

Response of sorption processes of MCPA to the amount and origin of organic matter in a long-term field experiment

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Summary

Changes in farming practices over long times can affect the sorption behaviour of MCPA ((4-chloro-2-methylphenoxy)acetic acid). We studied the adsorption–desorption mechanisms of MCPA on soil with varied amounts and origins of soil organic matter obtained from a long-term field experiment with various organic amendments. The origin of the soil organic matter seems to be crucial for the sorption behaviour of MCPA. Samples of soil amended with sewage sludge sorbed MCPA more strongly than the soil under any other treatment. Peat-amended soil was second followed by soil receiving animal manure, green manure, mineral fertilizer without N and the fallowed soil. Both the carbon content and the origin of the organic matter are important for the sorption. A decrease of carbon content of a soil does not necessarily imply a reduction of sorption capacity for polar organic acids such as MCPA. Nevertheless, our adsorption–desorption experiments suggest that with decreasing carbon content the role of mineral sorption mechanisms could become more pronounced. Our results showed that interactions of soil organic matter and soil minerals distinctly influence adsorption properties for MCPA.

Introduction

The leaching of pesticides into groundwater is receiving increasing attention. Adsorption on the soil matrix appears to be one of the most important factors affecting both leaching and behaviour and fate of pesticides in soil. Adsorption–desorption reactions of pesticides in soil are affected by the physicochemical characteristics of the pesticide, the composition and texture of the soil, and temperature and humidity.

The contribution of the individual factors to the possible migration of pesticides to the groundwater can be determined fundamentally by studying the adsorption, desorption, degradation and percolation (Socias-Viciano *et al.*, 1999). The pesticide sorption behaviour is related both to texture and properties of the soils and to the chemical structure of the organic substances.

Phenoxyalkanoic acid herbicides such as MCPA ((4-chloro-2-methylphenoxy)acetic acid), are broad-spectrum, post-emergent herbicides much used in agriculture. They have one polar carboxylic group and one lipophilic phenyl moiety, and

because of this structure they are suitable model substances for studying adsorption–desorption processes in soil (Celis *et al.*, 1999; Socias-Viciano *et al.*, 1999; Haberhauer *et al.*, 2000). Parker & Rate (1998) postulated that the interactions of the carboxylic groups with surfaces of organic matter and negatively charged clay via metal ion bridges dominate the sorption of acid herbicides. Benoit *et al.* (1996) thought that partition via lipophilic interactions in soil organic matter dominates. Soil pH can affect the protonation–deprotonation reaction of ionizable organic compounds, and therefore it can influence their sorption behaviour (Nicholls & Evans, 1991).

We believe that ionic interactions of carboxylic acids dominate sorption of phenoxyalkanoic acid herbicides on clay; nevertheless other reactions may also play a role in the sorption and leaching of acid pesticides in soil. Hydrogen bonds, van der Waals interactions of aliphatic groups and charge transfer interactions of the aromatic ring systems of humic substances with aromatic groups of pesticides may affect the strength of adsorption on soil constituents (Dec & Bollag, 1997; Gevaio *et al.*, 2000). Non-reversible and non-equilibrium conditions – within the timescale of the experiment – (e.g. slow diffusion into and partitioning in the soil matrix) can produce hysteresis when pesticides desorb.

However, the mechanism involved in such sorption has not yet been clearly demonstrated, one of the major reasons being the difficulty of isolating unaltered organic matter from the soil and characterizing its chemical and physical properties (Benoit *et al.*, 1996).

Hence, the origin, composition and content of the organic matter has an important impact on the sorption behaviour of the soil (Kile *et al.*, 1999; Perminova *et al.*, 1999). The content of organic matter of agricultural soils is related to farming practices including manuring. Thus, changes in farming practices on a long timescale will change organic matter content and therefore may change the adsorption–desorption properties for pesticides.

