Sorption of Anionic Metsulfuron-Methyl and Cationic Difenzoquat on Peat and Soil As Affected by Copper

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The effect of cationic copper (Cu^{2+}) on the sorption of anionic metsulfuron-methyl (Me) and cationic difenzoquat (DZ) to peat and soil was studied using a batch equilibration method. The results showed that Cu^{2+} increased the sorption of Me but diminished the sorption of DZ. The adsorption of Cu^{2+} on the surface of peat and soil neutralizes the negative charge, making the zeta potential (ζ) of peat and soil less negative, consequently decreasing the repulsion between the surface of peat or soil and Me and increasing the sorption of Me. Cu^{2+} may additionally form Cu–Me complexes in aqueous solution, which was preferentially sorbed to peat and soil over the anionic Me. In contrast, the decreased negative surface charge of soil and peat does not favor the sorption of cationic DZ. Fourier transform infrared showed that DZ may be sorbed through interaction with $-\text{OH}$ or $-\text{COOH}$ groups of peat and soil and that surface complexes of Cu^{2+} may form through these groups. A competitive sorption between Cu^{2+} and DZ for the same sorption sites is indicated, leading to mutual sorption inhibition of both cations.

Introduction

The environmental fate of both heavy metals and organic contaminants in the soil environment is governed by their sorption to soil and sediment, and numerous studies have focused on both the adsorption and desorption of heavy metals (1) and organic contaminants (2) in isolation from each other. However, it is commonly accepted that heavy metals and organic contaminants will in practice coexist as complex mixtures in real contaminated soils (3), such as may

be found in agricultural fields irrigated with wastewater. Currently, there is little detailed information available regarding the effects of heavy metals on the sorption of organic contaminants to soils and vice versa. Xiao et al. (4) observed that heavy metals increased the sorption of phenanthrene and 1,2,4,5-tetrachlorobenzene on bacteria. This was attributed to a mechanism that involved an altered structure of adsorbent being induced by the presence of the heavy metals and cation– π interactions between the heavy metals and the organic contaminants (5). For polar organic compounds, such as phenol, the sorption of phenol to activated sludge was inhibited by nickel or chromium due to competition between the metal and the polar organic compound for the deprotonated functional group binding sites (6, 7). Similarly, copper competed with Propisochlor for the sorption sites of carboxylic and phenolic groups and consequently altered the physical and chemical properties of the humic acids, resulting in a decrease in the sorption of Propisochlor (8). Adsorption of both glyphosate and copper on montmorillonite and soil was decreased when both compounds were simultaneously present, as compared to when glyphosate or copper was present in isolation (9, 10). This was attributed to the formation of a Cu–glyphosate complex that had a lower affinity for montmorillonite than either glyphosate or copper. Similar results were obtained by Arias et al., (11) who indicated that Cu–penconazole complexes had a greater affinity for soil colloids than penconazole itself. Maqueda et al. (12) observed that the cationic pesticide chlormimeform decreased the adsorption of copper on montmorillonite. Undabeytia et al. (13) also found that cadmium suppressed the sorption of chlormimeform. Pateiro-Moure et al. (14) studied the influence of copper on the adsorption and desorption of paraquat, diquat, and difenzoquat on untreated, Cu-enriched, and EDTA-treated soils. Competitive adsorption between copper and the herbicides revealed that copper was only capable of displacing difenzoquat from adsorption sites.

In our previous work, we studied the effect of Cu^{2+} and Pb^{2+} on the sorption of neutral *p*-nitrophenol (15) and 2,4,6-trichlorophenol (16) to peat and soil and showed that Cu^{2+} and Pb^{2+} diminished the sorption of *p*-nitrophenol and 2,4,6-trichlorophenol, but *p*-nitrophenol and 2,4,6-trichlorophenol had little effect on Cu^{2+} and Pb^{2+} adsorption. Several possible mechanisms may be responsible for the observed suppression of organic sorption by Cu^{2+} and Pb^{2+} : (1) Large hydrated metal associated ions may occupy a portion of the soil surface; (2) aggregation of colloidal particles may occur in the presence of Cu^{2+} and Pb^{2+} , and the aggregates may block soil pores; (3) Cu^{2+} and Pb^{2+} may compete with *p*-nitrophenol and 2,4,6-trichlorophenol for the same sorption sites.

