Influence of Molecular Structure on Sorption of Phenoxyalkanoic Herbicides on Soil and Its Particle Size Fractions

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The sorption and desorption behaviors of four phenoxyalkanoic acid herbicides and their metabolites on four agricultural soils and soil particle size fractions were examined. Generally, there was a trend of increasing adsorption and decreasing desorption in the order mecoprop < MCPA < dichlorprop < 2,4-D. The significant increase in adsorption of the phenolic metabolites can be explained by their lower polarity and enhanced partition in the organic soil matrix. Estimation of sorption distribution coefficients from particle size fraction adsorption data was possible for a sandy soil and a silty Cambisol soil only. It is suggested that increasing steric demand, for example, molecular volume, and slight changes in the polarity of the compounds affect their adsorption properties. Comparison of adsorption and desorption data of structurally similar compounds obtained from a variety of soils allows investigation of structure-induced differences in sorption strength.

INTRODUCTION

Adsorption on soil matrix appears to be one of the most important factors affecting the behavior and fate of pesticides in soil. Adsorption on clay materials, organic matter, and other soil properties influences the sorption behavior of organic pesticides (Borisover and Graber, 1997; McBride, 1989; Gao et al., 1998). Laboratory equilibrium sorption data are used to predict the partitioning of pesticides between different soil solids and solution phases and are an important indicator of pesticide mobility (Celis et al., 1998; Rütters et al., 1999). The release (desorption) of sorbed pesticides from soil particles is of importance for the final distribution determination of the pesticides in soil (Celis and Koskinen, 1999; Farrel, 1999). The sorption behavior is related both to the texture and properties of the soils and to the chemical structure of the organic substances (Dec and Bollag, 1997; Celis et al., 1997; Benoit et al., 1996).

Phenoxyalkanoic acid herbicides such as (2,4-dichlorophenoxy)acetic acid (2,4-D) or (4-chloro-2-methylphenoxy)acetic acid (MCPA) are broad-spectrum, postemergent herbicides extensively used in agriculture. The major metabolites of these phenoxyalkanoic acid herbicides are phenols. The resulting chlorophenols may bear an additional risk for groundwater pollution (Garrison et al., 1996). Due to their chemical structure—phenoxyalkanoic acid herbicides have one polar carboxylic group and one lipophilic phenyl moiety—they are suitable model substances for studying adsorption/desorption processes in soil (Celis et al., 1999; Bolan and Baskaran, 1996; Socias-Viciana et al., 1999; Susarla et al., 1997). Factors dominating the sorption of phenoxyalkanoic acid herbicides are postulated to be both interactions of the carboxylic groups with surfaces of organic matter and negatively charged clay via

metal ion bridges (Parker and Rate, 1998) and partition via lipophilic interactions in soil organic matter (Benoit et al., 1998; Pignatello and Xing, 1995). Some studies have been published on the adsorption of acidic pesticides and heavy metals onto clays when both classes of substances are present. It was shown that sorption processes are linked with both clay and heavy metal concentrations if the formation of complexes of pesticides with the heavy metals occurs either in soil solution or adsorbed on clay surfaces (Morillo et al., 1997).

Although ionic interactions of carboxylic acids are assumed to have an important effect of phenoxyalkanoic acid herbicides sorption on clay, other effects may also play a role in the overall picture of binding and leaching of pesticides in soil (Benoit et al., 1998). Lipophilic interactions such as interactions of the aromatic ring systems with aromatic groups that are present both in pesticides and in humic acids may also affect the strength of adsorption on soil constituents (Borisover and Graber, 1997; De Paolis and Kukkonen, 1997; Murphy et al., 1990).

Comparison of the sorption of two structurally similar organic substances and relation of the differences in sorption behavior to structural effects are difficult—if not impossible—if different soils are used for the experiments. Thus, the aim of this study was to examine the adsorption/desorption behavior of a set of phenoxyalkanoic acid herbicides, 2,4-D, dichlorprop, MCPA, and (4-chloro-2-methylphenoxy)propanoic acid) (mecoprop), and their main metabolites, 2,4-dichlorophenol (DCP) and 2-methyl-4-chlorophenol (MCP), on four different natural soils and their soil particle size fractions. The investigated soils vary broadly with regard to texture, organic carbon content, and pH. This set of sorption data was used (1) to examine the possibility of adsorption prediction on soil particle size fractions and (2) to estimate the effect of small structural variations of the pesticides on the sorption behavior to identify possible

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Table 1. Soil Characteristics

soil	origin	pH (CaCl₂)	% sand (2000−63 μm)	% silt (63−2 μm)	% clay (<2 μm)	% organic carbon
A	Speyer, Germany	6.00	88.20	9.30	2.50	0.59
B	Gumpenstein, Austria	4.60	48.00	43.00	9.00	2.40
C	Marchegg, Austria	6.50	78.00	12.00	10.00	0.54
D	Fuchsenbigl, Austria	7.90	22.00	55.00	23.00	2.70

sorption strength and mechanism related to certain structural moieties.