One long-term experiment was started on a homogeneous field 44 years ago in Sweden. Originally, all plots had the same mineral and organic composition. After adding different amendments over more than 35 years the soil organic matter, aggregate stability and pore sizes have been significantly altered (Gerzabek *et al.*, 1995; Kirchmann & Gerzabek, 1999). All these factors influence the adsorption of pesticides. Thus, long-term experiments supply samples of soil with differing amounts and qualities of organic matter (SOM), but all samples come from the same original soil. Adsorption experiments using such soils may become representative of the real environmental behaviour of the organic matter in agricultural soils subjected to pesticide treatments. Additionally, sorption depends on the nature and amount of surface ultimately exposed (Celis *et al.*, 1999). Thus, laboratory experiments in which certain amounts of organic matter are added to soil samples may give less conclusive results concerning the impact of such amendments than sorption experiments of soil with varying amounts of organic matter obtained from long-term trials.

The objective of this study was to examine the adsorption–desorption behaviour of MCPA as a model substance for anionic herbicides on soil to which had been added various organic materials over some 40 years, and to compare the sorption behaviour with respect to soil organic matter content and origin.

Materials and methods

Chemical

Analytical pure MCPA (4-chloro-2-methylphenoxy)acetic acid; Dr Ehrenstorfer GmbH, Augsburg, Germany) was used as analyte. Its solubility in water at 25°C was 825 mg l⁻¹, and its acid constant (p*K*_A) is 3.07. The agronomic dose of MCPA is between 1 and 2.5 kg ha⁻¹.

Soil

The soil was from a long-term experiment started in 1956 at Uppsala, Sweden on a Eutric Cambisol (FAO) with 37% clay

and 41% silt. The parent material consists of post-glacial clay with illite as the main clay mineral. Kirchmann *et al.* (1994) document the experiment and data fully. In 1956 the soil (0–20 cm depth) had 15 g kg⁻¹ of organic carbon, 1.7 g kg⁻¹ of nitrogen and a pH of 6.6. The experimental design is based on 14 differing treatments, laid out in a randomized block design with four replicates. The individual plots (2 m × 2 m) were separated by pressure-treated wooden frames. Six of the treatments, namely fallow (weeds removed), NoN (crop rotation with mineral P and K but without nitrogen fertilizer), green manure, animal manure (well decomposed), peat (sphagnum) and sewage sludge, were selected for this study. The application of organic amendments was based on equal amounts of ash-free organic matter amounting to 2000 kg C ha⁻¹ year⁻¹ on average. Organic matter was added in autumn in 1956, 1960, 1963 and thereafter every second year by hand. All plots received a dressing of 20 kg P ha⁻¹ in the form of superphosphate and 35–38 kg K ha⁻¹ in the form of potassium chloride annually in spring. Cereals (70%), rape (25%) and fodder beet (5%) were grown in rotation. There were no legumes in the rotation. At harvest the above-ground portion of the crop was completely removed. Samples of topsoil (0–20 cm) were taken in autumn 1998 from two replicates of each treatment. They were air-dried, passed through a 2-mm sieve, and then stored. Selected soil properties are shown in Tables 1 and 2. Particle-size distribution was determined by the method of Stemmer *et al.* (1998). This physical fractionation uses low-energy ultrasonication to disperse the soil and thus preserves stable microaggregates in the silt fraction. Total carbon (= total organic carbon) was measured in the soil samples using an elemental analyser (Carlo Erba Nitrogen Analyser 1500, Milano).

Adsorption experiments

Experimental batch sorption data were obtained as follows: 2 g of each soil sample was weighed into 50 ml centrifuge tubes made of polypropylene copolymer. Five millilitres of 0.01 M CaCl₂ aqueous solutions of MCPA containing initial pesticide concentrations (*C*₀) ranging between 0.1 and 100 mg l⁻¹ was added to each. The flasks were shaken for 24 h. Preliminary kinetic experiments had demonstrated that adsorption equilibrium was reached within less than 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 centrifuging, the supernatant solution was removed and the concentrations of MCPA in the supernatant solution, *C*_s, were determined by HPLC with a UV-detector (Beckman Instruments, Fullerton). As mobile phase a methanol–water mixture (ratio 65:35) was used with 0.5% acetic acid (isocratic elution). The analysis was done on a Hypersil 5 μm ODS, 250 mm × 4.0 mm column (C18-material, Merck, Darmstadt, Germany) at 40°C and a flow of 1 ml minute⁻¹. The MCPA was analysed at the wavelength of

