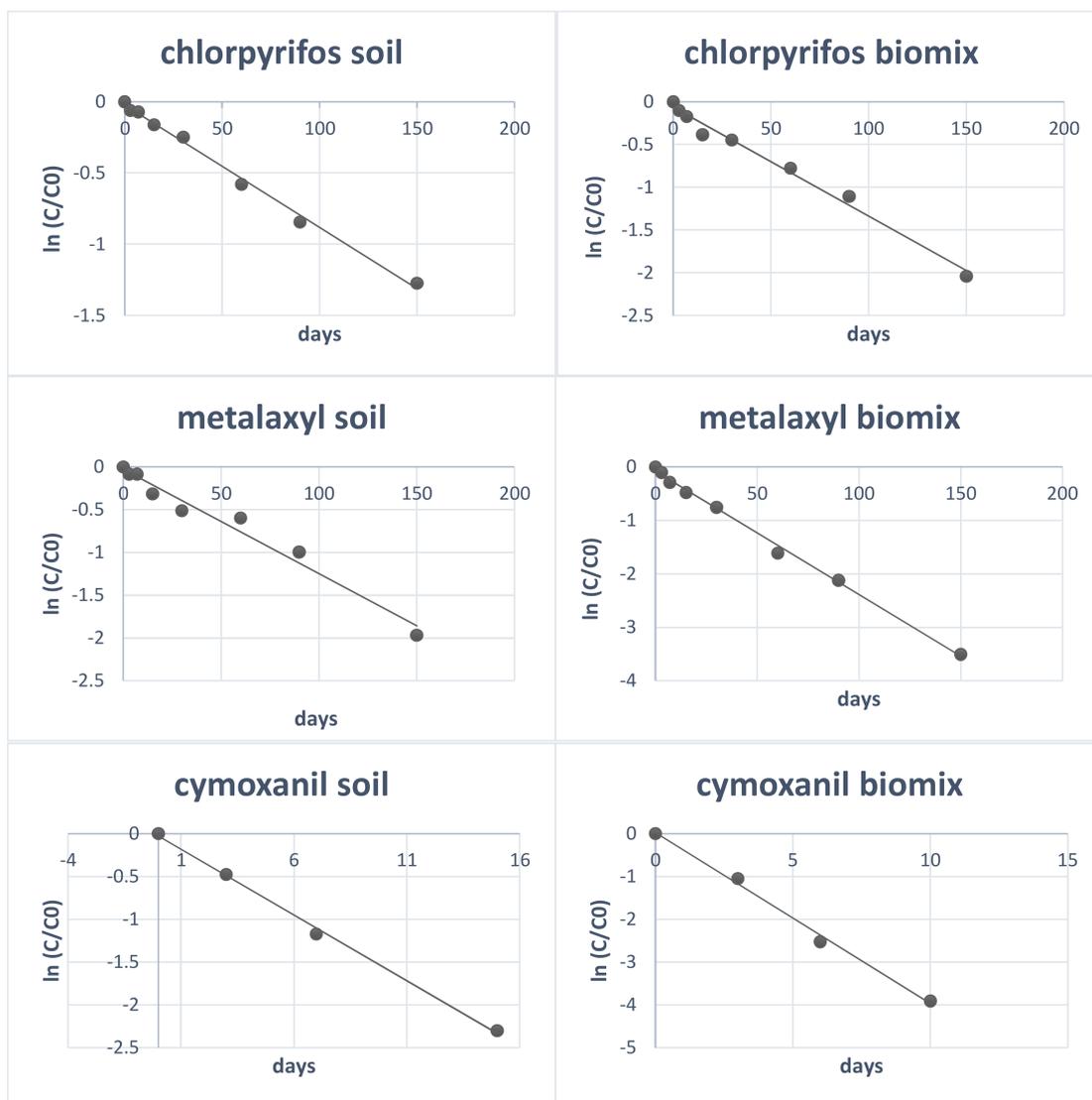


Figure 2. Degradation patterns of the three pesticides in the soil and in the biomix derived by applying first order kinetics to the data from the degradation laboratory experiment (data are the mean of three replicates; standard error even <2.1% both in soil and biomix samples); R^2 values always significant at $p < 0.001$ level.

Table 4. Degradation parameters of the three pesticides in soil and biomix derived by applying first order kinetics model to the degradation data (data are the mean of three replicates; standard error even <2.1% both in soil and biomix samples; low case letters represent least significant differences at $p < 0.05$ in soil and biomix, separately for each pesticides).

	k_{deg} (Days ⁻¹)		$t_{1/2}$ (Days)		R^2	
	Soil	Biomix	Soil	Biomix	Soil	Biomix
chlorpyrifos	0.0086	0.0127	80.6 ^a	54.6 ^b	0.994	0.988
metalaxyl	0.0122	0.0230	56.8 ^a	30.1 ^b	0.972	0.996
cymoxanil	0.1536	0.3992	4.5 ^a	1.7 ^b	0.998	0.995

The first-order model was well fitted with the degradation data, being significant at $p < 0.001$ level in all cases. The half-life values in soil, shown in Table 4, were higher for CH than ME and CY, in line with the half-life range reported in the PPDB [18] (Table 2) and in agreement with other authors:

Reeves [24] reported CH $t_{1/2}$ in different types of soils between 43 and 126 days, whilst Sukull and Spitteller [25] found ME $t_{1/2}$ in soil between 36 and 301 days.

The degradation for the three pesticides was found to be faster in the biomix than in the soil, indicating an important role of organic carbon and microbial population in promoting pesticide degradation, as reported by other authors [26,27]. Half-life values in the biomix decreased by 32.2%, 47.0% and 62.2% for CH, ME and CY, respectively. The half-life value for CH decreased less than those of ME and CY; Some authors [26] found that this behavior is caused by the main metabolite TCP (3,5,6-trichloro-2-pyridinol) which shows antimicrobial properties. On the contrary, the degradation of ME and CY in the biomix is faster than that of CH; the presence of organic carbon and a sound microbial population in the biomix could promote the faster degradation of the two pesticides, as reported by other authors [12,16].

4. Conclusions

This experiment has shown that the addition of organic substrates to soils improves pesticide adsorption and degradation, since organic matter is mainly responsible for pesticide–soil interactions. The most efficient fraction in pesticide adsorption is the humic carbon and, above all, the humic acid fraction. Pesticide degradation was enhanced by the addition of organic substrates to soils, even if the process was more evident for those pesticides which are less toxic or nontoxic for soil microflora.

The soil amendment with cheap and available organic wastes in the vineyard could reduce the impact of pesticides in this ecosystem and contribute to a sustainable management of chemicals in the environment.

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