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**Study of processes influencing bioavailability of pesticides in wood-soil systems:
Effect of different factors**

J. M. Marín-Benito^a, E. Herrero-Hernández^a, M. S. Rodríguez-Cruz^a, M. Arienzo^b, M. J. Sánchez-Martín^{a*}

^aInstituto de Recursos Naturales y Agrobiología de Salamanca, IRNASA-CSIC, Cordel de Merinas 40-52, 37008 Salamanca, Spain

^bDepartment of Earth Science, Environment and Resources, University of Naples Federico II, Largo San Marcellino 10, 80138 Naples, Italy.

*Corresponding author:

e-mail: mjesus.sanchez@irnasa.csic.es (M. J. Sánchez-Martín)

Telephone: +34 923219606; Fax: +34 923219609

ABSTRACT

Lignocellulosic wastes and by-products containing lignin are now available in large amounts from forestry and industrial activities, and could be promising organic materials for the biosorption of pesticides by soils in order to reduce point-source pollution. Adding these materials to soil requires understanding the process of pesticide sorption-desorption by wood-soils, as sorption capacity could increase, with changes in pesticide bioavailability and final fate. The objective of this work was to study the effect that pine and oak wood added to soils had on the sorption/desorption of the pesticides linuron, alachlor, and metalaxyl. Experiments were conducted with two sandy loam and sandy clay soils each amended with two wood doses (5% and 50%) after different incubation times (0, 5 and 12 months). A low wood dose (5%) had no significant impact on the sorption (K_f) of alachlor, but K_f increased for linuron (up to 5.4-1.7 times) and metalaxyl (up to 3.2 and 8.6 times) in all wood-soil systems. The results were not significantly different after different incubation times. The desorption results indicated that wood decreases the sorption irreversibility of alachlor, and increases that of linuron and metalaxyl, with a varying effect of the wood-soil incubation time. The addition of a high wood dose to soil (50%) was more significant for increasing the sorption of all the pesticides, and the sorbed amounts remaining after desorption (>49% for linuron, >33% for alachlor and >6% for metalaxyl), although there was no apparent discrimination between the two types of woods. The role of the nature of the wood (K_{oc} values) for sorption was evidenced for alachlor and metalaxyl, but not for linuron. These outcomes are of interest for extending wood application to soil as a barrier for avoiding environmental risk by point-source pollution due to the use and management of pesticides in farming systems.

Key words: Oak, pine, wood, soils, sorption, desorption, bioavailability, alachlor, linuron, metalaxyl.

1. Introduction

Pesticides are used in modern farming to increase food production. However, surface and ground water contamination has been detected in recent years, possibly due to inadequate pesticide management (Herrero-Hernández et al., 2013; Papadakis et al., 2015; Ccanccapa et al., 2016). Point-source pollution caused by accidental spillages when filling a tank or cleaning spraying equipment has been identified as a major contamination risk (Castillo et al., 2008; Karanasios et al., 2012). To reduce this pollution, the use of natural organic materials or modified inorganic materials as barriers for enhancing the retention of pesticides by soils has been attracting growing attention for some years now (Rodríguez-Cruz et al., 2007a; Marín-Benito et al., 2012a; Tran et al., 2015; Álvarez-Martín et al., 2016a; Centofanti et al., 2016), because organic matter (OM) plays an important role in the sorption of these compounds. These techniques enhance the initial immobilization of pollutants in the barrier, and their subsequent chemical, physical and biological transformation (De Wilde et al., 2009).

The biodegradation of pesticides after the addition of organic materials to soil may occur because the application of an additional source of OM, and sometimes microorganisms, accelerates the degradation of pesticides (Kravvariti et al., 2010; García-Delgado et al., 2015; Pinto et al., 2016). Most of these organic materials or biomasses can in fact allow the development of fungi producing extracellular ligninolytic enzymes that promote pesticide degradation (Castillo and Torstensson, 2007), preventing their transport to surface and ground waters (De Wilde et al., 2009). However, by decreasing the bioavailability of pesticides owing to their increased sorption capacity, the addition of an organic residue to soil may also decrease pesticide degradation (Briceño et al., 2007; Kravvariti et al., 2010; Álvarez-Martín et al., 2016b). Accordingly, there is increased interest in evaluating the sorption-desorption capacity of pesticides by the biomixtures of soil-organic residue as the principal component in the barrier system, which is the main

element controlling immobilization and degradation efficacy, and therefore pesticide dissipation (Karanasios et al., 2012).

One type of highly promising organic materials for biosorption are lignocellulosic wastes and by-products containing lignin, available in large amounts from forestry and industrial activities (Karanasios et al., 2010, 2012; Pintor et al., 2012; Abdolali et al., 2014; Muter et al., 2014). The literature has covered the use of bark, cork and woodchip residues as biomaterials or low-cost sorbents for point-source pollution barriers, or for creating sorbent zones in the soil to increase the sorption of organic pollutants and delay their mobility. There are studies on hydrophobic compounds such as toluene, benzene and o-xylene (MacKay and Gschwend, 2000), polynuclear aromatic hydrocarbons (Boving and Zhang, 2004), persistent organic pollutants (Olivella et al., 2011, 2013) and pesticides (Brás et al., 1999; Domingues et al., 2007; Rodríguez-Cruz et al., 2007b; Boudesocque et al., 2008; Esra Ilhan et al., 2012; Olivella et al., 2015; Mandal and Singh, 2016).

Besides lignin, wood contains cellulose and hemicellulose as its main components. Rodríguez-Cruz et al. (2009) have reported that lignin, the hydrophobic component of wood, has a high sorption capacity towards hydrophobic organic compounds and/or pesticides, which can be retained by different interaction mechanisms. The authors studied the sorption–desorption and interaction mechanisms of three non-ionic pesticides (linuron, alachlor and metalaxyl) and two ionic ones (paraquat and dicamba) by three commercial lignins (hydrophobic macromolecule) and cellulose (hydrophilic macromolecule) as wood components. The use of wood residues as a soil amendment and their potential to immobilize pesticides, and hence their potential to be used in technologies for preventing soil and water pollution, has not been widely reported. Some studies provide information on the properties of different woods and pesticides involved in the immobilization process (Rodríguez-Cruz et al., 2007b) or the effect of fixed wood barriers on the retention of pesticides under saturated flow conditions (Rodríguez-Cruz et al., 2011). However, a

further scale-up of such studies requires biomixing these biomasses with soils of different properties at both bench and pilot scales. Gathering information about this performance involves investigating the sorption capacity of pesticides by biomass-soil mixtures and their potential for desorption as an indicator of the bioavailability of the sorbed compounds. These processes depend on the characteristics of wood-soil systems and on the properties of pesticides (Chaplain et al., 2011).