maximum absorption (228 nm). The MCPA adsorbed, C_a , was calculated from the difference between the initial and final concentration of the CaCl_2 solution. Blanks containing no MCPA were included, and flasks containing only MCPA and no soil were analysed to determine adsorption on the surface of the flasks. All sorption experiments were done at least in duplicate. Linear isotherms were obtained ($C_a = K_D C_s$) with correlation coefficients always greater than 0.999. Distribution coefficients, K_D values, were obtained from the slope of the graph of C_a against C_s . Values of K_{OC} were calculated as follows:

$$K_{OC} = 100 K_D / \text{Organic carbon \%}.$$

Desorption experiments

Desorption experiments were done in two steps and commenced immediately after the corresponding adsorption experiment. The supernatant removed was replaced by the same amount (5 ml) of fresh 0.01 M CaCl_2 solution. The mixture was shaken for 24 h, and the soil and aqueous phases were separated as described above. This procedure was repeated in a second desorption step. All desorption experiments were performed at least in duplicate.

The MCPA adsorbed, C_{a-Des1} , C_{a-Des2} , after the first and second desorption step was calculated from the difference between the initial C_0 and final concentration of the CaCl_2 solution of the adsorption, C_s , first desorption, C_{s-Des1} , and second desorption step, C_{s-Des2} , respectively. Linear isotherms were obtained by plotting the corresponding adsorbed MCPA after desorption step against the concentration of MCPA in solution:

$$C_{a-Des1} = K_{D-Des1} C_{s-Des1}.$$

Distribution coefficients, K_D values, were obtained from the slope of a C_{a-Des1} against C_{s-Des1} .

Theoretical calculations

We made the initial calculations using the self-consistent field (SCF) Hartree–Fock method (Roothaan, 1951) and the 3-21G basis set (Binkley *et al.*, 1980) as implemented in Gaussian 98 (Gaussian, Inc., Pittsburgh, PA). The interaction energies between MCPA and the individual minerals and model compounds of the soil organic matter (Figure 3) were obtained as follows: first, the energies of minimized conformations of the single molecules were calculated, then the energies of minimized conformations of the whole complexes (MCPA plus model compound) were calculated. The formation energies of these complexes were obtained by subtracting the energies of the single molecules (residues) from the energies of the complex. This formation energy was used as an estimate of the interaction energy.

Results and discussion

After more than 40 years of the treatments the amount (Tables 1 and 2) and composition of soil organic matter has been altered (Gerzabek *et al.*, 1995, 1997; Kirchmann *et al.*, 1996).

The organic carbon contents of the topsoils changed distinctively during the 42 years of treatment. The topsoil on the continuous fallow plots had lost approximately one third of its organic matter. Arable cropping resulted in a less dramatic decrease of organic carbon (13%), and green manure maintained the humus status since 1956. In comparison with the other variants the carbon content has been increased significantly by peat and sewage sludge amendments. The organic matter content remained fairly constant in the soil of plots treated with green manure and increased in the plots receiving animal manure.

The C/N ratio in the topsoil ranged from 9.7 to 18.3 in 1998 (Table 1). The soil under all treatments except the peat had C/N ratios that are typical for agricultural soils (Scheffer & Schachtschabel, 1998). There were significant changes in the characteristics of the organic material extracted from the soil treated with peat, which differed considerably in its E_4/E_6 ratios, the ratios of fulvic to humic acids, and FTIR-spectra

Table 1 Soil characteristics of the treatments and elemental composition of organic amendments

