Relationship between The Adsorption Capacity of Pesticides by Wood Residues and The Properties of Woods and Pesticides

SONIA RODRIGUEZ-CRUZ,[‡]
MARIA S. ANDRADES,[†]
MARIA SANCHEZ-CAMAZANO,[‡] AND
MARIA J. SANCHEZ-MARTIN*,[‡]

Instituto de Recursos Naturales y Agrobiología, CSIC. Apdo, 257, 37071 Salamanca, Spain and Departamento Agricultura y Alimentación, Universidad de La Rioja, Madre de Dios, 51, 26006 Logroño, Spain

With the aim to explore the potential use of wood residues in technologies aimed at preventing the pollution of soil and water, we studied the adsorption of four non-ionic pesticides (linuron, alachlor, metalaxyl, and chlorpyrifos) and two ionic pesticides (dicamba and paraquat) with a K_{ow} range of -4.5 to 4.7 by nine types of wood with lignin content in the $18.2-26.9\%$ range. The Freundlich Kf values were considered as indicators of the adsorption capacity. A statistical study was carried out using simple and multiple correlations to establish the degree to which the different parameters of the woods and of the pesticides were involved in adsorption. In the case of the non-ionic pesticides, positive and negative significant correlations were observed between Kf and the lignin ($r = 0.73-0.83$, $p < 0.05-0.01$), and soluble C contents of the woods ($r = 0.66-0.84$), $p < 0.1-0.01$). For dicamba, a correlation between Kf and pH ($r = -0.66$, $p < 0.1$) of the woods was found, while for paraquat, this was seen between Kf and the cation exchange capacity ($r = 0.71$, $p < 0.1$) of the woods. No significant correlation was observed between Kf and the total C content of the woods. A highly significant correlation between Kf and K_{ow} values ($r \geq 0.93$, $p < 0.01$) was found in the adsorption of the pesticides by the woods (with the exception of paraquat) showing that this parameter is very important in this adsorption process. The determination coefficient of the multiple correlation between Kf and the parameters K_{ow}, soluble C, and lignin contents accounts for nearly 100% of the variability in adsorption for non-ionic pesticides. Based on the results of our study and of those of the literature related to the adsorption of aromatic hydrocarbons, we used the K_{ow} values to define a predictive model of adsorption of hydrophobic organic compounds in general by the woods.

Introduction

The number of studies addressing the development of new technologies aimed at mitigating the risk involved in the use of pesticides in agriculture has increased substantially over the past few years. Point sources of water pollution by pesticides are diverse and may be originated by leakages from the devices used to apply the compounds, from spills, and from incorrect disposal of wastes and wash water (*1*). Recent work has shown that the pollution derived from such point sources is more important than that derived from agricultural practices (*2, 3*). Owing to this, the development of new sustainable technologies or methods for reducing pollution point-sources is decisive to avoid later difficult decontamination processes of soil and water. In this sense, some studies reported in the literature have shown that biobeds are able to retain and degrade the pesticides responsible for the pollution resulting from the handling of utensils and machinery, significantly reducing the concentration of leached pesticides (*4, 5*). For the development of these technologies, it is necessary the investigation and selection of new adsorbent materials able to retain or immobilize pesticides and, if possible, at the same time able to facilitate their later degradation to prevent the transport of such compounds and, hence, the pollution of water.

A number of studies have indicated the effect of organic matter (OM) in the adsorption of hydrophobic organic compounds by natural soils (*6−8*) or soils amended with OM (*9−14*). The interaction mechanism involves a partition process of the compound between the water and the OM, in turn involving nonpolar hydrophobic interactions between the OM and non-ionic organic compounds. Some of these works have been aimed at investigating the potential use of organic materials or wastes (*11−13*) to solve problems of soil and water pollution due to organic compounds. In this sense, special attention has been paid to investigate the residual material adsorption capacity, in particular biomaterials. The interest is to convert them into useful products. Such residues offer unexplored natural resources and, in many cases, even pose serious problems as to their disposal.

Wood residues represent one of these residues. They include residues from the industrial transformation of wood (solid residues in the form of bark, sawdust, and shavings are available in large amounts from sawmills and related wood-processing industries) to forest wastes derived from tree harvesting and pruning. These residues could be used either as-is or after a suitable process of composting with a view to substituting the use of more expensive traditional adsorbents often proposed for such ends, such as activated carbon, peat, modified inorganic materials, etc. (*15−18*).

Wood, a material of plant origin, contains a series of organic compounds (cellulose, lignin, hemicellulose, resin, tannin...) (*19*). The presence of high proportions of lignin in wood could make this latter material a good adsorbent of hydrophobic organic compounds, as is the case of many pesticides used in agriculture. In fact, some studies have indicated the adsorbent capacity of this wood component for hydrocarbons and lipids (*20*). The capacity of lignin to adsorb and to control bioavailability and, consequently, biodegradation pesticides has also been reported previously in studies carried out to determine the influence of this material as a precursor of the soil OM, in the behavior of pesticides in soils (*21*), or to check its possible use as a pesticide-support in controlled-release formulations (*22*).

The literature contains several references concerning the effectiveness of natural untreated woods to adsorb heavy metals from industrial effluents (*23, 24*), together with a few studies on the adsorption of toxic organic compounds by sawdust or tree bark. The latter studies refer to hydrocarbons and dyes (*25−27*) and, in general, the authors use only one

* Corresponding author phone: 34 923219606; fax: 34 923219609; e-mail: mjesussm@usal.es.
† Universidad de La Rioja.
‡ Instituto de Recursos Naturales y Agrobiología.