MATERIALS AND METHODS

Chemicals. Analytical pure MCPA, mecoprop, 2,4-D, (2,4-dichlorophenoxy)propanoic acid (dichlorprop), DCP, MCP, and 4-chlorophenol (CP) (Dr. Ehrenstorfer GmbH, Augsburg, Germany) were used as analytes.

Soils. Four soils of different origin were used for the adsorption/desorption experiments. Three soils (soils B, C, and D) stem from agricultural areas in Austria. Soil A (German Standard soil 2.1) was purchased from LUFA (Speyer, Germany). The plow layers of the respective sites were sampled for the study. The soils were air-dried, passed through a 2 mm sieve, and stored. Selected soil properties are shown in Table 1. Soil particle size fractionation was performed according to the method of Stemmer et al. (1998). This physical fractionation procedure uses low-energy ultrasonication for dispersion of the soil samples and thus preserves stable microaggregates in the silt fraction. The sand, silt, and clay fractions were used for this experiment. The fraction containing the soluble components was not included in the experiment. Total carbon was measured in soil samples using an elemental analyzer (Carlo Erba 1500 nitrogen analyzer, Milan, Italy).

Sorption Experiments. Experimental sorption data were obtained as follows: Either 2 g of soil or 1 g of sand or 0.5 g of silt or 0.1 g of clay was weighed into a conical flask. After pre-equilibration (5 mL of 0.01 M CaCl₂, 24 h), 5 mL of 0.01 M CaCl₂ aqueous solutions containing the initial pesticide concentrations (C_0) ranging from 0.1 to 100 mg L⁻¹ was added. The flasks were shaken for 24 h. A 0.01 M solution of CaCl₂ was used to ease phase separation and to keep ionic strength similar to natural soil solutions. The experiments were carried out at 20 °C. After centrifugation, the equilibrium concentrations of the substances in the supernatant solution, C_s, were determined by HPLC with UV detection (System Gold; Beckman Instruments, Fullerton, CA). As mobile phase a methanol/water mixture (ratio = 65:35) was used with 0.5% acetic acid (isocratic elution). The analyses were performed on a Hypersil 5 μm ODS, 250 × 4.0 mm column (C18 material, Merck, Darmstadt, Germany) at 40 °C and a flow of 1 mL/min. The herbicides were analyzed at 228 nm, the wavelength of maximum absorption. Blanks containing neither pesticides nor phenols as well as flasks containing only the herbicide and no soil, to determine adsorption onto the surface of the flasks, were analyzed. Two replicates of each experiment were carried out for each series of experiments.

Desorption experiments were commenced immediately after the corresponding sorption experiment. The supernatant was removed and replaced by the same amount (5 mL) of fresh 0.01 M CaCl₂ solution. The shaking of the mixture (24 h) and the subsequent separation of soil and aqueous phase were conducted as described above. This procedure was repeated in a second desorption step. All sorption and desorption experiments were performed at least in duplicate.

The amount of substance adsorbed (micrograms) was calculated from the difference between the initial and final concentrations (micrograms per milliliter) of the CaCl₂ solution and multiplied by the amount of the CaCl₂ solution (5 mL). The concentrations of the substance in soil or soil fraction [C_a (micrograms per gram)] were calculated by relating the adsorbed amount to the amount of soil (2 g) or soil fraction (1 to 0.1 g). The concentrations in the solution (C_s) (micrograms per milliliter) were plotted against the calculated concentrations in the soil or soil fraction [C_a (micrograms per gram)]. A
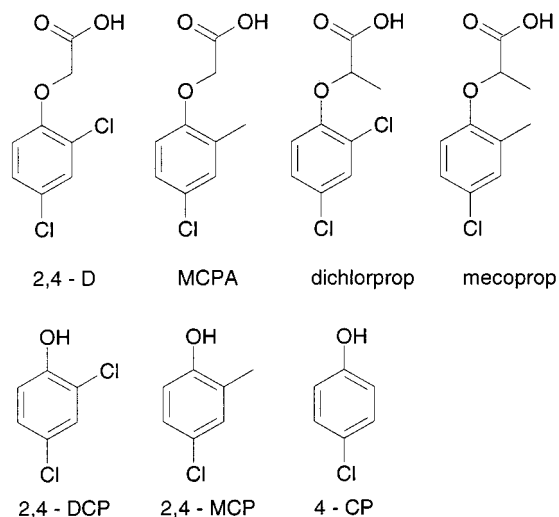
Figure 1. Chemical structures of the investigated phenoxyalkanoic acid herbicides and their metabolites.

linear adsorption model (exponent of the Freundlich isotherm = 1) was applied to the data ($C_a = K_D C_s$). Distribution coefficients (K_D values) were obtained from the slope of a C_s versus C_a plot.