Treatment	pH	Organic C /%	N /%	C/N	Organic amendments	Organic C /%	N /%	C/N
Fallow (FA)	6.3	1.1 (0.1)	0.12 (0.02)	9.8				
NoN	6.5	1.3 (0.1)	0.13 (0.02)	9.7				
Animal manure (AM)	6.3	2.2 (0.1)	0.22 (0.03)	10.1	Animal manure (AM)	39.5 (2.0)	1.76 (0.21)	22.4
Green manure (GM)	6.7	1.8 (0.1)	0.17 (0.01)	10.4	Green manure (GM)	41.4 (1.4)	1.83 (0.23)	22.6
Peat (PE)	5.8	3.2 (0.2)	0.17 (0.02)	18.3	Peat (PE)	45.9 (1.5)	0.77 (0.11)	69.6
Sewage sludge (SE)	5.8	2.6 (0.2)	0.27 (0.01)	9.7	Sewage sludge (SE)	30.4 (1.3)	3.29 (0.15)	9.2

Standard errors are given in parentheses.

from that under all other treatments (see Gerzabek *et al.*, 1997).

Adsorption

The adsorption of MCPA on the different treatments in batch experiments revealed the differences induced by farming practices. Figure 1 shows adsorption isotherms. There were significant differences in the adsorption behaviour between the peat, sewage sludge, animal manure plots and the other

treatments. The soil amended with sewage sludge adsorbed more strongly than on soil treated with peat (PE). The soil that received animal manure (AM) adsorbed slightly more strongly than that to which green manure was added (GM), the unfertilized soil (NoN) and the fallowed soil (FA). Concerning adsorption of MCPA, no significant difference was observed between GM, NoN and FA. The adsorption distribution coefficients, K_{D-Ads} , obtained from a linear adsorption model ranged from 0.86 to 2.12 for FA and SE treatments, respectively. We were surprised to find no significant

Table 2 Soil texture characteristics of the treatments and elemental composition of the particle-size fractions

Treatment	Texture ^a /%					Organic C in particle-size fractions ^a /weight %				
	CS	FS	Silt	Clay I	Clay II	CS	FS	Silt	Clay I	Clay II
Fallow (FA)	4.0	16.1	47.9	25.3	4.1	0.3	0.2	1.2	1.6	1.8
NoN	4.4	15.9	46.9	25.6	3.2	0.3	0.2	1.4	1.7	2.1
Animal manure (AM)	4.5	15.1	52.0	24.9	3.7	0.6	0.4	2.1	2.1	3.0
Green manure (GM)	3.8	15.4	50.0	24.7	2.7	0.9	0.4	2.4	2.4	2.9
Peat (PE)	4.2	15.0	49.3	22.0	1.7	1.3	1.2	4.7	2.7	4.1
Sewage sludge (SE)	4.7	15.1	55.2	21.5	1.5	1.0	0.7	2.9	2.6	5.0

^aCS, coarse sand (2000–200 μm); FS, fine sand (200–63 μm); silt (63–2 μm); clay I (2–0.1 μm); clay II (<0.1 μm).