Linuron, alachlor and metalaxyl are compounds from urea, chloroacetanilide and alaninate that constitute some of the most important groups of pesticides used in agriculture. They have very different properties in terms of water solubility, hydrophobicity and GUS mobility index (PPDB, 2016). These compounds could be considered models for (i) studying the effect different factors have on sorption-desorption by wood-soil systems, and (ii) extending the information to other pesticides widely used in farming, involving biobed systems supported with wood residues.

The objective of this work was to study the effect that two woods, pine (softwood) and oak (hardwood), added as sawdust to sandy loam and sandy clay soils, had on the immobilization of three pesticides with different characteristics: linuron, alachlor, and metalaxyl. Assays were conducted on the sorption/desorption of such compounds in the two soils amended with two doses of wood and in soil-wood systems after different incubation times (0, 5 and 12 months) in order to i) evaluate such processes under more extended conditions, and ii) better simulate real field scenarios for the retention of pesticides from point sources of pollution.

2. Materials and Methods

2.1. Soil and wood samples

Samples of two soils with different properties were collected from the surface layer (0-15 cm depth) of an agricultural field located in Aldearrubia (AL-soil) (41° 0' 29.16" N,

5° 29' 51" W) and in Castellano de Moriscos (CM-soil) (41° 01' 10.92" N, 5° 35' 33" W), both in the province of Salamanca (Spain). The soils were left overnight at room temperature to reduce moisture content, and then sieved (<2 mm). The pH was determined in a soil/water suspension (1/2.5 w/v), and particle size distribution was determined using the pipette method. Organic carbon (OC) content was determined by oxidation (Walkley–Black method). AL-soil was a Fluventic Eutrochrepts soil (Soil Survey Staff, 2010) of a sandy loam texture (11.8% clay, 13.6% silt, and 74.5% sand), with 0.51% OC content, a pH of 6.3, and a cation exchange capacity of 4.8 cmol kg⁻¹, whereas CM-soil was a Typic Rhodolxeralfs soil of a sandy clay texture (38.1% clay, 5.8% silt, and 56.1% sand), with 1.04% OC content, a pH of 6.9 and a cation exchange capacity of 20.5 cmol kg⁻¹ (Bremner, 1996). The clay minerals identified by X-ray diffraction indicated the presence of illite and kaolinite (AL-soil), and of montmorillonite, illite and kaolinite (CM-soil). The water holding capacities were 34% and 44% for AL-soil and CM-soil, respectively.

Pine and oak sawdust (<1 mm) was obtained from a local industry in Salamanca (Spain). The woods' main physicochemical properties have been determined in a previous work (Rodríguez-Cruz et al., 2007b). They have a similar total OC content, 38.5 (oak) - 41.6% (pine), but different soluble organic carbon (DOC), 6.86% for oak and 1.62% for pine, and different lignin contents: 18.2% for oak and 24.4% for pine.

2.2. Chemicals

Alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide) was supplied by Chem Service (West Chester, USA) (99.5% purity). It is a solid herbicide with a water solubility of 240 µg mL⁻¹ at 20°C. Linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea) was supplied by Riëdel de Haën (Hannover, Germany) (>99% purity). It is a solid herbicide with water solubility of 63.8 µg mL⁻¹ at 20°C. Metalaxyl (methyl N-(methoxyacetyl)- N-(2,6-xylyl)-DL-alaninate) was supplied by Riëdel de Haën (Hannover,

Germany) (>98% purity). It is a solid fungicide with a water solubility of 8400 $\mu\text{g mL}^{-1}$ at 22°C. The log K_{ow} values for these compounds at pH 7 and 20°C were 3.09 for alachlor, 3.00 for linuron, and 1.75 for metalaxyl. The GUS index values (1.08 for alachlor, 2.34 for linuron, and 2.79 for metalaxyl) (Table S1 in the Supplementary Material, PPDB, 2016) indicate the low or moderate leaching potential of these compounds for moving toward groundwater, although literature data support their frequent presence in it (Herrero-Hernández et al., 2013). The ^{14}C -labelled pesticides with a specific activity of 2.31 MBq mg^{-1} and 97.0% purity (alachlor), 4.13 MBq mg^{-1} and 98% purity (linuron), and 1.37 MBq mg^{-1} and 97.2% purity (metalaxyl) were supplied by International Isotopes (Munich, Germany).

2.3. Treatment of soils with oak and pine wood

A bulk sample of 2 kg dry weight (dw) of soil was placed in a glass laboratory biobed (40 x 30 x 15 cm), and amended with oak and pine sawdust (<1 mm) at a dose of 5% w/w, equal to 40 t C ha^{-1} , similar to other organic residues (Rodríguez-Cruz et al., 2012), and ten times higher at 50% w/w, equal to 400 t C ha^{-1} , to examine the effect of the wood dose and its nature. The soils' initial moisture content was adjusted to 40% of their maximum water-holding capacity. A fraction of unamended AL-soil and CM-soil and both soils amended with the low dose (5%) of wood was incubated in a thermostated chamber at 20°C and 40% of water-holding capacity for 0, 5 and 12 months. Sub-samples were analyzed to assess OC content. The results are included in Table 1.

2.4 Effect of the incubation time of wood-amended soils on pesticide sorption/desorption

The isotherms of the sorption of ^{14}C -linuron, ^{14}C -alachlor and ^{14}C -metalaxyl by the soils and wood-soil mixtures after 0, 5 and 12 months of incubation were obtained using the batch equilibrium technique. Triplicate samples (5 g) of both AL-soil and CM-soil

amended with oak and pine at dose 5% were treated with 10 mL of an aqueous solution of each pesticide at concentrations of 1, 5, 10, 15, 20, and 25 mg L⁻¹, and at an activity of 100 kBq L⁻¹. The soil:solution ratio was adapted to obtain a suitable sorption according to the OECD guideline (OECD/OCDE, 2000). The suspensions were shaken intermittently at 2-3 h intervals for 24 h in a thermostated chamber at 20°C. They were subsequently centrifuged at 5045 g for 15 min, and the pesticide concentrations were determined. Preliminary experiments showed that a contact for 24 h was long enough for equilibrium to be reached. The amount of pesticide sorbed (C_s) was considered to be the difference between that initially present in the solution (C_i) and that remaining after equilibration (C_e) with the soil or wood-soil. After sorption equilibrium had been reached, 5 mL of supernatant was removed from the sorption equilibrium solution and immediately replaced by 5 mL of deionized water for the desorption study of pesticides. The resuspended samples were shaken at 20°C for 24 h, after they were centrifuged, and the amount of pesticide desorbed was measured. This desorption procedure was repeated four times for each sample.

The sorption and desorption data of all the pesticides were fitted to the linearised form of the Freundlich equation: $\log C_s = \log K_f + n_f \log C_e$ or $\log C_s = \log K_{fd} + n_{fd} \log C_e$, where C_s (mg kg⁻¹) is the amount of sorbed pesticide, C_e (mg L⁻¹) is the equilibrium concentration of pesticide in solution, and K_f or K_{fd} (mg^{1-nf} kg⁻¹ L^{nf}) and n_f or n_{fd} are the Freundlich sorption or desorption coefficients and nonlinearity coefficients, respectively. The hysteresis coefficients of the desorption isotherms (H) were also calculated ($H = n_f/n_{fd}$).