The distribution coefficients of the total soil were estimated from sorption data of the particle size fractions using the equation

$$K_{D-estimated} = X_{sand} K_{D-sand} + X_{silt} K_{D-silt} + X_{clay} K_{D-clay}$$

where X is the fraction of the corresponding size fraction ($X_{sand} + X_{silt} + X_{clay} = 1$) and K_D is the distribution coefficient of the corresponding size fraction, which is obtained as described above.

Free standard adsorption (desorption) energies (ΔG^0) were calculated as

$$\Delta G^0 = -RT \ln(K_D)$$

where T is the temperature in Kelvin and R is the general gas constant (8.314 J/mol).

$\Delta\Delta G°$ values are obtained as outlined in the following example:

$$\Delta\Delta G^0_{adsorption/desorption \ of \ MCPA} = \Delta G^0_{desorption \ of \ MCPA} - \Delta G^0_{adsorption \ of \ MCPA}$$

$\Delta\Delta G^0$ values were calculated for each substance and all investigated soils.

RESULTS AND DISCUSSION

Four different soils were used for the adsorption/desorption studies. A sandy soil (A), a silty Cambisol (B), a sandy Luvisol (C), and a calcic Chernozem (D) with high contents of clay, silt, and organic carbon were chosen (Table 1). These soils exhibit a wide range of particle size distributions and pH. Adsorption/desorption experiments of the four herbicides and the three possible metabolites (Figure 1) were carried out using

Table 2. Distribution Coefficients (K_D) of Adsorption and Desorption Experiments

soil		% particle fraction of bulk soil	organic carbon	K_D						
				MCPA	mecoprop	2,4-D	dichlorprop	4-CP	2,4-DCP	2,4-MCP
				Adsorption						
A	sand	88.20	0.34	0.47	0.56	0.73	0.62	0.80	1.93	0.77
	silt	9.30	1.39	1.58	2.16	2.13	2.36	3.39	9.79	3.05
	clay	2.50	2.81	3.93	4.29	6.48	5.64	9.12	27.9	7.46
	total soil		**0.6**	**0.46**	**0.55**	**0.68**	**0.61**	**1.15**	**2.64**	**1.05**
B	sand	48.00	0.82	0.99	0.58	1.22	0.80	1.06	2.20	1.38
	silt	43.00	2.49	2.47	1.66	3.66	2.05	3.29	5.36	4.11
	clay	9.00	3.00	8.04	5.96	11.6	7.93	9.10	18.7	14.1
	total soil		**2.40**	**1.94**	**1.39**	**2.81**	**1.73**	**2.29**	**4.39**	**2.97**
C	sand	78.00	0.22	0.46	0.59	0.60	0.70	1.01	2.62	1.19
	silt	12.00	1.06	1.70	2.08	2.96	2.58	4.88	7.75	4.50
	clay	10.00	2.29	4.93	6.62	8.48	8.57	13.9	26.3	14.4
	total soil		**0.54**	**0.53**	**0.62**	**0.74**	**0.70**	**1.23**	**2.60**	**1.41**
D	sand	22.00	0.43	0.64	0.50	0.86	0.50	1.55	2.98	2.11
	silt	55.00	1.84	1.54	1.47	2.62	1.60	4.05	8.28	6.30
	clay	23.00	3.32	5.27	4.83	8.45	4.73	12.8	25.8	21.4
	total soil		**2.70**	**1.07**	**0.89**	**1.55**	**0.93**	**2.61**	**5.02**	**3.72**
				Desorption						
A	sand	88.20	0.34	0.68	0.80	0.74	0.72	1.79	2.51	1.52
	silt	9.30	1.39	5.53	7.72	7.57	6.40	15.45	17.93	14.16
	clay	2.50	2.81	21.1	36.5	30.1	35.1	72.6	96.3	58.8
	total soil		**0.6**	**0.73**	**0.94**	**0.82**	**0.87**	**1.95**	**2.18**	**1.61**
B	sand	48.00	0.82	1.00	0.47	1.26	1.34	1.90	2.39	2.30
	silt	43.00	2.49	4.79	3.65	5.87	4.51	9.34	9.51	8.64
	clay	9.00	3.00	27.3	27.0	39.4	26.3	50.9	58.7	67.6
	total soil		**2.40**	**1.63**	**1.68**	**2.06**	**1.93**	**3.06**	**3.73**	**4.37**
C	sand	78.00	0.22	0.98	0.94	1.17	0.91	2.37	3.72	2.97
	silt	12.00	1.06	2.39	3.40	3.21	2.41	5.60	7.60	6.33
	clay	10.00	2.29	11.9	20.3	17.1	20.3	45.3	72.4	39.1
	total soil		**0.54**	**0.78**	**0.95**	**1.12**	**0.97**	**1.98**	**2.97**	**2.20**
D	sand	22.00	0.43	1.30	0.72	1.32	1.32	4.11	2.47	3.52
	silt	55.00	1.84	5.21	4.91	8.48	5.82	18.1	14.4	11.3
	clay	23.00	3.32	30.1	36.7	50.8	37.8	120	114	85.7
	total soil		**2.70**	**1.86**	**1.73**	**2.48**	**1.70**	**5.17**	**4.73**	**4.94**