TABLE 1. Characteristics of Wood Samples

wood (species)	humidity (%)	ash (%)	total C (%)	soluble C[a] mg/L	soluble C[a] (%)	CEC (meq/100 g)	pH	surface area (m²/g)	lignin content (%)
holm (*Quercus rotundifolia*)	5.3	1.3	32.2	159	4.94	10.3	5.2	<1	22.6
oak (*Quercus rubra*)	5.9	0.4	38.5	264	6.86	9.91	4.0	<1	18.2
beech (*Fagus sylvatica*)	7.0	0.4	38.1	110	2.89	7.61	4.9	<1	22.2
walnut (*Juglans nigra*)	6.8	0.5	37.9	97.1	2.56	12.2	5.2	<1	22.3
elm (*Ulmus minor*)	6.5	0.9	40.4	69.9	1.73	14.2	6.4	<1	26.9
pine (*pinus sylvestris*)	6.4	0.2	41.5	67.2	1.62	7.02	5.0	<1	24.4
poplar (*Populus sp*)	6.3	0.2	38.4	68.4	1.78	6.22	4.9	<1	22.1
plane (*Platanus hibrida*)	5.0	2.0	48.0	178	3.71	11.2	5.4	<1	19.2
maple (*Acer negundo*)	5.6	3.3	46.0	186	4.04	10.5	6.0	<1	21.6

[a] Soluble C content in the wood extracts determined under the conditions in which the study was carried out (wood/water suspension of 1/100 ratio after 24 h of agitation at 20 °C) and expressed in mg/L or as percentage of total C

or two types of wood to which they assign a theoretical value of the lignin content depending their hard or soft nature. Mackay and Gschwend (*28*) have reported the use of fir wood sticks and pine chips as sorbents of toluene, benzene, and *o*-xylene. Trapp et al. (*29*) used willow wood splints for the removal of lipophilic organic compounds, and Boving and Zang (*30*) used aspen wood fibers to remove polynuclear aromatic hydrocarbons from water. In general, such studies indicate a good adsorption capacity of the hydrophobic organic pollutants. Accordingly, wood wastes could be used in point-source pollution as barriers or for creating adsorbent zones in the soil to increase the adsorption of organic pollutants and delay their mobility.

To date, however, no basic studies have been carried out to determine the potential use of wood wastes as adsorbents of pesticides in technologies aimed at preventing the pollution of soil and water. Pesticides have a structure with different polar groups that differentiate them from the organic pollutants studied; therefore, the previous work carried out with these compounds may not be directly applicable. According to this, the objective of the present work was to investigate the adsorption capacity of pesticides by different types of woods as a function of the wood parameters, of the non-ionic or ionic nature of the pesticide(s), and of the K_{ow} parameter, indicative of the hydrophobic character of the pesticide. The originality of this work lie in the following aspects: (1) Use of a series of pesticides with different structure, four non-ionic (linuron, alachlor, metalaxyl, and chlorpyrifos) and two ionic pesticides (dicamba and paraquat) (K_{ow} range from −4.5 to 4.7), (2) Use of nine types of wood with lignin content (experimentally determined) ranging between 18.2 and 26.9% (holm, oak, beech, walnut, elm, pine, poplar, maple, and plane), (3) The possibility to establish sound relationships, not shown before by other authors, between the adsorption coefficients of the pesticides by woods and the wood and pesticide properties, and to set up a model for predicting the adsorption of these compounds by wood residues.

Materials and Methods

Woods. Nine samples representative of the different types of hard and soft woods were used in this study. Holm, oak, beech, walnut, elm, pine, and poplar woods were obtained from a local industry in Salamanca (Spain), while plane and maple wood samples were from the pruning of city trees. The woods were used in the form of sawdust. They were grounded in a ball mill and the fraction <1 mm was selected by sieving and kept in an controlled humidity atmosphere for later use. The characteristics of these samples (total and soluble C, CEC, pH, and surface area) determined by the methods described elsewhere (*16*) (Table S-1 in the Supporting information) are included in Table 1. Lignin content was determined according to UNE 57100:1986 regulation.

The samples were used untreated since it was considered of interest to know their properties and behavior in natural form. However, some experiments were carried out with treated pine and oak woods. They were washed with deionized water, with a 1 N HCl solution or with a 0.5 M NaOH solution for 8 h at 60 °C (*23, 27*) until no dissolved organic carbon was left in solution.

Pesticides. Unlabeled and ¹⁴C-labeled pesticides were used in the study. ¹⁴C-linuron (specific activity 4.13 MBq/mg and 98% purity) and ¹⁴C-alachlor (specific activity 2.31 MBq/mg and 97.0% purity) were supplied by International Isotopes (Munich, Germany). ¹⁴C-metalaxyl (specific activity 1.37 MBq/mg and 97.2% purity) and the same pesticide unlabeled (>98% purity) was supplied by Novartis Crop Protection AG (Basel, Switzerland). Unlabeled linuron, alachlor, chlorpyrifos, and dicamba were supplied by Riëdel de Haën (Hannover, Germany) (all >97.5% purity), and paraquat chloride tetrahydrate (99% purity) was supplied by Chem-Service (West Chester, PA, U.S.). The characteristics of these compounds are shown in Table S-2 (Supporting Information) (*31*).