2.5 Effect of wood dose on pesticide sorption/desorption by soils

The sorption of ¹⁴C-linuron, ¹⁴C-alachlor and ¹⁴C-metalaxyl by triplicate samples of wood-soil at the dose of 50% w/w was determined as a single-point concentration based on the highest concentration used for the isotherms (25 mg L⁻¹). The procedure to determine

the amount of pesticide sorbed was similar to that previously indicated. Distribution coefficients, K_d ($L\ kg^{-1}$), were determined for comparing the pesticide's capacity for sorption by the wood-soil mixtures at low and high doses. They were calculated from the relationship between C_s ($mg\ kg^{-1}$) and C_e ($mg\ L^{-1}$) ($K_d = C_s/C_e$). K_d values normalised to 100% OC (K_{oc}) were also obtained as $K_d\ 100/\%OC$.

Pesticide desorption was also studied as previously indicated (i.e. desorption procedure was carried out four times for each sample), with calculation of the amounts of pesticides initially sorbed (Sorb%), desorbed (Des%) and sorbed after desorption or net sorption (n-Sorb %), i.e., sorption minus desorption.

2.6 Analytical determination of pesticides

The quantity of ^{14}C -alachlor, ^{14}C -linuron and ^{14}C -metalaxyl after sorption was determined on a Beckman LS6500 liquid scintillation counter (Beckman Instruments Inc., Fullerton, CA). The equilibrium solution's radioactivity was measured in disintegrations per minute (dpm), and was determined in 1 mL of supernatant to which 4 mL of scintillation cocktail (Ecoscint TMA, National Diagnostics, Atlanta, GA) had been added. The dpm value recorded was related to the dpm obtained for aliquots of the respective standards of the pesticide solutions. Determinations were performed in duplicate for all the solutions, and the coefficient of variation was always $<2\%$. Solution quenching was corrected with chemical quench curves generated using ^{14}C -standards purchased from Beckman.

2.7 Statistical analysis

Standard deviations (SD) were used to indicate variability in the sorption coefficients among triplicates. Sorption constant values were subjected to an analysis of variance, and the least significant difference (LSD) was determined at a confidence level of

95% to measure the effects of different treatments on the sorption of pesticides by soils.
The IBM SPSS Statistics 22.0 software for Windows was used.

3. Results and Discussion

3.1 Effect of the incubation time of wood-soils on pesticide sorption/desorption by soils

Fig. 1-3 include the sorption-desorption isotherms of linuron, alachlor and metalaxyl for AL-soil and CM-soil amended with the low dose (5%) of wood after 0 (0 m), 5 (5 m) and 12 (12 m) months of incubation. All the isotherms fitted the Freundlich sorption equation ($r \geq 0.96$; $p < 0.01$ (sorption) and $r \geq 0.89$; $p < 0.05$ (desorption)), and Tables S2-S4 in the Supplementary Material show the sorption and desorption coefficients (K_f and n_f , K_{fd} and n_{fd}) determined from this equation.

All the isotherms obtained for linuron and some of those obtained for alachlor were nonlinear L-type (Fig. 1 and 2), with n_f values ranging from 0.77 to 0.93 (Tables S2-S3 in the Supplementary Material); whereas those of metalaxyl were linear for wood-soils (Fig. 3) (n_f values 0.95-1.07) and of S-type (n_f values 1.12-1.67) for both unamended soils (Table S4 in the Supplementary Material). For alachlor, these isotherms can be considered linear at 0 m and 12 m, and resemble a C-type (Fig. 2) because the n_f values fall within the range established by Pignatello et al. (2006) for an isotherm to be considered linear, with n_f values merely from 0.95 to 1.02 for both combinations of both soils amended with oak and pine (Table S3 in the Supplementary Material). This isotherm variability indicates that different sorption mechanisms may exist between pesticides and soil components and/or wood components (lignin and cellulose). Nonlinear isotherms have been reported for the sorption of non-ionic compounds of a polar nature by humic acid and the humin fractions of a peat soil, and additional specific interactions of the solute with the active groups of OM have been suggested (Chiou et al., 2000). In addition, Xing et al. (1994) have described the sorption of different non-ionic organic compounds, such as phenol, toluene, xylene, and

benzene by lignins and humic acids as linear isotherms, suggesting partitioning as a sorption mechanism.

The K_f values of pesticides sorbed by the unamended soils indicate that sorption was in the order: alachlor>linuron>metalaxyl, with the parameters obtained in CM-soil being higher than in AL-soil for alachlor and linuron (Tables S2 and S3 in the Supplementary Material). These sorption coefficients were 3.29 (AL-soil) - 5.90 (CM-soil) (alachlor), 1.60 (AL-soil) - 4.30 (CM-soil) (linuron), and 0.20 (AL-soil) - 0.13 (CM-soil) (metalaxyl). The highest sorption by CM-soil of a sandy clay texture could be explained by its higher clay content and the presence of montmorillonite clay mineral, which should favour the sorption of pesticides of a polar nature (Álvarez-Martín et al., 2016a). The K_f values of these pesticides sorbed by soils to a greater or lesser extent and the influence of soil properties have been reported in the literature (Sánchez-Camazano et al., 2000; Andrades et al., 2001, Sakaliene et al., 2007).

The effect that the application of pine or oak woods to the soils at the lower dose (5%) had on pesticide sorption varied, increasing or decreasing, depending on different factors. This effect was negative for the sorption of alachlor by wood-soils. Initially, the sorption of alachlor by oak amended AL-soil was similar to unamended AL-soil ($LSD=0.569$, $p=0.08$), while the sorption of alachlor by oak or pine amended CM-soil decreased significantly relative to unamended soil ($LSD=0.593$, $p=0.001$) (Table S3 in the Supplementary Material). Compared to the non-incubated wood-soils, the K_f coefficients did not record any significant change after the incubation of wood-soil for five and 12 months. The evolution of the wood applied to soil was evident over time, since the OC content of the wood-soil systems decreased by 20%-35% (Table 1). However, the sorption capacity of this herbicide was not significantly modified except for AL-soil+oak. The results indicate that the application of wood to soil at the low dose (5%) did not report an increase in alachlor sorption, although considerable sorption of alachlor by pine and oak

woods (without soil) has been observed (Rodríguez-Cruz et al., 2007b). Some studies have reported that alachlor K_d values increase in soils amended with other organic materials, such as lignocellulosic residue and cattle waste (Dorado et al., 2005) or swine wastewater (Dal Bosco et al., 2012). The behaviour of alachlor observed here could occur if wood had contributed to masking of sorption sites. Bonfleur et al. (2016) observed a decreased sorption of alachlor, bentazon and imazethapyr in tropical soils and indicated that organomineral interactions may lead to greater blockage of sorption sites on OM in these soils than in subtropical soils. Celis et al. (2006) have also indicated that clay inorganic constituents play a major role in binding soil OM, with the mineral-bound organic material being less accessible for incorporating hydrophobic organic compounds than free organic material. Accordingly, the mainly decreased affinity of alachlor by CM-soil with montmorillonite clay mineral may be explained after wood addition.