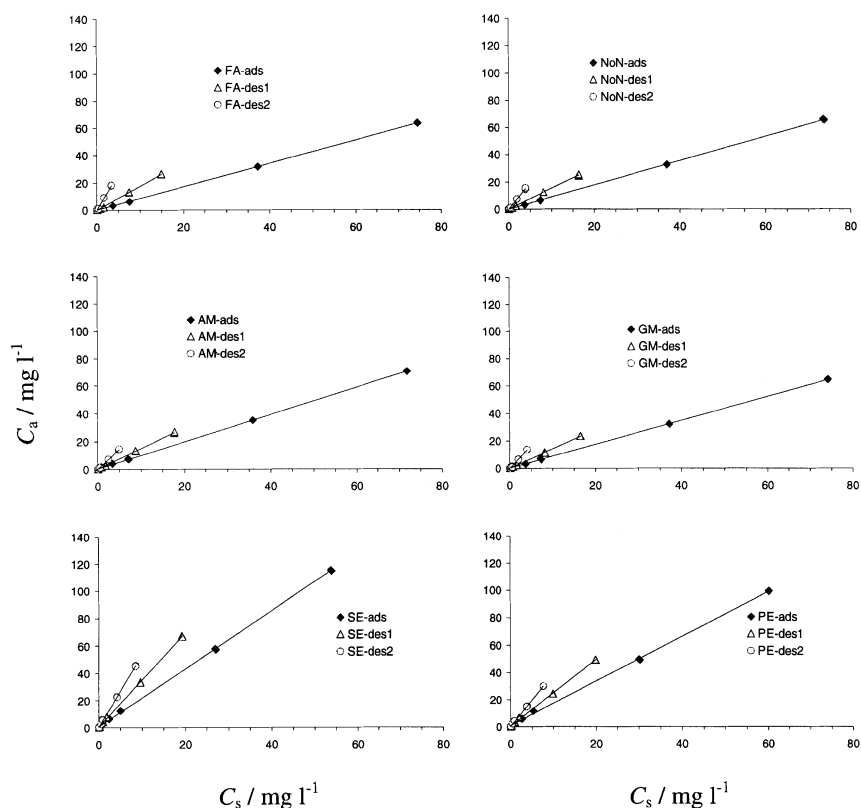


Figure 1 Adsorption and desorption isotherms of MCPA on soil of different treatments. The amount of MCPA sorbed, C_a , is plotted against the amount in solution, C_s , of the adsorption step (ads) and of the first (des1) and second desorption step (des2).

Table 3 Distribution coefficients, K_D , of adsorption and two-step desorption, K_{D-Des1} , K_{D-Des2} , experiments

	K_{D-Ads}	K_{D-Des1}	K_{D-Des2}	K_{OC}	K_{D-Ads}/K_{D-Des1}
Fallow (FA)	0.86 (0.01)	1.78 (0.02)	5.46 (0.05)	76	0.48
NoN	0.89 (0.02)	1.54 (0.03)	3.93 (0.11)	71	0.58
Animal manure (AM)	0.99 (0.02)	1.50 (0.03)	2.88 (0.08)	45	0.66
Green manure (GM)	0.87 (0.02)	1.43 (0.02)	3.20 (0.04)	48	0.61
Peat (PE)	1.63 (0.02)	2.43 (0.02)	3.83 (0.03)	51	0.67
Sewage sludge (SE)	2.12 (0.02)	3.45 (0.03)	5.31 (0.04)	81	0.61

Standard errors are given in parentheses.

correlation between the total carbon content of the samples and their MCPA adsorption behaviour. The K_{D-Ads} value increases from GM, AM to peat and sewage sludge (Table 3 and Figure 2), which accords with increasing carbon content, but the nearly equal K_{D-Ads} of GM, NoN and FA does not correlate with the decrease of organic carbon content from 1.8% (GM) to 1.1% (FA). The fallowed soil adsorbed more strongly than the soil under treatments GM and AM when the large differences in organic matter are taken into account. Additionally adsorption of MCPA on the peat-amended soil was less than that on receiving sludge, although the carbon content is distinctly greater. These findings can be emphasized by calculating K_{OC} values. Nearly the same K_{OC} values (70–80) were obtained for the soil of the fallow and sludge treatments (Table 2), while the K_{OC} was only 50 for the AM, GM and PE treatments. A comparison of the adsorption behaviours of the soil that received peat, which contains the most organic carbon, and that amended with sludge suggests that the origin of the organic matter is crucial for the ability to interact with MCPA. It is obvious that an increase in carbon content in soil alone does not necessarily result in greater adsorption, since the number of adsorption sites for interactions between MCPA and the organic matter depends on the origin of the material (sewage sludge or peat). Organic matter originating from peat, which is a lipophilic and inert amendment (Gerzabek *et al.*, 1997), is less polar and therefore has fewer sites for polar sorption with MCPA than organic matter from sludge. The sludge provides additional adsorption sites for MCPA, as demonstrated by our sorption experiments.