Analytical Determination of Unlabeled and Labeled Pesticides. Quantitative determination of ¹⁴C-linuron, ¹⁴C-alachlor, and ¹⁴C-metalxyl was accomplished on a Beckman LS6500 (Beckman Instruments Inc., Fullerton, CA) liquid scintillation counter (*16*). Quantitative determination of chlorpyrifos and dicamba was accomplished with HPLC. The chromatograph used (Waters Associates, Mildford, MA, U.S.) was equipped with an autosampler, two detectors (photo-diode array (DAD) and mass spectrometer (MS)), and a data acquisition and processing system (Empower software). Quantitative determination of paraquat was accomplished with a Varian Cary 100 UV spectrophotometer (Varian Australia Pty. Ltd, Mulgrave, Australia) (See Table S-2 in the Supporting information).

Sorption Experiments. Sorption of pesticides was determined using a batch equilibrium method described elsewhere (*16*). Duplicate 100-mg wood samples were equilibrated with 10 mL of an aqueous solution of each pesticide at concentrations in different ranges, depending on the pesticide solubility in water or its adsorption characteristics (See Table S-2 in the Supporting Information). For the determination of chlorpyrifos, dicamba, and paraquat in equilibrium solutions, calibration curves with external standards were used. Concentrations ranged between 0.1 and 0.8 μg/mL (chlorpyrifos), 2.5 and 25 μg/mL (dicamba), and 1 and 25 μg/mL (paraquat) ($r^2 \geq 0.99$, $p < 0.001$).

The pesticide amount adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the wood. Sorption data were fitted to the Freundlich equation. The linearized form of this adsorption equation is log Cs = log Kf + nf log Ce, where Cs (μg/g) is the amount of sorbed pesticide, Ce (μg/
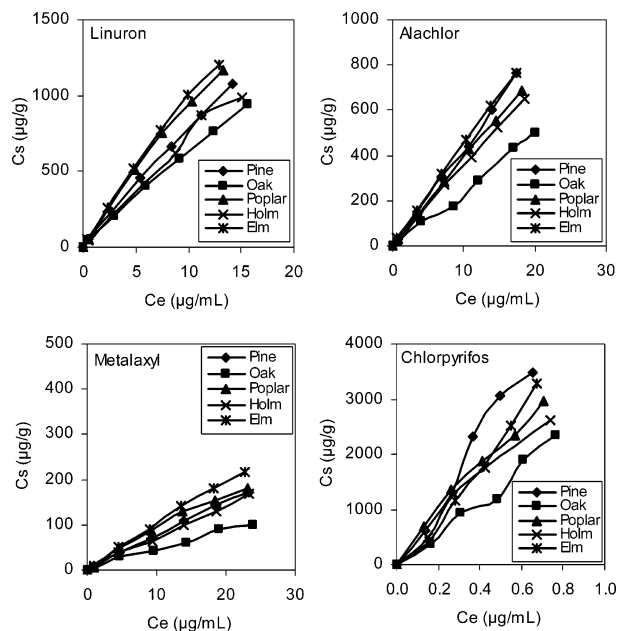
FIGURE 1. Adsorption isotherms of non-ionic pesticides by selected woods.
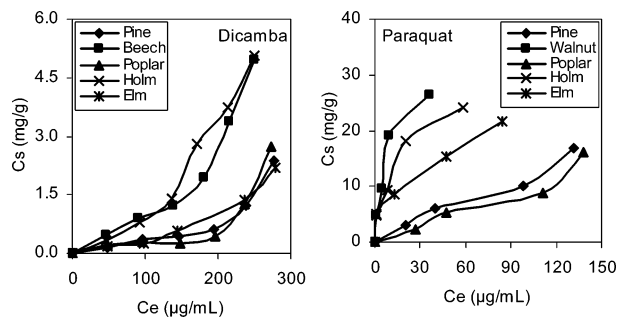
FIGURE 2. Adsorption isotherms of ionic pesticides by selected woods.

mL) is the equilibrium concentration of pesticide in solution, and Kf ($\mu g^{1-nf} mL^{nf} g^{-1}$) and nf are the Freundlich affinity and nonlinearity coefficients, respectively.

Statistical Analysis. Standard error (SE) were used to indicate variability in the Kf values among duplicates. Simple and multiple linear regression models were used to relate adsorption with properties of woods and pesticides. The SPSS 12.0 software package was used.

Results and Discussion

Adsorption isotherms of all pesticides by the woods used in the study were obtained. Figures 1 and 2 show some representative isotherms for each of the pesticides, and Table 2 shows the adsorption coefficients, Kf and nf, obtained as a result of fitting all the isotherms to the Freundlich equation with r values ≥0.94.

According to the classification of Giles et al. (*32*), the isotherms obtained for the non-ionic pesticides were, in general, of type L, close to C; i.e., almost linear. C-type isotherms point to partitioning mechanism of the adsorbate in the adsorbent and they have been seen in the adsorption of different pesticides by organic materials (*15*). The adsorption isotherms of chlorpyrifos were of the S/C or L/C type (nonlinear), indicating greater increase in adsorption at low pesticide concentrations than at high concentrations of pesticide in solution. Nonlinear isotherms have also been found for the adsorption of polynuclear aromatic hydrocarbons with high K_{ow} values (>2.36) by aspen wood (*30*).