Conversely, the K_f coefficients of linuron and metalaxyl for the wood-soils increased significantly compared to the corresponding unamended soil (Tables S2 and S4 in the Supplementary Material). However, the influence of the type of wood (pine or oak) on the sorption of both pesticides was not significant, although Rodríguez-Cruz et al. (2007b) have reported the higher sorption of pesticide by pine than by oak due to its higher lignin content. The K_f sorption constants of the pesticides for the wood-soils after different incubation times increased by up to 4.8 and 5.4 times in AL-soil with oak or pine, by up to 1.76 and 1.70 times in CM-soil with oak and pine for linuron, by up to 3.2-4.4 times in AL-soil with oak or pine, and by 8.6-8.0 times in CM-soil with oak and pine for metalaxyl. The K_f values obtained after the incubation times were only significantly different for linuron in the AL-soil.

A significant simple linear correlation coefficient between the sorption constants K_f and the soil OC contents of soils and wood-soils was found for linuron ($r=0.56$, $p<0.05$) and metalaxyl ($r=0.59$, $p<0.05$), in spite of the different hydrophobic nature of these pesticides.

The influence of the OC content of unamended soils or soils amended with organic residues from different origins, such as sewage sludge, grape marc, and spent mushroom substrate (SMS), was indicated for the sorption of linuron (Sánchez-Camazano et al., 2000; Rodríguez-Cruz et al., 2012). Similarly, an increase in the sorption of metalaxyl by soils amended with SMS or solid wine distillery wastes has been reported (Andrades et al., 2004; Marín-Benito et al., 2012b), in spite of the hydrophilic nature of this compound, according to its log K_{ow} and water solubility.

The reversibility of pesticide sorption by wood-soils was studied by desorption isotherms from samples initially treated with 25 mg L⁻¹ of linuron, alachlor and metalaxyl after 0, 5 and 12 months of wood-soil incubation (Fig. 1-3). As the desorption data did not match those of the sorption isotherm, the desorption isotherms showed hysteresis in varying degrees for all the pesticides and treatments considered. The hysteresis coefficients obtained were constantly > 1 for both unamended and wood-soils (Tables S2-S4 in the Supplementary Material), indicating that the desorption process was not fully reversible.

According to the H coefficients, the higher hysteresis was obtained for alachlor desorption (Table S3 in the Supplementary Material). The H values for the unamended soils were very high (16.2 (AL-soil) - 11.3 (CM-soil)), being 2.5 and 1.5 times higher than the mean H values for wood-soils. The presence of wood at the dose of 5% in the soils enhanced alachlor desorption. These results are in agreement with the sorption ones, since higher sorption irreversibility was observed for the unamended soils, and decreased in the wood-soils. The K_{fd} values for the AL-soil+oak were in general higher than for the AL-soil+pine (LSD=3.184, p=0.001), and an increase in sorption irreversibility at the longer incubation time was observed in both systems. However, in the CM-soil, the K_{fd} values for soil+pine or oak were not significantly different (LSD=4.113, p= 0.000), and sorption irreversibility either decreased or was similar with incubation time. Accordingly, the bioavailability of alachlor in the wood-soils would depend on the type of amended soil,

being enhanced over time in the CM-soil, with a higher sorbent capacity after the addition of wood.

The desorption isotherms of linuron showed hysteresis, although the K_{fd} values of the unamended soils were not statistically different to the wood-soils, which indicates that the wood did not enhance the desorption of linuron, as occurred in the case of alachlor. Furthermore, in the wood-soils, K_{fd} value increased with the incubation time in the CM-soil+pine or oak (LSD=7.941, $p=0.031$), and AL-soil+pine (LSD=7.430, $p=0.259$), which meant an increase in desorption hysteresis (Table S2 in the Supplementary Material). The formation of bound residues of this herbicide has been reported in soils amended with sewage sludge, grape marc or SMS (Marín-Benito et al., 2014), and could explain the increase in sorption irreversibility because its bioavailability decreased over time.

When considering the desorption data of metalaxyl, it is interesting to note that the desorption coefficients increased significantly in the wood-soils (LSD=1.973, $p=0.001$ (AL-soil) and LSD=3.022, $p=0.043$ (CM-soil)). In the AL-soil, K_{fd} values were higher for AL-soil+oak than for AL-soil+pine, but this was not observed in the CM-soil (Table S4 in the Supplementary Material). Sorption irreversibility increased in both wood-soils, although it decreased over time due to a significant increase in desorption, conversely to the desorption results for linuron and alachlor indicated above. Hence, an initial increase in metalaxyl sorption by the wood-soils would be followed by an increase in its bioavailability over time. A similar effect has been reported by Marín-Benito et al. (2012b) for metalaxyl in soils amended with SMS after different incubation times.

3.2 Effect of wood dose on pesticide sorption/desorption by soils

The effect of the application of a high dose (50%) of wood as a soil amendment was studied to evaluate its use in real scenarios for the retention of the pesticides involved in point-source pollution. Table 2 and Fig. S1 in the Supplementary Material include the

sorption and desorption results of linuron, alachlor and metalaxyl by AL-soil and CM-soil with the high dose (50%) of the two woods applied, and with the low dose (5%) for comparison purposes at an initial concentration of pesticides ($25 \mu\text{g mL}^{-1}$). The results are expressed in terms of K_d distribution coefficients, sorbed amounts relative to initial amount added (Sorb%), desorbed amounts (Des%), and net-sorbed amounts (remaining after desorption) (n-Sorb%) of pesticides for soils and wood-soils after four consecutive desorption cycles.

Among the different pesticides, the maximum sorption and minimum desorption corresponded to alachlor in the unamended soils. Thus, a maximum peak of n-Sorb% of 25.9% was determined for this pesticide in CM-soil, whereas only minimum peaks of n-Sorb% of 1.53-1.78% were observed for metalaxyl in both soils (Table 2). When the woods were applied at a low dose, only n-Sorb% of linuron and metalaxyl increased, but pesticide sorption by soils increased in all the conditions when the woods were applied at a high dose ($p < 0.05$). Pesticide sorption by wood-soils recorded a maximum peak of n-Sorb% $> 49\%$ for linuron in both soils with a high dose of wood applied, whereas values of n-Sorb% $> 33\%$ and $> 6\%$ were observed for alachlor and metalaxyl in similar conditions.