all four soils and their soil particle size fractions (sand, silt, and clay) as adsorbents.

Linear adsorption behavior was found for all soils and soil fractions and has also been reported for adsorption of phenoxyalkanoic acids in other studies (Bolan and Baskaran, 1996). The K_D values are presented in Table 2.

A general trend of increased adsorption on smaller particle size fractions (sand to silt to clay) can be observed. This can be related to both the increasing surface of the clay fraction and the increasing organic carbon content of the clay fractions (Parker and Rate, 1998). Adsorption and desorption K_D values of each phenoxyalkanoic acid and each metabolite showed a significant correlation to the soil organic carbon content. Differences among the fractions were obtained when K_D values were related to the organic carbon content of the fractions. This could be explained by differences in the nature of organic matter among fractions, as was shown by Stemmer et al. (1998) using the same fractionation procedure.

Adsorption (K_D) on clay particles was found to be increased by a factor of ~10 ± 2 in comparison to adsorption on sand particles. Adsorption of the phenols (4-CP, 2,4-DCP, and 2,4-MCP) was stronger than adsorption of the phenoxyalkanoic acid derivatives (MCPA, mecoprop, 2,4-D, and dichlorprop). This was true for all examined soils and all particle size fractions and was also reported by Benoit et al. (1996, 1998).

Soil pH can affect sorption behavior of ionizable organic compounds (Nicholls and Evans, 1991). Although the phenols will exist as neutral species, the phenoxyalkanoic acids [pK_a ranging from 2.6 to 3.78 for 2,4-D and mecoprop, respectively (Tomlin, 1994)] will exist primarily as anions. However, soil surfaces are more acidic than the bulk pH (Parker and Rate, 1998), which could have an influence on the sorption behavior of phenoxyalkanoic acids on soil B, which has a pH of 4.6. Phenoxyalkanoic acids seem to be slightly more strongly sorbed at the lower pH of soil B compared to soil D (similar percent organic carbon, but pH 4.6 for soil B and pH 7.9 for soil D) (Table 2).

Desorption distribution coefficients of all bulk soil experiments were ~1.3 ± 0.3 times higher than the corresponding adsorption distribution coefficients (K_{D-ads}). A similar ratio of K_{D-des} relative to K_{D-ads} was found for the sand fractions (1.6 ± 0.5), whereas a much higher increase of K_{D-des} relative to K_{D-ads} was obtained for the silt (2.5 ± 1.1) and clay fractions (4.9 ± 2.1). An artificial introduction of new strong adsorption sites due to the fractionation process may be an explanation for that finding. Desorption from these new adsorption sites may be more inhibited than desorption from the adsorption sites of the unfractionated soil, which could lead to the observed decrease in desorption efficiency. We also attempt to estimate the adsorption or desorption behavior from the adsorption or desorption behavior of the corresponding soil particle size fractions. For that purpose the estimated K_D values were calculated using both the relative amount of each particle size fraction (sand, silt, and clay) and their respective K_D values (for details see Materials and Methods). The relationship between the estimated and experimentally measured K_D values is plotted in Figure 2 for the adsorption behavior. Although prediction of K_{D-ads} seems to be possible for all substances on soils A and B, prediction of K_{D-ads} for