The aim of the present work was to study the effect of Cu^{2+} on the sorption of Me and DZ on peat and soil. Anionic Me and cationic DZ were chosen as representative anionic and cationic organic contaminants that are widely used in Chinese agriculture. DZ accumulates readily in soils and Me has a long soil half-life (17) such that residue Me can inhibit the growth of rice seedlings in the growing season after application. Similarly, we chose to study copper as an example of a heavy metal, since it is an essential trace element for both plants and animals and can be accumulated to a very high levels in soils through the land application of fertilizers, sewage sludge, or wastewater irrigation (18). Coexistence of copper and either DZ or Me is common in Chinese soils, but little is known about how they interact with each other, and the presence of such mixed contaminants may affect individual contaminant sorption and their ultimate fate in

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the soil environment. Here, we examine the interactive effects between copper and organic contaminants (DZ or Me) on soil and peat sorption and use FTIR and zeta potential (ζ -potential) analysis to provide an insight to the relevant mechanisms.

Materials and Methods

Materials. Peat and soil were the same adsorbents used previously (16). A black chernozem soil (a clay loam Mollisol) was collected from the surface horizon (0–20 cm) in Heilongjiang Province, northeastern China. Soil was air-dried, ground, and homogenized to pass a 1.0 mm sieve. The peat sample was also collected from the Heilongjiang Province and was dried at 105 °C, ground, and homogenized to pass through a 0.15 mm sieve. Characteristics of peat and soil were determined by the methods of Nelson and Sommers (19) and Sumner and Miller (20), and their properties are listed in Table S1.

The two herbicides, Me and DZ (purity of >98%), were purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI) and have the structures and properties shown in Table S2. $\text{Cu}(\text{NO}_3)_2$, NaNO_3 , NaOH , and HNO_3 were all reagent grade chemicals; methanol was HPLC grade.

Effect of pH on the Sorption of Me and DZ. Me and DZ were dissolved in 0.01 M NaNO_3 solution, to which NaN_3 (0.1 g L^{-1}) was added to suppress the growth of bacteria. A batch sorption equilibration method was performed in triplicate in 50 mL glass centrifuge tubes by mixing soil (1.0 g) or peat (0.1 g) with 0.05 mM Me solution (20 mL). For DZ sorption experiments, only 0.10 g of soil was used due to the high sorption ability for DZ. The concentration of DZ used in this experiment was 0.4 mM. The pH was adjusted from 3.0 to 7.5 for peat and soil by addition of 0.1 M HNO_3 or NaOH . The suspension was then rotated continuously for 24 h at room temperature (23 ± 1 °C) and centrifuged at 1667g for 20 min to separate the liquid and solid phases. The supernatant was subsequently used for HPLC and UV–visible spectrophotometric analyses.

Effect of Cu^{2+} on the Sorption of Me and DZ. Batch equilibration sorption experiments were carried out in triplicate by mixing soil (1.0 g) or peat (0.10 g) with a 0.01 M NaNO_3 solution (20 mL) containing various concentrations of Me (0.005, 0.013, 0.026, 0.052, 0.078, and 0.104 mM) and Cu^{2+} as nitrate (0.1, 0.5, and 2.0 mM) in 50 mL glass centrifuge tubes sealed with Teflon-lined screw caps. As described above for DZ, only 0.10 g of soil or peat was used in the sorption experiments. The initial concentrations of DZ were 0.04, 0.1, 0.2, 0.4, 0.6, and 0.8 mM. The addition of 0.5 mM Cu^{2+} represents a concentration near the Third Environmental Quality Standard for soils (500 mg kg^{-1}) in China assuming all of the Cu^{2+} in solution is adsorbed by the soil. The pH of the adsorbent suspension was adjusted by dropwise addition of 0.1 M HNO_3 or NaOH three times during the equilibration period. The final pH of the solution was 5.0 ± 0.2 after 24 h equilibration. Under such conditions, Me and DZ were present in solution as an anion and cation, respectively. Our previous experiments also indicated that coprecipitation of Me and Cu^{2+} was unlikely at pH 5.0 (data not shown). The suspension was rotated continuously for 24 h at room temperature (23 ± 1 °C) to reach apparent equilibrium. After centrifugation at 1667g for 20 min, the concentrations of Me and DZ in the supernatant were determined by HPLC and UV–visible spectrophotometric analysis, respectively.