The Kf values for the adsorption of these pesticides by the different woods, considered as a measure of the adsorption capacity, were very high for chlorpyrifos (the pesticide with the greatest hydrophobicity), varying between 3176 and 6559, and they lay in a narrower range, between 74.4 and 123, 22.4−48.8, and 4.95−10.9 for linuron, alachlor, and metalaxyl respectively. The lowest Kf values generally corresponded to adsorption by oak wood, with the lowest lignin content, and the highest ones to adsorption by pine or elm, with the highest lignin contents. These Kf constants are higher than those reported by Mackay and Gschwend (*28*) for the adsorption of aromatic hydrocarbons by pine and fir. Additionally, and only as a comparison, we indicated these Kf values are higher than those obtained in the adsorption of same pesticides by other natural inorganic and organic adsorbents, such as clay minerals (*16*, *33*), soils rich in clay minerals (*17*, *33*), or soils amended with residual OM (*13*, *15*, *34*, *35*). However, the adsorption capacity of the woods studied here is lower than that of commercial humic acid (*36*) and that of clays and soils modified with long-chain cationic surfactants (*16*, *17*) (See Table S-3 in the Supporting Information).

The adsorption isotherms of dicamba and paraquat (Figure 2) are of the S type and of S/C type, respectively, in the range of concentrations studied (50−300 $\mu g/mL$). The Kf values for the adsorption of dicamba shown in Table 2 range between 0.29 and 2.37. They are higher than those obtained by adsorption of dicamba by soils (*37*) but they are lower than those obtained for the adsorption of this pesticide by organoclays (*18*). The Kf values for the adsorption of paraquat range between 79.7 and 5071; the highest values correspond to adsorption by holm, walnut, and elm. A wide range of Kf values for adsorption of paraquat by clays, OM, and soils is also found in the bibliography (*38*).

Using a statistical approach, a study was carried out on the effect of the properties of the woods and of the pesticides on the adsorption of these compounds. The simple linear correlation coefficients between wood properties themselves and between adsorption constants, Kf, and wood properties, such as content in total C, lignin and soluble C, pH, and CEC were obtained (Table 3). First, it may be seen that there is no correlation between the adsorption Kf constants and the total C content. This means that not all the polymers of the woods contributing to their total C contents affect the adsorption of the pesticides studied. Accordingly, the indicators usually employed to estimate the adsorption of organic compounds by soils and other organic adsorbents, the content in total C and K_{oc} (*6*), cannot be used as indicators of the adsorption of the pesticides by the woods. A significant linear relationship was found for the non-ionic pesticides between the values of Kf and the soluble C and the lignin contents of the woods. It is indicated that these wood parameters are significantly correlated (Table 3) although soluble C comes from an extractive minor fraction of woods and not from the lignin content (*19*, *23*, *27*). Also, a significant correlation was found between Kf and pH for linuron and alachlor.

The negative correlation between soluble C contents (%) (Table 1) and Kf values indicate the possible influence of soluble C to decrease the adsorption capacity of the pesticides by woods because these compounds must be partially adsorbed by the soluble organic compounds of the woods. In this sense, the literature contains references indicating the effect of dissolved OM present in solution on the adsorption of hydrophobic organic compounds by soils and OM (*13*, *35*). This process of pesticide adsorption by the soluble OM of the woods was checked experimentally in the study of the adsorption of linuron and metalaxyl by two representative woods, pine and oak, previously subjected to different washings with water or solutions of HCl or NaOH. The Freundlich Kf values for the adsorption of these pesticides

TABLE 2. Freundlich Adsorption Coefficients of Different Pesticides by Woods (Kf, nf), Adsorption Coefficients Normalized to 100% of Lignin Content (Kf_{lignin})[a], Mean Values, and Coefficients of Variation (CV) of these Adsorption Coefficients