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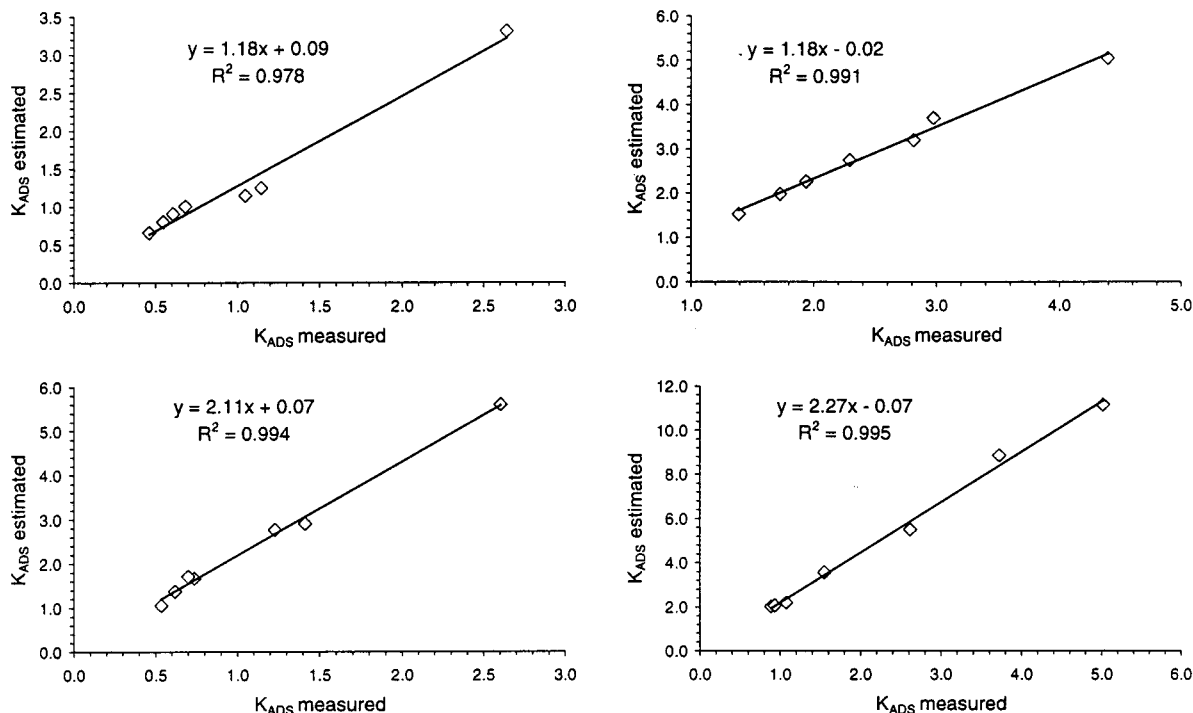
Figure 2. Estimated distribution coefficients of all investigated substances and soils obtained from adsorption behavior onto soil particle size fractions versus measured distribution coefficients [soils A (top, left), B (top, right), C (bottom, left), and D (bottom, right)].

Table 3. Differences in Free Standard Sorption Energies between Desorption and Adsorption Behaviors of the Investigated Substances ($\Delta\Delta G^0 = \Delta G^0_{\text{desorption}} - \Delta G^0_{\text{adsorption}}$)

| | kJ/mol | | | | | | |
soil	MCPA	mecoprop	2,4-D	dichlorprop	4-CP	2,4-DCP	2,4-MCP
A	−1.13	−1.35	−0.44	−0.88	−1.30	0.46	−1.06
B	0.42	−0.46	0.76	−0.27	−0.71	0.40	−0.94
C	−0.91	−1.05	−1.02	−0.81	−1.17	−0.33	−1.09
D	−1.34	−1.64	−1.16	−1.48	−1.67	0.15	−0.70
av ± SD	−0.74 ± 0.79	−1.12 ± 0.51	−0.46 ± 0.87	−0.86 ± 0.50	−1.21 ± 0.40	0.17± 0.36	−0.95 ± 0.18

soils C and D showed a significant and systematic overestimation by a factor of >2 even if good correlation between the estimated and measured K_D was obtained. This finding supports the assumption that stronger adsorption sites are introduced during the fractionation process. The particle fractionation process seems to uncover a number of new, strong adsorption sites, which are not accessible for sorption in the original macro- and microaggregate architecture. This behavior seems not to correlate with texture or organic carbon content of the soils; for one of the soils containing a very high sand content (soil A), adsorption parameters for soil size fractions could be used to predict the adsorption of the original soil, whereas for the other soil (soil C), a high deviation between the estimated and measured K_D values was found.