Adsorption Isotherms of Cu^{2+} in the Absence or Presence of Me or DZ. Soil (1.0 g for Me and 0.10 g for DZ) and peat (0.10 g) were immersed in a 0.01 M NaNO_3 background electrolyte solution (10 mL) in 50 mL centrifuge tubes and stirred for 4 h, which was equal to the hydration time of peat and soil. After this pre-equilibration step, Cu^{2+} was added together with Me or DZ. Control samples were identical to

other samples, except no Me or DZ was added. The initial concentrations of Cu^{2+} ranged from 0.10 to 4.0 mM, whereas the initial concentrations of Me and DZ were 0.5 and 0.8 mM, respectively. The pH of all sorbent solutions was maintained at 5.0 ± 0.2 by addition of 0.1 M HNO_3 or NaOH during the equilibration period. The final volume of the equilibrium solution was adjusted to 20 mL using background electrolyte. The adsorption equilibration time was 24 h. After reaching equilibrium, the suspension was centrifuged at 1667g for 20 min to separate the liquid and solid phases, and the concentrations of Cu^{2+} in the supernatants was determined by ICP-AES. Adsorption experiments were carried out in triplicate.

Analysis. The concentrations of Me in the equilibrium solutions was determined using a HPLC (Agilent 1100 HPLC) equipped with a diode array detector (DAD) set at 254 nm and an extended polar selectivity reversed-phase C18 column (15 cm $\times$ 4.6 mm i.d.). Isocratic elution was performed at a flow rate of 0.7 mL/min using a methanol/water (80:20, v:v) mobile phase (pH 3.0, adjusted with acetic acid). The concentrations of DZ in the equilibrium solutions were measured using a UV–visible HP 8452 A spectrophotometer at 254 nm ($\epsilon = 21\,100\text{ M}^{-1}\text{ cm}^{-1}$). The concentrations of total Cu in the equilibrium solutions and free Cu^{2+} in the presence and absence of Me were determined by ICP-AES (Plasma Quad3, Manchester, U.K.) and a copper ion selective electrode, respectively. The sorbed Me, DZ, and Cu^{2+} were calculated from the differences between the initial and final equilibrium concentrations. The recoveries of Me and DZ without soil and peat added were >98%, indicating no significant degradation or other loss of organic compounds during the sorption experiment.

Data Analysis. Sorption data were fitted to the Freundlich equation, $Q = K_f C^n$, where Q (mM/g) is the amount of Me or DZ sorbed by the soil or peat, C (mM) is the equilibrium concentration in solution, and K_f and n are empirical constants representing the intercept and the slope of isotherms, respectively.

Zeta Potential (ζ) Measurement. The suspension for ζ -potential measurements was prepared by mixing peat (0.1 g) or soil (1.0 g) with 0.01 M NaNO_3 solution (20 mL) containing different concentrations of Cu^{2+} (0, 0.5, 2.0 mM). The suspension was rotated continuously for 24 h at room temperature (23 ± 1 °C). The solution pH was adjusted to 2–6.5 using 0.1 M HNO_3 or NaOH . The ζ -potentials were determined on the basis of microelectrophoresis measurements on a Zetasizer 2000 (Malvern Instruments, U.K.). The voltage applied to the capillary cell was set at 150 V and the Henry function [$f(\text{Ka})$] of 1.5 was used to directly calculate ζ -potentials. The electrophoretic capillary cell was rinsed three times with 50 mL of deionized water (18 M Ω) before each analysis. Five independent ζ -potential measurements were collected for each sample to ensure accurate and reproducible data.