pesticide/parameter	holm	oak	beech	walnut	elm	pine	poplar	plane	maple	mean value	CV
Linuron											
Kf	79.9 ± 1.28[b]	74.4 ± 0.63	90.9 ± 0.13	92.7 ± 1.89	123 ± 5.67	96.2 ± 0.07	103 ± 0.91	92.9 ± 0.06	92.7 ± 0.63	93.9	14.7
nf	0.95 ± 0.02	0.93 ± 0.10	0.93 ± 0.00	0.90 ± 0.00	0.90 ± 0.01	1.00 ± 0.00	0.97 ± 0.01	0.94 ± 0.01	0.93 ± 0.00		
Kf_{lignin}[a]	353	408	409	415	459	394	466	483	429	424	9.51
Alachlor											
Kf	39.2 ± 0.27	22.4 ± 1.23	42.3 ± 6.05	37.3 ± 0.24	48.8 ± 0.28	41.4 ± 1.91	43.6 ± 0.73	42.1 ± 1.92	35.1 ± 0.31	39.1	18.9
nf	0.96 ± 0.00	1.03 ± 0.03	0.92 ± 0.06	0.96 ± 0.00	0.97 ± 0.00	1.02 ± 0.02	0.95 ± 0.01	0.97 ± 0.02	0.97 ± 0.02		
Kf_{lignin}	173	123	190	187	162	169	220	219	162	178	16.9
Metalaxyl											
Kf	8.13 ± 0.13	4.95 ± 0.71	7.26 ± 0.21	8.85 ± 0.25	10.9 ± 0.55	8.28 ± 0.38	10.8 ± 0.11	7.36 ± 0.53	6.73 ± 0.01	8.14	23.3
nf	0.95 ± 0.04	0.98 ± 0.05	0.97 ± 0.05	0.92 ± 0.03	0.97 ± 0.01	0.99 ± 0.01	0.93 ± 0.00	0.96 ± 0.01	0.85 ± 0.04		
Kf_{lignin}	35.9	27.2	32.7	39.7	40.7	33.9	48.5	38.3	31.2	36.5	17.1
Chlorpyrifos											
Kf	4002 ± 635	3176 ± 630	4794 ± 689	3702 ± 273	5911 ± 477	6559 ± 1174	3926 ± 2.56	3297 ± 396	3389 ± 168	4309	28.0
nf	1.11 ± 0.05	1.15 ± 0.30	1.71 ± 0.02	1.67 ± 0.18	1.33 ± 0.06	1.18 ± 0.07	0.84 ± 0.19	0.98 ± 0.39	0.82 ± 0.09		
Kf_{lignin}	17707	17450	21594	16600	21973	26881	17764	17171	15689	19203	18.7
Dicamba											
Kf	0.53 ± 0.27	1.78 ± 1.87	2.37 ± 0.95	1.85 ± 0.54	0.65 ± 0.04	0.52 ± 0.05	1.21 ± 0.61	0.72 ± 0.07	0.29 ± 0.04	1.10	66.6
nf	1.65 ± 0.75	1.17 ± 0.12	1.28 ± 0.03	1.41 ± 0.05	1.30 ± 0.07	1.41 ± 0.43	1.23 ± 0.03	1.34 ± 0.52	1.51 ± 0.23	5.13	
Kf_{lignin}	2.35	9.78	10.7	8.30	2.42	2.13	5.48	3.75	1.34		69.8
Paraquat											
Kf	4665 ± 9.70		82.5 ± 5.15	5071 ± 928	4692 ± 552	233 ± 19.1	79.7 ± 7.19	88.3 ± 11.3	290 ± 51.8	1900	127
nf	0.41 ± 0.02		1.12 ± 0.13	0.49 ± 0.06	0.31 ± 0.03	0.86 ± 0.02	1.05 ± 0.01	1.48 ± 0.24	1.05 ± 0.04		
Kf_{lignin}	20641		371	22739	17442	954	360	459	1342	8039	127

[a] Kf_{lignin} = 100 Kf/%lignin   [b] Standard error of two duplicates

TABLE 3. Simple Correlation Coefficients (*r*) between Wood Parameters and between Adsorption Constants (Kf) of Pesticides and Wood Parameters

wood parameters	total carbon	soluble carbon	lignin content	pH	CEC
total carbon	1				
soluble carbon	0.14	1			
lignin content	−0.20	−0.73[a]	1		
pH	0.36	−0.48	0.64[c]	1	
CEC	0.13	0.12	0.20	0.57	1
pesticide					
Linuron	0.25	−0.80[b]	0.77[a]	0.72[a]	0.30
Alachlor	0.10	−0.84[b]	0.73[a]	0.65[c]	0.01
Metalaxyl	−0.17	−0.81[b]	0.76[a]	0.52	0.10
Chlropyrifos	−0.01	−0.66[c]	0.83[b]	0.28	0.01
Dicamba	−0.35	0.11	−0.32	−0.66[c]	0.20
Paraquat	−0.57	0.11	0.46	0.34	0.71[c]

[a] $p < 0.05$. [b] $p < 0.01$. [c] $p < 0.1$.

by washed woods (Table S-4 in the Supporting Information) show, in general, an increase in adsorption, especially by the woods washed with HCl. Thus, the results indicate the possibility to improve the efficiency of the woods in the adsorption of pesticides by previous washing.

The significant correlation coefficients (*r*) of the corresponding linear regressions between the adsorption constants and the lignin content of the woods were 0.77 ($p < 0.05$) (linuron), 0.73, ($p < 0.05$) (alachlor), 0.76 ($p < 0.05$) (metalaxyl), and 0.83 ($p < 0.01$) (chlorpyrifos). This indicates that this parameter would explain more than 50% of the variability in the adsorption of non ionic pesticides by different types of wood. These results point to the involvement of the lignin in the adsorption of linuron, alachlor, metalaxyl, and chlorpyrifos. We have also carried out the adsorption of the same pesticides by commercial wood components, lignin and cellulose (*36*). Results revealed that the adsorption constants obtained with lignin were one order higher than those seen with cellulose. Other authors (*28*), also studying the adsorption efficiency of organic compounds by isolated wood polymers, lignin and cellulose, reported that only lignin is responsible for the adsorption of organic compounds by wood.

The adsorption constants, referred to the contents in lignin of the respective woods Kf$_{lignin}$ (Kf$_{lignin}$= 100 Kf/%lignin) are shown in Table 2. These constants may be considered a measure of the adsorption capacity of the lignin contained in the woods. The normalization with respect to the lignin content reduces the variability in adsorption for each of the non-ionic pesticides as indicated by the coefficients of variation (CV) of the adsorption constants included in Table 2. The proximity of the Kf$_{lignin}$ values (CV ≤ 18.7%) for the adsorption of each individual pesticide by the woods used here is in agreement with the correlation found between the adsorption constants and the lignin content. The variability of Kf$_{lignin}$ values is much less than the variability found usually between sorption coefficients of pesticides by soils normalized to the soil OC content (K_{oc}) (*39*) and ascribed to the different nature of the soil OM. According to this, it may be indicated that the differences in the structure of the lignin from the different types of wood (hard and soft), with respect to the amount of methoxyl, phenolic, hydroxyl, benzyl alcohol, and carbonyl groups (*19*), do not become very evident for adsorption. The pesticides with different degrees of hydrophobicity must be adsorbed by partitioning in the hydrophobic polymer lignin, a compound with hydrophobic phenylpropane units, as indicated for other compounds. The mean Kf$_{lignin}$ value obtained for metalaxyl, 36.5, was fairly similar to the adsorption coefficient of this compound by