Good correlation was also found for the estimated $K_{D-\text{des}}$ and measured $K_{D-\text{des}}$ ($R^2 = 0.96$ and 0.90 for soils A,B and C,D, respectively). However, the estimated values exhibited a systematic overestimation by a factor of 2.8 and 7.4 for soils A,B and D,C, respectively. Like for the adsorption behavior, the power of the prediction of the desorption behavior depends more on the type of soil than on the molecular structure of the analyte. Because a similar power of prediction was observed for soils A,B and C,D for all investigated compounds and adsorption as well as desorption, the estimation of $K_{D-\text{des}}$ or $K_{D-\text{ads}}$ using data of the particle size fractions

strongly depends on the type of soil and not on the different structures of the investigated compounds. If it was possible to fractionate the soil without increasing the number of adsorption sites, their original $K_{D-\text{ads}}$ values could be deduced simply from the additive contribution of the different fractions.

Comparison of the adsorption and desorption behaviors of the same investigated compound reveals a general trend toward inhibited desorption (hysteresis) ($\Delta\Delta G^0 < 0$) (Table 3). Such trends were significant for mecoprop, dichlorprop, 2,4-CP, and 2,4-MCP. The 2,4-D and 2,4-DP metabolite 2,4-DCP desorbed to almost the same extent from the soil as it was adsorbed on the soil matrix, which is reflected by the insignificant differences between the standard free energies.

To estimate overall adsorption or desorption changes induced by the structural changes within the group of phenoxyalkanoic acid herbicides and metabolites on all four investigated soils, averages in standard free energies were calculated (Table 4). Differences in standard free sorption energy values can be straightforwardly used for interpretation of adsorption strength. For example, a negative $\Delta\Delta G^0$ value between adsorption of analytes of a group A (e.g., MCPA and mecoprop) and of a group B (e.g., 2,4-D and dichlorprop) on the same soil means that the adsorption of the analytes of group B is stronger than of group A and vice versa for positive $\Delta\Delta G^0$ values. The most pronounced structure-related

Table 4. Differences in Free Standard Sorption Energies Induced by Structural Changes ($\Delta\Delta G^0 = \Delta G^0_{II} - \Delta G^0_I$)

$\Delta G^0_I \Rightarrow \Delta G^0_{II}$	kJ/mol, **av** $\pm$ SD	
	adsorption	desorption
phenyl$-$CH$_3$ (MCPA, mecoprop) $\Rightarrow$ phenyl$-$chloride (2,4-D, dichlorprop)	$-$**0.60** $\pm$ 0.34	$-$**0.33** $\pm$ 0.43
phenyl$-$CH$_3$ (2,4-MCP) $\Rightarrow$ phenyl$-$chloride (2,4-DCP)	$-$**1.36** $\pm$ 0.68	$-$**0.25** $\pm$ 0.58
phenyl$-$H (4-CP) $\Rightarrow$ chlorophenyl (2,4-DCP)	$-$**1.77** $\pm$ 0.22	$-$**0.39** $\pm$ 0.50
phenol$-$H (2,4-DCP, 2,4-MCP) $\Rightarrow$ phenoxyacetic acid (dichlorprop, MCPA)	**2.36** $\pm$ 0.90	**2.15** $\pm$ 0.43
phenol$-$H (2,4-DCP, 2,4-MCP) $\Rightarrow$ phenoxypropionic acid (dichlorprop, mecoprop)	**2.78** $\pm$ 0.95	**2.18** $\pm$ 0.49
acetic (MCPA, 2,4-D) $\Rightarrow$ propionic acid (mecoprop, dichlorprop)	**0.42** $\pm$ 0.64	**0.03** $\pm$ 0.49

adsorption effect was observed for the comparison of the phenols to the phenoxyalkanoic acids. Due to the introduction of the acidic and more polar moiety, water solubility is enhanced and the tendency toward soil sorption decreases. The significantly higher adsorption of the phenols can be explained by their lower polarity and therefore higher partition in the organic soil matrix as well as their smaller steric requirements (size), which results in higher mobility within the organic matrix (Dec and Bollag, 1997). Similar differences in $\Delta\Delta G^0$ were obtained when the desorption behaviors of phenols and phenoxyalkanoic acids were compared. This finding confirms that different sorption strengths are involved in the sorption of phenols and phenoxyalkanoic acids.