The mean increases or decreases in n-Sorb% were 1.4-1.3 times (linuron), 2.4-2.3 times (metalaxyl), and 0.9-0.7 times (alachlor) in AL-soil and CM-soil with a low dose of wood. Increases were observed in all cases for n-Sorb% by AL-soil and CM-soil with the high dose of wood compared with the unamended soils: 6.6-4.7 times (linuron), 2.0-1.4 times (alachlor), and 4.1-3.6 times (metalaxyl).

The results were outstanding for soils with a high dose of wood applied, and they were consistent with the high increase in OC content of wood-soils with respect to the unamended ones (24-33 times (AL-soil) and 11-17 times (CM-soil)) (Table 1). A significant linear correlation was found between sorption parameters (K_d , %Sorb and n-Sorb%) and the OC contents including all the samples examined for each pesticide. These

simple linear correlation coefficients (r) were in the 0.964-0.985 ($p<0.001$) range for linuron, 0.920-0.981 ($p<0.001$) for alachlor, and 0.933-0.975 ($p<0.001$) for metalaxyl. However, only a significant negative correlation was found between %Des and OC content for linuron ($r=0.704$ $p<0.05$), indicating that OC helped to increase linuron sorption, but did not enhance its desorption, and hence decreased the bioavailability of the compound sorbed by the wood-soil system.

In relation to the effect of the OC nature of the unamended soil and soils with oak and pine wood with different lignin content, values of K_d related to 100% of OC (K_{oc}) were calculated (Table 2). K_{oc} values corresponding to linuron sorption by unamended and wood-soils were very similar ($VC=18.3-25.5\%$), indicating that this sorption depended on the OC content of both soils according to the relationship indicated above, with the nature of this OC (from unamended and wood-soils) being less important for the sorption of this compound. This corroborates previous results on linuron sorption by soils amended with other organic amendments (Rodriguez-Cruz et al. 2012). However, the K_{oc} values corresponding to the sorption of alachlor and metalaxyl by unamended and wood-soils are very different, with VCs varying in a wide range (105-92.2% and 62.4-86.6%, respectively). The K_{oc} values found for unamended soils were much higher than those found for wood-soils, indicating the importance of the OC nature on the sorption of these pesticides. The higher K_{oc} values of alachlor and metalaxyl in the unamended soils than in wood-soils indicated the highest capacity of natural soil OC for the sorption of these pesticides or the influence of other soil parameters on this process. In addition the nature of wood was not evident despite the different composition of oak or pine wood. The contrasting behaviour of the pesticides is probably linked to their different interaction mechanisms with the wood or soil components. The less hydrophobic pesticide metalaxyl might interact through hydrogen bond with OH functional groups of wood components (lignin and cellulose) or with the organic and inorganic moieties of the soil, and alachlor

and linuron could be sorbed mainly through a hydrophobic mechanism or by formation of bonds via charge transfer. These interaction mechanisms have been reported by Rodriguez-Cruz et al. (2009) in a FTIR study of the pesticides sorbed by lignin and cellulose.

4. Conclusions

The results reveal that the addition of wood to soils did not significantly increase the sorption of all the pesticides by both the soils studied. The response of the soil to oak or pine wood treatment at a low dose (5%) was more evident for linuron and metalaxyl in both soils, and for alachlor in the sandy loam soil, because alachlor sorption by the wood-sandy clay soil at a low dose decreased compared to sorption by the unamended soil. This trend was not observed when increasing the wood dose (50%) because the sorption of all the pesticides increased under all conditions. Alachlor desorption and/or its possible bioavailability from wood-soils was enhanced, although depending on the type of soil this trend changed after 12 months of incubating wood-soil systems. However, the presence of wood did not enhance linuron desorption and/or possible bioavailability in any soil sample or the initial desorption of metalaxyl, although this trend changed with incubation time when metalaxyl desorption was increased. The results obtained indicate that the application of a suitable dose of wood to soils may favour pesticide retention by soils even after extended incubation times, but the nature of the soils and pesticides needs to be considered if the subsequent degradation/dissipation of pesticides is to avoid the leaching of these compounds in farming systems.

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584

FIGURE LEGENDS

Fig. 1. Sorption-desorption isotherms of linuron for unamended soils (AL-soil and CM-soil) and soils amended with the low dose (5%) of oak and pine wood after 0 (0 m), 5 (5 m) and 12 (12 m) months of incubation. Closed symbols correspond to sorption; open symbols correspond to desorption (C_e , pesticide equilibrium concentration (mg L^{-1}) and C_s , pesticide sorbed concentration (mg kg^{-1})). Error bars represent standard deviation of the mean value ($n=3$). Least significant difference (LSD95%) among treatments and incubation times for each soil are included in Table S2.

Fig. 2. Sorption-desorption isotherms of alachlor for unamended soils (AL-soil and CM-soil) and soils amended with the low dose (5%) of oak and pine woods after 0 (0 m), 5 (5 m) and 12 (12 m) months of incubation. Closed symbols correspond to sorption; open symbols correspond to desorption (C_e , pesticide equilibrium concentration (mg L^{-1}) and C_s , pesticide sorbed concentration (mg kg^{-1})). Error bars represent standard deviation of the mean value ($n=3$). Least significant difference (LSD95%) among treatments and incubation times for each soil are included in Table S3.

Fig. 3. Sorption-desorption isotherms of metalaxyl for unamended soils (AL-soil and CM-soil) and soils amended with the low dose (5%) of oak and pine woods after 0 (0 m), 5 (5 m) and 12 (12 m) months of incubation. Closed symbols correspond to sorption; open symbols correspond to desorption (C_e , pesticide equilibrium concentration (mg L^{-1}) and C_s , pesticide sorbed concentration (mg kg^{-1})). Error bars represent standard deviation of the mean value ($n=3$). Least significant difference (LSD95%) among treatments and incubation times for each soil are included in Table S4.

Table 1.

Organic carbon content (OC) of AL-soil and CM-soil unamended and amended with oak or pine wood at two doses (5% and 50%) and incubated at different times (0 (0m), 5 (5m) and 12 (12m) months).

Sample	Organic carbon (%)		
	0m	5m	12m
AL-soil	0.51	-	-
CM-soil	1.04	-	-
AL-soil+oak 5%	2.05	1.88	1.57
AL-soil+oak 50%	12.5	-	-
AL-soil+pine 5%	2.70	2.33	2.00
AL-soil+pine 50%	16.9	-	-
CM-soil+oak 5%	2.67	1.98	1.72
CM-soil+oak 50%	12.3	-	-
CM-soil+pine 5%	3.25	2.55	2.25
CM-soil+pine 50%	18.7	-	-

Table 2.