commercial lignins, 32.7, obtained by us in a previous work (*36*). In the case of the more hydrophobic pesticides, the mean Kf$_{lignin}$ values were 424, 178, and 19203 for linuron, alachlor, and chlorpyrifos, respectively, and they are 2−5-fold higher than those obtained by commercial lignins: 138, 79.2, and 3792 for linuron, alachlor and chlorpyrifos, respectively. The adsorption properties of commercial lignins must be more or less altered during the procedure used to extract them from their natural form in wood. Similar results have also been reported by Rupp et al. (*40*).

The Kf$_{lignin}$ values for the ionic pesticides dicamba and paraquat varied over a broad range (CV ≥ 69.8%) for the different types of wood, also in agreement with the absence of correlation between the adsorption constants and the lignin content for these pesticides. The mean values obtained for these Kf$_{lignin}$ were 5.13 for dicamba and 8039 for paraquat. Neither these are similar to the adsorption coefficients found for commercial lignins. In general, these were higher for dicamba and lower for paraquat than the Kf$_{lignin}$ values (*36*). The adsorption of these pesticides by the woods must occur through different adsorption mechanisms than in the case of the non-ionic pesticides. In this sense, it should be noted that in the correlation analysis between the adsorption constants and the characteristics of the woods, a significant negative correlation coefficient was obtained between Kf and the pH of the woods for dicamba ($r = -0.66$; $p < 0.1$), together with a positive correlation coefficient between Kf and the CEC of the woods for paraquat ($r = 0.71$; $p < 0.1$), in agreement with the respective anionic and cationic nature of these pesticides. Paraquat would be adsorbed via cation exchange with the exchange cations of wood. Dicamba must be more adsorbed in neutral form and through the same mechanism as the non-ionic pesticides. According to Severtson and Banerjee (*41*), the neutral form dominates partitioning if pH is less than two units above the solute's pKa value in the adsorption of organic acids.

A study was also made of the correlation between the Kf adsorption constants and the values of K_{ow} of the pesticides for each of the woods used. The log form of both parameters was used to decrease the uncertainty of the results. No correlation was found between either parameter when all the pesticides were considered. However, when paraquat was excluded, highly significant correlation coefficients (*r*) were obtained (0.93−0.99, $p < 0.01$). Also highly significant ($r = 0.97$, $p < 0.001$) was the linear regression between log Kf and log K_{ow} on considering linuron, alachlor, metalaxyl, chlorpyrifos, and dicamba, and all the types of wood together ($n = 44$). The corresponding equation was as follows: log Kf = 0.693 (±0.28) log K_{ow} + 0.025 (±0.079). This equation is similar to that reported by Boving and Zang (*30*) for the adsorption of naphthalene, fluorine, anthracene, and pyrene by aspen wood and similar our calculations from the data reported by MacKay and Gschwend for the adsorption of benzene, toluene, and xylene by Ponderosa pine and Douglas fir (*28*) (See Figure S-1 in the Supporting Information).

The results of all the above authors concerning the adsorption of aromatic hydrocarbons and those obtained in the present work for the adsorption of pesticides by different types of wood were plotted jointly to study the possible linear correlation between the adsorption coefficients Kf (in all cases determined from the Freundlich equation) and the K_{ow} values of the different types of compounds studied by both those authors and ourselves, with a greater K_{ow} range (−0.55−5.13). Although the plot combines three sets of data collected under different experimental conditions, it is strongly linear (see Figure S-1 in the Supporting Information), with a highly significant correlation coefficient ($r = 0.94$, $p < 0.001$). Therefore, the equation obtained, log Kf = 0.651 (±0.032) log K_{ow} + 0.003 (±0.095), may offer a model that could allow the adsorption prediction of organic compounds (hydrocarbons

and pesticides) from very different structures and with hydrophobicities within a broad range from their log K_{ow} value.

Moreover, taking into account the significant simple correlations obtained for each of the pesticides with the different parameters of the woods (Table 3) we sought to calculate Kf by combining the properties of the pesticides, such as K_{ow}, with those of the woods, such as the lignin and soluble C contents of the woods, through a multiple correlation. In this case, the values corresponding to dicamba and paraquat were discarded since there was no correlation between Kf and the lignin content for either pesticide or between the value of Kf and K_{ow} for paraquat. The equation obtained: $\log Kf = -0.989\ (\pm 0.176) + 0.923\ (\pm 0.010)\log K_{ow} + 0.015\ (\pm 0.007)$ lignin $-0.026\ (\pm 0.01)$ soluble C, with a correlation coefficient of $r = 0.998$ ($p < 0.001$), again indicates that the K_{ow} parameter is the main factor governing adsorption. The contribution of the other two parameters, even though it is low, will allow us to determine almost 100% of the variability in the adsorption of pesticides by woods. According to this, we could establish that the woods with a greater lignin content (i.e., softwoods), would be more suitable to retain pesticides. However, considering the low weight of lignin content in comparison K_{ow} of pesticide, it could indicate the usefulness of most woods as adsorbents in the development of environmental technologies for removal of pesticides.