A comparison of the dichlorophenyl-containing herbicides (2,4-D and dichlorprop) to the chloromethylphenyl-containing herbicides (MCPA and mecoprop) showed that the substitution of a methyl by a chlorine group (e.g., MCPA versus 2,4-D) results in increased adsorption of the substance (negative $\Delta\Delta G^0 = -0.60 \pm 0.37$ kJ/mol). This effect is even stronger for the investigated metabolites MCP and 2,4-DCP ($\Delta\Delta G^0 = -1.4 \pm 0.7$ kJ/mol). The difference in adsorption standard free energy between 4-CP and 2,4-DCP of almost -1.8 ± 0.2 kJ/mol again demonstrates the increase in adsorption induced by an additional chlorine atom, in this case by replacement of a hydrogen atom. A slight change in polarity due to the introduction of a chlorine group might allow additional weak interactions with the soil matrix and therefore stabilize and increase adsorption.

A comparison of the acetic acid derivatives (MCPA and 2,4-D) to the propionic acid derivatives (mecoprop and dichlorprop) shows a slight but not significant deviation toward increased adsorption of the acetic acid derivatives.

Much less pronounced $\Delta\Delta G^0$ values were found for the desorption process. Changes of the molecular structure by replacing a methyl group or hydrogen atom by a chlorine group did not affect the desorption behavior significantly [e.g., 2,4-MCP versus 2,4-DCP $\Delta\Delta G^0 = -0.25 \pm 0.58$ kJ/mol for desorption in contrast to -1.3 kJ/mol for adsorption (Table 4)]. Similar effects can be observed for structural changes of the acid moiety (acetic versus propionic acid).

The polarity of the phenoxyalkanoic acid herbicides is mainly governed by the carboxylic and ether groups. The slight change in polarity introduced by a chlorine group may favor additional weak dipole$-$dipole interactions and enlarges the number of possible adsorption sites, which are higher for, for example, 2,4-D or 2,4-DCP, than for MCPA or 2,4-MCP, respectively. However, the strengths of interaction might still be similar or the same. Consequently, the desorption behavior for these two compound groups might not be significantly different. This is in agreement with the results found in our study. On the other hand, the comparison of the $\Delta\Delta G^0$ values for adsorption and desorption of phenols and the phenoxyalkanoic acids suggests that the differences in adsorption cannot be explained only by steric reasons (enlargement of the molecular structure) and consequently different access to adsorption sites. The introduction of a carboxylic acid function and the strong increase in polarity involved additionally induces a change in the type of sorption mechanism.

SUMMARY AND CONCLUSIONS

For almost all investigated soil and soil particle size fractions sorption of the phenols (4-CP, 2,4-DCP, and 2,4-MCP) was stronger than sorption of the phenoxyalkanoic acid herbicides (MCPA, mecoprop, 2,4-D, and dichlorprop). The significant increase in adsorption of the phenols can be explained by their less pronounced polarity and therefore higher solubility in the organic soil matrix and additionally by lower steric requirements, which results in higher mobility within the organic matrix.

Desorption behavior was well correlated with adsorption behavior. However, hysteresis was observed, and a substantial part of the sorbed substances remains on the soil.

The power of the estimation of sorption distribution coefficients from sorption data of particle size fractions strongly depends on the type of soil and not on the structure of the investigated substances. A good correlation between the estimated and experimentally determined sorption distribution coefficients was found for all four investigated soils, but the prediction of sorption distribution coefficients was possible for only two of them. The particle fractionation process seems to introduce new adsorption sites, which are not accessible for the analyte when adsorption experiments are carried out using the original soil.

The strength of adsorption can be related to the structures of the compounds investigated. Averaged over all investigated soils mecoprop showed the weakest adsorption. Adsorption is increased when the methyl group of the phenoxy ring is replaced by a chlorine (dichlorprop) and additionally increased when the propionic moiety is substituted by an acetic acid moiety (2,4-D). This structural change affects the volume and polarity of the examined analytes. Both the increasing steric demand and slight changes in polarity affect the adsorption of these substances.

However, the strengths of possible adsorption interactions (charge interactions of the acid group and dipole$-$dipole and van der Waals interactions of other functional groups) are still similar or the same. This can be shown by the desorption data of the herbicide structures investigated. A further comparison of adsorption and desorption data of a group of structurally similar compounds on a large variety of soils could be a powerful strategy for future investigations of structure-induced differences in adsorption strength and mechanisms.

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LITERATURE CITED

Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, U.K., 1998.

Benoit, P.; Barriuso, E.; Houot, S.; Calvet, R. Influence of the nature of soil organic matter on the sorption−desorption of 4-chlorophenol, 2,4-dichlorophenol and the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). *Eur. J. Soil Sci.* **1996**, *47*, 567−578.

Benoit, P.; Barriuso, E.; Calvet, R. Biosorption characterization of herbicides, 2,4-D and Atrazine, and two chlorophenols on fungal mycelium. *Chemosphere* **1998**, *37*, 1271−128.