Effect of pine and oak at doses of 5% and 50%, as amendments of AL-soil and CM-soil on the sorption and desorption of linuron, alachlor and metalaxyl. Distribution coefficients (K_d ($L\ kg^{-1}$)), sorbed (Sorb%), desorbed (Des%) and net-sorbed (after desorption) (n-Sorb%) pesticide percentages are indicated as mean values $\pm$ standard deviation.

Sample	$K_d \pm SD^a$	K_{oc}^b	Sorb $\pm SD\%$	Des $\pm SD\%$	n-Sorb $\pm SD\%$
Linuron					
AL-soil	1.39 $\pm$ 0.17a	274	12.2 $\pm$ 1.79a	31.5 $\pm$ 1.03a	8.34 $\pm$ 1.15a
AL-soil+oak 5%	3.83 $\pm$ 0.03a	187	30.9 $\pm$ 1.14b	60.8 $\pm$ 2.54b	12.1 $\pm$ 0.89a
AL-soil+oak 50%	27.5 $\pm$ 0.19b	220	73.3 $\pm$ 0.18c	33.4 $\pm$ 0.04a	48.9 $\pm$ 3.44b
AL-soil+pine 5%	4.63 $\pm$ 0.61a	171	32.9 $\pm$ 1.22b	63.5 $\pm$ 2.32b	12.0 $\pm$ 0.19a
AL-soil+pine 50%	35.4 $\pm$ 6.13b	209	77.9 $\pm$ 2.9c	29.3 $\pm$ 3.61a	55.1 $\pm$ 0.73c
VC% ^c	108	18.3	63.2	38.7	83.2
LSD ^d 95%	8.07	-	6.17	18.5	6.19
CM-soil	2.86 $\pm$ 0.10a	275	22.3 $\pm$ 0.81a	51.8 $\pm$ 1.53b	10.7 $\pm$ 0.78a
CM-soil+oak 5%	4.54 $\pm$ 0.31a	170	32.2 $\pm$ 1.23b	54.3 $\pm$ 5.12b	14.7 $\pm$ 2.12a
CM-soil+oak 50%	26.5 $\pm$ 5.11b	215	72.6 $\pm$ 3.71c	31.4 $\pm$ 1.14a	49.8 $\pm$ 1.75b
CM-soil+pine 5%	4.94 $\pm$ 0.13a	152	33.7 $\pm$ 0.56b	57.4 $\pm$ 6.54b	14.3 $\pm$ 1.75a
CM-soil+pine 50%	31.4 $\pm$ 0.30b	167	75.8 $\pm$ 0.18c	33.3 $\pm$ 0.71a	50.5 $\pm$ 0.65b
VC%	97.8	25.5	52.7	26.9	72.4
LSD 95%	8.33	-	6.54	13.9	5.54
Alachlor					
AL-soil	3.16 $\pm$ 0.09a	624	24.0 $\pm$ 0.73a	14.2 $\pm$ 0.25a	20.6 $\pm$ 0.11b
AL-soil+oak 5%	3.15 $\pm$ 0.16a	154	26.8 $\pm$ 0.83a	29.8 $\pm$ 0.67bc	18.8 $\pm$ 0.73ab
AL-soil+oak 50%	10.2 $\pm$ 0.39b	81.6	50.5 $\pm$ 0.95b	33.3 $\pm$ 0.59bc	33.7 $\pm$ 0.34c
AL-soil+pine 5%	3.88 $\pm$ 0.12a	144	27.6 $\pm$ 0.64a	38.4 $\pm$ 4.23c	17.0 $\pm$ 0.82a
AL-soil+pine 50%	13.5 $\pm$ 0.43c	79.8	57.4 $\pm$ 0.79c	26.6 $\pm$ 0.78b	42.1 $\pm$ 0.14d
VC%	70.5	105	41.5	31.9	41.4
LSD 95%	1.56	-	4.48	11.1	2.93
CM-soil	4.47 $\pm$ 0.02b	429	30.9 $\pm$ 0.12b	16.3 $\pm$ 3.63a	25.9 $\pm$ 3.43ab
CM-soil+oak 5%	3.51 $\pm$ 0.10a	131	27.6 $\pm$ 0.51a	30.7 $\pm$ 2.03b	19.0 $\pm$ 0.23a
CM-soil+oak 50%	10.6 $\pm$ 0.06c	86.2	51.4 $\pm$ 0.15c	33.4 $\pm$ 0.29b	33.9 $\pm$ 0.25bc
CM-soil+pine 5%	3.35 $\pm$ 0.05a	103	26.2 $\pm$ 0.25a	25.4 $\pm$ 0.76ab	19.5 $\pm$ 0.02a
CM-soil+pine 50%	12.5 $\pm$ 0.09d	67.1	55.7 $\pm$ 0.18d	33.9 $\pm$ 1.86b	36.8 $\pm$ 1.15c
VC%	62.0	92.2	36.6	26.2	30.1
LSD 95%	0.39	-	1.86	11.7	9.17
Metalaxyl					
AL-soil	0.34 $\pm$ 0.02a	66.8	3.27 $\pm$ 0.18a	53.1 $\pm$ 0.18b	1.53 $\pm$ 0.14a
AL-soil+oak 5%	0.60 $\pm$ 0.03a	29.1	5.52 $\pm$ 0.56a	34.3 $\pm$ 2.69a	3.63 $\pm$ 0.05ab
AL-soil+oak 50%	2.88 $\pm$ 0.06b	23.1	22.4 $\pm$ 0.34b	71.8 $\pm$ 6.39c	6.30 $\pm$ 1.51b
AL-soil+pine 5%	0.58 $\pm$ 0.04a	21.6	5.15 $\pm$ 0.35a	38.8 $\pm$ 5.70ab	3.15 $\pm$ 1.19ab
AL-soil+pine 50%	3.16 $\pm$ 0.27b	18.7	24.0 $\pm$ 1.54b	74.6 $\pm$ 0.26c	6.10 $\pm$ 0.46b
VC%	91.5	62.4	84.6	33.8	49.1
LSD 95%	0.46	-	2.79	14.6	3.22
CM-soil	1.19 $\pm$ 0.02a	114	10.6 $\pm$ 0.14b	83.2 $\pm$ 3.0c	1.78 $\pm$ 0.21a
CM-soil+oak 5%	1.02 $\pm$ 0.05a	38.3	10.2 $\pm$ 0.39ab	60.5 $\pm$ 3.45a	4.01 $\pm$ 0.89ab
CM-soil+oak 50%	2.95 $\pm$ 0.06b	23.9	22.7 $\pm$ 0.37c	73.6 $\pm$ 1.41b	6.00 $\pm$ 0.42bc
CM-soil+pine 5%	0.95 $\pm$ 0.01a	29.2	8.51 $\pm$ 0.08a	61.2 $\pm$ 2.75a	3.31 $\pm$ 0.81a
CM-soil+pine 50%	3.85 $\pm$ 0.20c	20.5	27.8 $\pm$ 1.05d	75.3 $\pm$ 0.86bc	6.86 $\pm$ 0.50c
VC%	66.6	86.6	54.5	13.7	46.6
LSD 95%	0.35	-	1.94	9.08	2.25

^a K_d were calculated from the relationship between C_s ($mg\ kg^{-1}$) and C_e ($mg\ L^{-1}$), SD, standard deviation of the mean value ($n=3$). ^b K_{oc} , distribution coefficient normalized to organic carbon (OC) content ($K_d \cdot 100/OC\%$). ^cVC, Variation coefficient. ^dLSD, Least significant difference among treatments for each soil. Means followed by the same letter do not differ significantly at $p<0.05$.