The large K_{OC} value of the fallowed soil (least organic matter) and NoN variants might be explained both by variations in polarity of the organic matter (Kile *et al.*, 1999) and by an additional contribution to the sorption of the inorganic soil constituents. We know that clay minerals have reactive surfaces that are normally coated by organic matter (Parker & Rate, 1998). The smaller amount of organic matter as found especially in the fallow plots might make these surface edges more accessible to direct interactions between MCPA and minerals. This explanation accords with the macroaggregates (1–2 mm) being less stable (Gerzabek *et al.*, 1995) and containing more clay-sized particles in the fallow soil (Table 2).

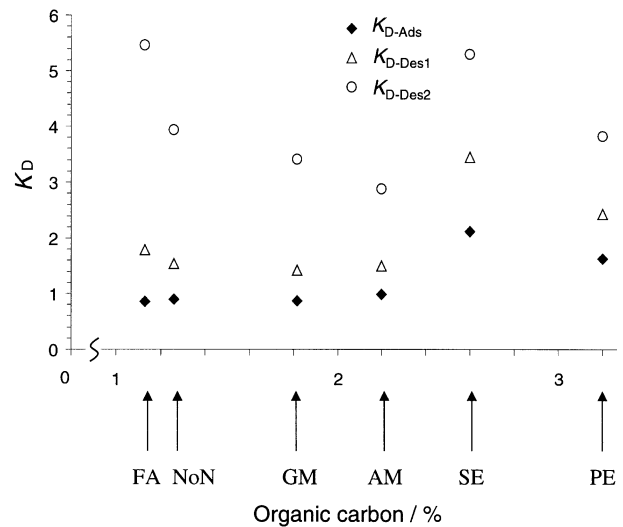


Figure 2 K_D values of the adsorption and desorption steps against organic carbon content of all treatments.

The degree of dissociation of organic acids such as MCPA affects their sorption behaviour (Nicholls & Evans, 1991). The pH of the soil amended with peat and sludge (pH=5.8) is less than that of the soil under the other treatments (6.3–6.7) but still more than two orders of magnitude greater than the pK_A value of MCPA ($pK_A=3.07$). However, the pH of the soil solution near soil surfaces decreases. A larger portion of the neutral form of MCPA may increase partitioning of MCPA in the lipophilic soil matrix. Thus, besides containing more organic matter the somewhat greater acidity of the soil amended with peat and sludge might contribute to the greater adsorption of MCPA in comparison with the other treatments.

Desorption

The desorption behaviour of MCPA was similar to the adsorption behaviour. The largest K_{D-Des} values were obtained for the soil treated with peat and sludge followed by the FA, NoN and AM treatments (Table 3). The quotient of the K_{D-Ads}/K_{D-Des1} shows the hysteresis of the sorption process. While

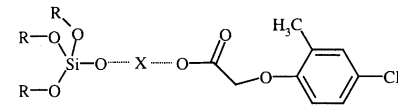
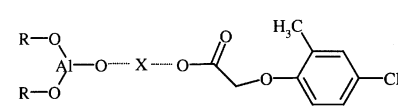
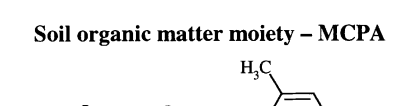
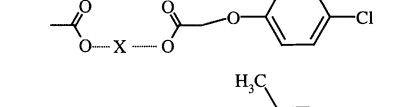
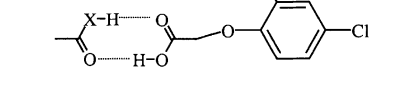
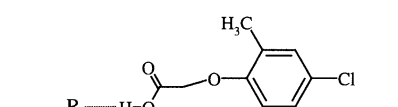
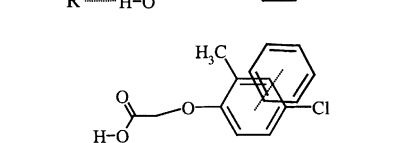
Mineral moiety – MCPA	Type of interaction	Estimated interaction energy (kJ mol ⁻¹)
	Electrostatic X is Mg	-329
	Electrostatic X is H	-127
	Electrostatic X is Mg	-152
Soil organic matter moiety – MCPA		
	Electrostatic X is H	-139
	Hydrogen bonds X is O (carboxylic acid) X is NH (amide)	-112 -110
	Hydrogen bond R is carbonyl group R is phenol R is imidazol	-69 -73 -99
	Aromatic interactions	-12