Bolan, N. S.; Baskaran, S. Biodegradation of 2,4-D herbicide as affected by ist adsorption−desorption behaviour and microbial activity of soils. *Aust. J. Soil Res.* **1996**, *34*, 1041−1053.

Borisover, M. D.; Graber, E. R. Specific interactions of organic compounds with soil organic carbon. *Chemosphere* **1997**, *34*, 1761−1776.

Celis, R.; Koskinen, W. C. An isotopic exchange method for the characterization of the irreversibility of pesticide sorption−desorption in soil. *J. Agric. Food Chem.* **1999**, *47*, 782−790.

Celis, R.; Cox, L.; Hermosin, M. C.; Cornejo, J. Sorption of Thiazafluron by Iron- and Humic acid-coated Montmorillonite. *J. Environ. Qual.* **1997**, *26*, 472−479.

Celis, R.; Barriuso, E.; Hout, S. Effect of liquid sewage sludge addition on Atrazine sorption and desorption by soil. *Chemosphere* **1998**, *37*, 1091−1107.

Celis, R.; Hermonsin, M. C.; Cox, L.; Cornejo, J. Sorption of 2,4-Dichlorophenoxyacetic Acid by model particles simulating naturally occurring soil colloids. *Environ. Sci. Technol.* **1999**, *33*, 1200−1206.

Dec, J.; Bollag, J.-M. Determination of covalent and noncovalent binding interactions between xenobiotic chemicals and soil. *Soil Sci.* **1997**, *162*, 858−874.

De Paolis, F.; Kukkonen, J. Binding of organic pollutants to humic and fulvic acids: Influence of pH and the structure of humic material. *Chemosphere* **1997**, *34*, 1693−1704.

Farrel, J.; Grassian, D.; Jones, M. Investigation of mechanisms contributing to slow desorption of hydrophobic organic compounds from mineral solids. *Environ. Sci. Technol.* **1999**, *33*, 1237−1243.

Gao, J. P.; Maguhn, J.; Spitzauer, P.; Kettrup, A. Sorption of pesticides in the sediment of the Teufelsweiher pond (southern Germany). I: Equilibrium assessments, effect of organic carbon content and pH. *Water Res.* **1998**, *32*, 1662−1672.

McBride, M. B. Surface chemistry of soil minerals. In *Minerals in Soil Environments*; Soil Science Society of America Book Series; Dixon, J. B., Weed, S. B., Eds.; SSSA: Madison, WI, 1989.

Morillo, E.; Undabeytia, T.; Maqueda, C. Adsorption of Glyphosate on the clay mineral Montmorillonite: Effect of Cu-(II) in solution and adsorbed on the mineral. *Environ. Sci. Technol.* **1997**, *31*, 3588−3592.

Murphy, E. M.; Zachara, J. M.; Smith, S. C. Influence of mineral-bond Humic substances on the sorption of hydrophobic organic compounds. *Environ. Sci. Technol.* **1990**, *24*, 1507−1516.

Nicholls, P. H.; Evans, A. A. Sorption of ionisable organic compounds by field soils. Part I: Acids. *Pestic. Sci.* **1991**, *33*, 319−330.

Parker, A., Rate, J. E. Eds. *Environmental Interactions of Clays−Clays and the Environment*; Springer-Verlag: Berlin, Germany, 1998.

Pignatello, J. J.; Xing, B. Mechanism of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* **1995**, *30*, 1−11.

Rütters, H.; Höllrigl-Rosta, A.; Kreuzig, R.; Bahadir, M. Sorption behavior of Prochloraz in different soils. *J. Agric. Food Chem.* **1999**, *47*, 1242−1246.

Socias-Viciana, M. M.; Fernandez-Perez, M.; Villafranca-Sanchez, M.; Gonzales-Pradas, E.; Flores-Cespedes, F. Sorption and Leaching of Atrazine and MCPA in natural and peat-amended calcareous soils from Spain. *J. Agric. Food Chem.* **1999**, *47*, 1236−1241.

Stemmer, M.; Gerzabek, M. H.; Kandeler, E. Organic matter and enzyme activity in particle-size fractions of soils obtained after low-energy sonication. *Soil Biol. Biochem.* **1998**, *30*, 9−17.

Susarla, S.; Bahaskar, G. V.; Bhamidimarri, R. Competitive adsorption−desorption kinetics of phenoxyacetic acids and a chlorophenol in volcanic soil. *Environ. Technol.* **1997**, *18*, 937−943.

Tomlin, C., Ed. *The Pesticide Manual*; Britsh Crop Protection Council: Farnham, U.K., 1994.