Fig. 1

Fig. 2

Fig. 3

Supplementary Material

Study of processes influencing bioavailability of pesticides in wood-soil systems: Effect of different factors

J. M. Marín-Benito^a, E. Herrero-Hernández^a, M. S. Rodríguez-Cruz^a, M. Arienzo^b, M. J. Sánchez-Martín^{a*}

^aInstituto de Recursos Naturales y Agrobiología de Salamanca, IRNASA-CSIC, Cordel de Merinas 40-52, 37008 Salamanca, Spain

^bDepartment of Earth Science, Environment and Resources, University of Naples Federico II, Largo San Marcellino 10, 80138 Naples, Italy.

*Corresponding author:

e-mail: mjesus.sanchez@irnasa.csic.es (M. J. Sánchez-Martín)

Telephone: +34 923219606; Fax: +34 923219609

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Table S1.Chemical structure and physicochemical properties of pesticides studied^a

Common name IUPAC name	Chemical structure	pK _a	Log K _{ow}	WS (mg L ⁻¹)	GUS index
Linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea)		-	3.00	63.8	2.34
Alachlor 2-chloro-2',6'-diethyl-N-(methoxymethyl)		0.62	3.09	240	1.08
Metalaxyl (methyl N-(methoxyacetyl)-N-(2,6-xyllyl)-DL-alaninate)		-	1.75	8400	2.79

^a From PPDB, Pesticide Properties DataBase (2015) <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>. WS solubility in water at 20 °C, K_{ow} octanol/water partition coefficient at pH 7 and 20°C, pK_a dissociation constant at 25°C.

Table S2.

Freundlich constants for sorption (K_f ($\text{mg}^{1-n_f} \text{kg}^{-1} \text{L}^{n_f}$), n_f) and desorption (K_{fd} ($\text{mg}^{1-n_{fd}} \text{kg}^{-1} \text{L}^{n_{fd}}$), n_{fd}), hysteresis coefficients (H) of linuron by unamended AL-soil and CM-soil and these soils amended with a low dose (5%) of oak and pine wood at different times of incubation wood-soil (no-incubation (0m), five months of incubation (5m) and twelve months of incubation (12m)).

Sample	$K_f \pm \text{SD}^a$	$n_f \pm \text{SD}$	r^2	$K_{fd} \pm \text{SD}$	$n_{fd} \pm \text{SD}$	r^2	$H \pm \text{SD}$
AL-soil	1.60 $\pm$ 0.50a	0.93 $\pm$ 0.56	0.99	20.00 $\pm$ 0.55ab	0.17 $\pm$ 0.05	0.78	5.47 $\pm$ 0.64
AL-soil+oak 0m	5.33 $\pm$ 0.23b	0.90 $\pm$ 0.007	0.99	17.69 $\pm$ 1.12ab	0.52 $\pm$ 0.13	0.99	1.73 $\pm$ 0.21
AL-soil+oak 5m	6.87 $\pm$ 1.12bcd	0.90 $\pm$ 0.11	0.99	20.04 $\pm$ 0.99ab	0.49 $\pm$ 0.12	0.99	1.84 $\pm$ 0.22
AL-soil+oak 12m	7.70 $\pm$ 0.90bcd	0.89 $\pm$ 0.10	0.98	23.56 $\pm$ 2.12ab	0.46 $\pm$ 0.01	0.99	1.93 $\pm$ 0.58
AL-soil+pine 0m	5.94 $\pm$ 1.12bc	0.92 $\pm$ 0.12	0.99	16.80 $\pm$ 2.25a	0.56 $\pm$ 0.12	0.99	1.65 $\pm$ 0.23
AL-soil+pine 5m	8.70 $\pm$ 0.85d	0.77 $\pm$ 0.12	0.99	21.69 $\pm$ 1.25ab	0.45 $\pm$ 0.12	0.99	1.70 $\pm$ 0.23
AL-soil+pine 12m	8.67 $\pm$ 1.25cd	0.87 $\pm$ 0.32	0.97	24.59 $\pm$ 4.54c	0.44 $\pm$ 0.23	0.99	1.97 $\pm$ 0.23
LSD ^b 95%	2.748			7.430			
CM-soil	4.30 $\pm$ 0.56a	0.84 $\pm$ 0.05	0.99	19.63 $\pm$ 3.90a	0.36 $\pm$ 0.06	0.98	2.34 $\pm$ 0.33
CM-soil+oak 0m	6.70 $\pm$ 0.49b	0.88 $\pm$ 0.01	1.00	24.44 $\pm$ 1.20ab	0.42 $\pm$ 0.02	0.99	2.10 $\pm$ 0.23
CM-soil+oak 5m	7.37 $\pm$ 0.25b	0.86 $\pm$ 0.16	0.99	24.99 $\pm$ 1.25ab	0.43 $\pm$ 0.13	0.99	2.00 $\pm$ 0.34
CM-soil+oak 12m	7.58 $\pm$ 0.21b	0.91 $\pm$ 0.11	0.97	35.01 $\pm$ 1.12c	0.35 $\pm$ 0.12	0.99	2.60 $\pm$ 0.21
CM-soil+pine 0m	7.10 $\pm$ 0.24b	0.89 $\pm$ 0.01	0.99	22.51 $\pm$ 2.25ab	0.46 $\pm$ 0.13	0.99	1.93 $\pm$ 0.23
CM-soil+pine 5m	7.16 $\pm$ 0.28b	0.86 $\pm$ 0.16	0.99	23.69 $\pm$ 2.25ab	0.46 $\pm$ 0.15	0.99	1.87 $\pm$ 0.32
CM-soil+pine 12m	7.31 $\pm$ 1.12b	0.88 $\pm$ 0.12	0.99	30.16 $\pm$ 3.21bc	0.36 $\pm$ 0.11	0.99	2.44 $\pm$ 0.25
LSD ^b 95%	1.065			7.941			

^aSD, standard deviation of the mean value (n=3). ^bLSD, Least significant difference among treatments and times for each soil. Means followed by the same letter do not differ significantly at $p < 0.05$.

Table S3.