Acknowledgments

Supporting Information Available

Tables S-1, S-2, S-3, S-4, and Figure S-1. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Torstensson, L.; Castillo, M. dP. Use of biobeds in Sweden to minimise environmental spillages from agricultural spray equipment. *Pestic. Outlook* **1997**, *8*, 24–27.

(2) Mason, P. J.; Foster, I. D. L.; Carter, A. D.; Walker, A.; Higginbothams, S.; Jones, R. L.; Hardy, I. A. J. Relative importance of point source contamination of surface waters: river Cherwell catchment monitoring study. In *Proceedings of the XI Symposium on Pesticide Chemistry, Human and Environmental Exposure to Xenobiotics*; Del Re, A. A. M., Brown, C. D., Capri, E., Errera, G., Evans, S. P., Trevisan, M., Eds.; La Goliarda Pavese: Pavia, Italy, 1999; pp 405–412.

(3) Müller, K.; Bach, M.; Hartmann, H.; Spiteller, M.; Frede, H. G. Point- and nonpoint-source pesticide contamination in the Zwester Ohm catchment, Germany, *J. Environ. Qual.* **2002**, *31*, 309–318.

(4) Fogg, P.; Boxall, A. B. A.; Walker, A.; Jukes. A. Effect of Different Soil Textures on Leaching Potential and Degradation of Pesticides in Biobeds. *J. Agric. Food Chem.* **2004**, *52*, 5643–5652.

(5) Fogg, P.; Boxall, A. B. A.; Walker, A.; Jukes. A. Leaching of pesticides from biobeds: Effect of biobed depth and water loading. *J. Agric. Food Chem.* **2004**, *52*, 6217–6227.

(6) Koskinen, W.; Harper, S. The retention process: mechanisms. In *Pesticides in the Soil Environment: Processes, Impacts, and Modelling*, book series 2; Cheng, H. H., Bailey, G. W., Green, R. E., Spencer, W. F., Eds.; Soil Science Society of America: Madison, WI, 1990; pp 51–77.

(7) Sánchez- Martín, M. J.; González-Pozuelo, J. M.; Sánchez-Camazano, M. Adsorption of ethofumesate by agricultural and natural soils. *Weed Res.* **1993**, *33*, 479–486.

(8) Sánchez-Martín, M. J.; Andrades, M. S.; Sánchez-Camazano, M. Soil properties influencing the adsorption and mobility of penconazole in vineyard soils. *Soil. Sci.* **2000**, *165*, 951–960.

(9) Barriuso, E.; Houot, S.; Serra-Wittling, C. Influence of compost addition to soil on the behaviour of herbicides. *Pestic. Sci.* **1997**, *49*, 65–75.

(10) Sánchez-Camazano, M.; Iglesias-Jiménez, E.; Sánchez-Martin, M. J. City refuse compost and sodium dodecyl sulphate as modifiers of diazinon leaching in soil. *Chemosphere* **1997**, *35*, 3003–3012.

(11) Sánchez-Camazano, M.; Sánchez-Martín, M. J.; Delgado-Pascual, R. Adsorption and mobility of linuron in soils as influenced by soil properties organic amendments and surfactants. *J. Agric. Food Chem.* **2000**, *48*, 3018–3026.

(12) Sánchez, L.; Romero, E.; Peña, A. Ability of biosolids and a cationic surfactant to modify methidation leaching. Modelling with pescol. *Chemosphere* **2003**, *53*, 843–850.

(13) Andrades, M. S.; Rodríguez-Cruz, M. S**.**; Sánchez-Martín, M. J.; Sánchez-Camazano, M. Effect of the addition of wine distillery wastes to vineyard soils on the adsorption and mobility of fungicides. *J. Agric. Food Chem.* **2004**, *52*, 3022–3029.

(14) Dorado, J.; López-Fando, C.; Zancada, M. C.; Almendros, G. Sorption-desorption of alachlor and linuron in a semiarid soil as influenced by organic matter properties after 16 years of periodic inputs. *J. Agric. Food Chem.* **2005**, *53*, 5359–5365.

(15) Iglesias-Jiménez, E.; Poveda, E.; Sánchez-Martín, M. J.; Sánchez-Camazano, M. Effect of the nature of exogenous organic matter on pesticide adsorption by the soil. *Arch. Environ. Contam. Toxicol.* **1997**, *33*, 127–134.

(16) Sánchez-Martín, M. J.; Rodríguez-Cruz, M. S.; Andrades, M. S.; Sánchez-Camazano, M. Efficiency of different clay minerals modified with a cationic surfactant in the adsorption of pesticides. Influence of clay type and pesticide hydrophobicity. *Appl. Clay Sci.* **2006**, *31*, 216–228.

(17) Rodriguez-Cruz, M. S.; Sánchez-Martín, M. J.; Andrades, M. S.; Sánchez-Camazano, M. Comparison of pesticide sorption by physicochemically modified soils with natural soils as a function of soil properties and pesticide hydrophobicity. *Soil Sediment Contam.* **2006**, *15*, 401–415.

(18) Carrizosa, M. J.; Koskinen, W. C.; Hermosin, M. C.; Cornejo, J. Dicamba adsorption-desorption on organoclays. *Appl. Clay Sci.* **2001**, *18*, 223–231.