Figure 3 Examples of some possible molecular interactions of MCPA with inorganic and organic moieties in soil.

similar quotients were calculated for AM, GM, PE and SE (0.61–0.67) distinctly smaller quotients were obtained for the NoN and even smaller ones for the fallow variant. Desorption relative to adsorption of MCPA is least favoured in soil from the fallowed plots.

Such hysteresis is commonly found in sorption experiments. For example, diffusion-limited processes and strong or irreversible binding are thought to contribute to the hysteresis (Pignatello & Xing, 1996).

A set of possible molecular interactions of MCPA with mineral or organic matter is shown in Figure 3. The binding sites considered consist of either a mineral moiety, which can be regarded as a model for a mineral surface edge, or an organic molecule representing a structural moiety of SOM and MCPA (Figure 3). Both interactions of the neutral (X=H) and ionic forms (X=Mg) of MCPA are included. Interaction energies were estimated using quantum chemical calculations to allow a relative comparison. Interaction energies in the range of –12 to –112 kJ mol⁻¹ were calculated for charge transfer and several hydrogen bond interactions which are likely to occur in sorption of polar molecules (such as MCPA) on organic matter (Dec & Bollag, 1997). The interaction energies obtained are in good agreement with published data, where similar systems were investigated (Leach, 1996; Aquino

et al., 2000; Tunega *et al.*, 2000). While a value of about –12 kJ mol⁻¹ is in the range of weak van der Waals interactions, the other values are typical for polar dipole interactions (Leach, 1996; Kubicki & Apitz, 1999). Electrostatic interactions with silicate, aluminate or organic matter showed distinctly larger interaction energies (up to –329 kJ mol⁻¹). If such electrostatic sites are accessible for MCPA, they are likely to be involved in the sorption of MCPA (McBride, 1989; Cox *et al.*, 1997). Due to the large interaction energy, desorption of molecules bound to such adsorption sites seems less probable (Burgos *et al.*, 1996; Pignatello & Xing, 1996), and sorption of MCPA may be less reversible (within the experimental time span) the more such binding sites are present.

The significantly smaller adsorption–desorption quotients (Table 3) from samples from the fallowed soil in comparison with ones from the other treatments may be partly due to their having more polar and electrostatic binding sites. Since the fallowed soil contains the least organic matter the enhanced contribution of inorganic compounds (Murphy *et al.*, 1990; Celis *et al.*, 1997; Shen, 1999) could be one factor explaining the differences in adsorption–desorption behaviour. However, since other factors, such as changes in entropy, hydration enthalpy or in diffusion processes, are not available from such

simple interaction models, we cannot obtain any quantitative estimates of the contribution of each of the factors to the overall sorption behaviour.

Conclusions

Different farming practices over a long time changed the adsorption–desorption properties of soil for MCPA. The origin of organic matter seems to play an important role in the sorption, which was significantly altered by the different amendments. Sewage sludge had the largest effect. The other treatments were peat amendment, animal manure, green manure, inorganic fertilizers without N, and fallow, in that order. The increased sorption of MCPA on the soil receiving peat and sewage sludge can be related both to an increase in carbon content and to a decrease in pH relative to the other treatments. However, besides the content the origin and characteristics of the soil organic matter seem to be crucial for the sorption behaviour. Adsorption of MCPA was less on the peat-amended soil than on the soil treated with sewage sludge, even though the former contained more organic carbon. Additionally, the fallowed soil, which contains the least organic carbon, adsorbed MCPA similarly to the soil that received green manure and animal manure. Both the different origin of soil organic matter and an increasing role of mineral sorption with decreasing carbon content could contribute to this behaviour.

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