Freundlich constants for sorption (K_f ($\text{mg}^{1-n_f} \text{kg}^{-1} \text{L}^{n_f}$), n_f) and desorption (K_{fd} ($\text{mg}^{1-n_{fd}} \text{kg}^{-1} \text{L}^{n_{fd}}$), n_{fd}), hysteresis coefficients (H) of alachlor by unamended AL-soil and CM-soil and these soils amended with a low dose (5%) of oak and pine wood at different times of incubation wood-soil (no-incubation (0m), five months of incubation (5m) and twelve months of incubation (12m)).

Samples	$K_f \pm \text{SD}^a$	$n_f \pm \text{SD}$	r^2	$K_{fd} \pm \text{SD}$	$n_{fd} \pm \text{SD}$	r^2	$H \pm \text{SD}$
AL-soil	3.29±0.08a	0.97±0.003	0.99	50.96±0.96e	0.06±0.01	0.93	16.2±1.33
AL-soil+oak 0m	4.27±0.24b	0.91±0.02	0.99	42.44±0.85d	0.16±0.02	0.99	5.69±0.23
AL-soil+oak 5m	3.62±0.23a	0.88±0.01	0.99	29.49±0.28a	0.18±0.01	0.99	4.89±0.12
AL-soil+oak 12m	3.53±0.12a	0.97±0.01	0.99	43.15±0.25d	0.09±0.02	0.95	10.8±0.55
AL-soil+pine 0m	3.68±0.21a	1.02±0.02	0.99	34.06±1.25b	0.25±0.01	0.99	4.08±0.21
AL-soil+pine 5m	3.62±0.16a	0.88±0.02	0.99	27.09±1.21a	0.21±0.05	0.99	4.19±0.22
AL-soil+pine 12m	3.83±0.12ab	0.95±0.01	0.99	39.06±1.24c	0.12±0.03	0.99	7.92±0.01
LSD ^b 95%	0.569			3.184			
CM-soil	5.90±0.32b	0.90±0.02	0.99	63.01±0.25d	0.08±0.07	0.91	11.3±0.12
CM-soil+oak 0m	3.75±0.14a	0.98±0.12	0.99	41.98±0.25bc	0.18±0.11	0.99	5.44±0.33
CM-soil+oak 5m	3.88±0.22a	0.89±0.12	0.99	29.13±0.11a	0.20±0.09	0.99	4.45±0.22
CM-soil+oak 12m	3.86±0.23a	0.94±0.01	0.99	39.68±0.25b	0.12±0.03	0.99	7.53±0.22
CM-soil+pine 0m	3.94±0.21a	0.95±0.02	0.99	44.70±3.65c	0.14±0.02	0.99	6.79±0.89
CM-soil+pine 5m	3.62±0.25a	0.89±0.03	0.99	31.18±2.25a	0.17±0.02	0.99	5.24±0.32
CM-soil+pine 12m	3.59±0.22a	0.97±0.02	0.99	39.91±2.23b	0.14±0.06	0.99	7.13±1.12
LSD ^b 95%	0.592			4.113			

^aSD, standard deviation of the mean value (n=3). ^bLSD, Least significant difference among treatments and times for each soil. Means followed by the same letter do not differ significantly at $p < 0.05$.

Table S4.

Freundlich constants for sorption (K_f ($\text{mg}^{1-n_f} \text{kg}^{-1} \text{L}^{n_f}$), n_f) and desorption (K_{fd} ($\text{mg}^{1-n_{fd}} \text{kg}^{-1} \text{L}^{n_{fd}}$), n_{fd}), hysteresis coefficients (H) of metalaxyl by unamended AL-soil and CM-soil and these soils amended with a low dose (5%) of oak and pine wood at different times of incubation wood-soil (no-incubation (0m), five months of incubation (5m) and twelve months of incubation (12m)).

Samples	$K_f \pm \text{SD}^a$	$n_f \pm \text{SD}$	r^2	$K_{fd} \pm \text{SD}$	$n_{fd} \pm \text{SD}$	r^2	$H \pm \text{SD}$
AL-soil	0.20±0.02a	1.12±0.01	0.96	3.85±0.25a	0.19±0.12	0.86	5.89±0.22
AL-soil+oak 0m	0.6±0.32b	1.00±0.01	0.99	9.45±0.56e	0.12±0.02	0.90	8.33±0.85
AL-soil+oak 5m	0.72±0.12b	0.98±0.05	0.99	9.34±1.22cd	0.17±0.05	0.81	5.76±0.85
AL-soil+oak 12m	0.64±0.25b	0.95±0.12	0.99	8.26±0.65cd	0.15±0.12	0.97	6.46±0.33
AL-soil+pine 0m	0.62±0.12b	0.98±0.11	0.99	7.38±0.23bc	0.16±0.05	0.95	6.13±0.25
AL-soil+pine 5m	0.73±0.25b	0.98±0.11	0.99	5.70±0.22ab	0.30±0.12	0.96	3.26±0.12
AL-soil+pine 12m	0.88±0.12b	0.95±0.12	0.99	4.35±0.22a	0.35±0.12	0.97	2.60±0.33
LSD ^b 95%	0.385			1.973			
CM-soil	0.13±0.02a	1.67±0.25	0.99	2.49±0.22a	0.72±0.12	0.97	2.32±0.36
CM-soil+oak 0m	1.02±0.25b	1.00±0.12	0.99	8.30±1.22c	0.28±0.12	0.80	3.57±0.65
CM-soil+oak 5m	0.99±0.12b	1.02±0.25	0.99	6.80±1.12bc	0.39±0.12	0.98	2.62±0.22
CM-soil+oak 12m	1.12±0.22b	0.99±0.22	0.99	5.13±1.12ab	0.48±0.02	0.94	1.03±0.25
CM-soil+pine 0m	0.96±0.12b	1.00±0.12	0.99	6.95±0.55bc	0.30±0.11	0.90	3.33±0.22
CM-soil+pine 5m	0.86±0.12b	1.07±0.22	0.99	5.41±0.32abc	0.45±0.11	0.95	2.38±0.45
CM-soil+pine 12m	1.04±0.12b	1.05±0.12	0.99	5.50±1.12abc	0.47±0.02	0.94	2.33±0.22
LSD ^b 95%	0.413			3.022			

^aSD, standard deviation of the mean value (n=3). ^bLSD, Least significant difference among treatments and times for each soil. Means followed by the same letter do not differ significantly at $p < 0.05$.

Fig. S1. Sorption distribution coefficients (K_d , $L\ kg^{-1}$), sorbed amounts relative to $25\ \mu g\ mL^{-1}$ initial concentration added (Sorb%), desorbed amounts after four successive desorption stages (Des%), and net-sorbed amounts (remaining after desorption, n-Sorp%) of linuron, alachlor and metalaxyl for unamended AL-soil and CM-soil and both soils amended with the low dose (5%) and high dose (50%) of oak and pine woods without incubation. Error bars represent standard deviation of the mean value ($n=3$). Different letters in bars indicate significant differences among treatments for each parameter and soil ($p<0.05$).