(19) Sjöström, E. *Wood Chemistry: Fundamentals and Applications*; Academic Press: New York, 1993.

(20) Dizhbite, T.; Zakis, G.; Kizima, A.; Lazareva, E.; Rossinskaya, G.; Jurkjane, V.; Telysheva, G.; Viesturs, U. Lignin—a useful bioresource for the production of sorption-active materials. *Bioresour. Technol.* **1999**, *67*, 221–228.

(21) Benoit, P.; Barriuso, E.; Soulas, G. Degradation of 2,4-D, 2,4-dichlorophenol, and 4-chlorophenol in soil after sorption on humified and nonhumified organic matter. *J. Environ. Qual.* **1999**, *28*, 1127–1135.

(22) Riggle, B. D.; Penner, D. Kraft lignin adsorption of alachlor and chloramben as a controlled-release function evaluation. *J. Agric. Food Chem.* **1994**, *42*, 2631–2633.

(23) Gaballah, I.; Kilbertus, G. Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks. *J. Geochem. Explor.* **1998**, *62*, 241–286.

(24) Yu, B.; Zhang, Y.; Shukla, A.; Shukla, S. S.; Dorris, K. L. The removal of heavy metals from aqueous solutions by sawdust adsorption, removal of lead and comparison of its adsorption with copper. *J. Hazard. Mater.* **2001**, *B84*, 83–94.

(25) Bràs, I. P.; Santos, L.; Alves, A. Organochloride pesticides removal by pinus bark sorption. *Environ. Sci. Technol.* **1999**, *33*, 631–634.

(26) Shukla, A.; Zhang, Y. -H.; Dubey, P.; Margrave, J. L.; Shukla, S. S. The role of sawdust in the removal of unwanted materials from water. *J. Hazard. Mater.* **2002**, *B95*, 137–152.

(27) Haussard, M.; Gaballah, I.; Kanari, N.; de Donato, Ph.; Barrès, O.; Villieras, F. Separation of hydrocarbons and lipid from water using treated bark. *Water Res.* **2003**, *37*, 362–374.

(28) MacKay, A. A.; Gschwend, P. M. Sorption of monoaromatic hydrocarbons to wood. *Environ. Sci. Technol.* **2000**, *34*, 839–845.

(29) Trapp, S.; Migliranza, K. S. B.; Mosbek, H. Sorption of lipophilic organic compounds to wood and implications for their environmental fate. *Environ. Sci. Technol.* **2001**, *35*, 1561–1566.

(30) Boving, T. B.; Zhang, W. Removal of aqueous-phase polynuclear aromatic hydrocarbons using aspen wood fibers. *Chemosphere* **2004**, *54*, 831–839.

(31) Tomlin, C. *The Pesticide Manual*; British Crop Protection Council: Cambridge, UK, 2000.

(32) Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption

mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* **1960**, *111*, 3973−3993.

(33) Rodríguez-Cruz, S.; Aatouf, N.; Draoui, K.; Del Hoyo, C.; Sánchez-Martín, M. J. Adsorción de cloropirifos por minerales de la arcilla y suelos de Marruecos en sistema acuoso. *Macla* **2006**, *6*, 399−402.

(34) Rodríguez-Cruz, M. S.; Andrades, M. S.; Sánchez-Martín, M. J.; Sánchez-Camazano. M. Efecto de la aplicación de lodos de aguas residuales al suelo en la persistencia del herbicida linuron en condiciones de campo. In *Estudios de la zona no saturada del suelo*; Alvarez-Benedi, J., Marinero, P., Eds.; ITACYL: Valladolid, Spain, 2003; Vol. VI, pp 349−354.

(35) Cox, L.; Fernandes, M. C.; Zsolnay, A.; Hermosin, M. C.; Cornejo, J. Changes in dissolved organic carbon of soil amendments with aging: Effect on pesticide adsorption behaviour. *J. Agric. Food Chem.* **2004**, *52*, 5635−5642.

(36) Valderrábano, M.; Rodríguez-Cruz, M. S.; del Hoyo, M. C.; Sánchez-Martín, M. J. Physicochemical study of the adsorption of pesticides by wood components. In *Bioavailability of Pollutants and Soil Remediation*; Ortega-Calvo J. J., Ed.; IRNASE, CSIC: Sevilla, Spain, 2006; p 35.

(37) Menasseri, S.; Koskinen, W. C.; Yong Yen, P. Sorption of aged dicamba residues in soil. *Pest Manag. Sci.* **2003**, *60*, 297−304.

(38) Bromilow, R. H. Paraquat and sustainable agriculture. *Pest. Manag. Sci.* **2003**, *60*, 340−349.

(39) Papiernik, S. K.; Koskinen, W. C.; Cox, L.; Rice, P. J.; Clay, S. A.; Werdin-Pfisterer, N. R.; Norberg, K. A. Sorption-desorption of imidaclorprid and its metabolites in soil and vadose zone materials. *J. Agric. Food Chem.* **2006**, *54*, 8163−8170.

(40) Rupp, E.; Zuman, P.; Sestáková, I.; Horák, V. Polarographic determination of some pesticides. Application to a study of their adsorption on lignin. *J. Agric. Food Chem.* **1992**, *40*, 2016−2021.

(41) Severtson, S. J.; Banerjee, S. Sorption of chlorophenols to wood pulp. *Environ. Sci. Technol.* **1996**, *30*, 1961−1969.