FTIR Studies. FTIR spectra were obtained on a NEXUS 670 spectrophotometer equipped with deuterated triglycine and mercury–cadmium–telluride detectors, a KBr beam splitter, and a sample bench purged with dry air. The spectral resolution was 2.0 cm^{-1} from collection of 64 scans per spectrum. The sample preparation conditions were the same as described in the sorption experiments. The initial solution concentrations of Me, DZ, or Cu^{2+} were 0.2, 0.8, or 2.0 mM, respectively. For Me, the sorption process was repeated three times due to the lower sorption capacity of Me on peat. The sorbed amounts of Cu^{2+} , Me, and DZ on peat were 0.37, 0.03, and 0.15 mM g^{-1} , respectively. The aqueous suspension containing Me-, DZ-, or Cu^{2+} -sorbed peat was passed through a 0.45 μm hydrophilic polyethersulfone membrane on a Millipore holder. The resulting Me-, DZ-, or Cu^{2+} -peat deposit on the filter was air-dried overnight and removed from the

FIGURE 1. Adsorption isotherms of Me (a, b) and DZ (c, d) on Heilongjiang soil and peat as affected by different concentrations of Cu^{2+} in 0.01 M NaNO_3 solution and by different ionic strength at $\text{pH } 5.0 \pm 0.2$. ($\square$) 0.001 M NaNO_3 ; ($\circ$) 0.01 M NaNO_3 ; ($\triangle$) 0.1 M NaNO_3 ; (∇) 0.1 mM Cu^{2+} ; ($\blacklozenge$) 0.5 mM Cu^{2+} ; (left-pointing triangle) 2.0 mM Cu^{2+} .

TABLE 1. Freundlich Parameters of Me and DZ Sorption onto Soil and Peat ($n = 3$)

Cu^{2+} (mM)	Me			DZ		
	K_f	n	r	K_f	n	r
Soil						
0	0.010	0.764	0.998	4.104	0.460	0.979
0.5	0.012	0.727	0.982	2.953	0.470	0.987
2.0	0.021	0.640	0.993	2.335	0.461	0.981
Peat						
0	0.065	1.008	0.994	7.019	0.423	0.993
0.5	0.222	0.857	0.986	7.145	0.386	0.985
2.0	0.123	0.841	0.997	4.511	0.409	0.991

filter by running the filter and peat deposit over a knife edge. Although air drying aqueous samples may sometimes result in the formation of copper hydroxide and carbonate precipitates, a preliminary comparison between air-dried and freeze-dried peat samples revealed no differences in the FTIR spectra of Me and DZ between sample preparation methods, and therefore, air drying was used for all subsequent FTIR experiments. The FTIR spectra were recorded from pellets obtained by pressing a mixture of peat (1 mg) and dried KBr (100 mg) under pressure.

Results and Discussion

Effect of Cu^{2+} on the Sorption of Me and DZ. Sorption isotherms of Me and DZ on peat and soil in the absence and presence of Cu^{2+} (0.1, 0.5, and 2.0 mM) fit the Freundlich equation well (Figure 1). Sorption of Me increased with increasing Cu^{2+} concentrations, especially at 2.0 mM Cu^{2+} , where the sorption of Me on soil and peat was about 1.4–2.0 times the control (Figure 1a and b). Figure 1c and d shows the sorption isotherms of DZ on peat and soil in the absence and presence of Cu^{2+} (0.1, 0.5, and 2.0 mM). When DZ and Cu^{2+} were sorbed simultaneously, the adsorbed DZ was always lower than when DZ was sorbed alone. When the concentration of Cu^{2+} increased to 2.0 mM, the sorbed amount of 0.5 mM DZ decreased by ~30% for peat and by ~25% for soil. When DZ or Cu^{2+} was previously adsorbed the suppression of DZ sorption by Cu^{2+} was similar to that observed when Cu^{2+} and DZ were simultaneously sorbed (Figure S1). This indicated that Cu^{2+} and DZ competed for

FIGURE 2. Adsorption isotherms of Cu^{2+} on Heilongjiang peat and soil at $\text{pH } 5.0 \pm 0.2$ in the absence and presence of 0.5 mM Me or 0.8 mM DZ.

FIGURE 3. ζ -Potential as a function of pH for Heilongjiang peat and soil: without Cu^{2+} ($\bullet$), with 0.5 mM Cu^{2+} ($\circ$), and 2.0 mM Cu^{2+} ($\triangle$).

the same sorption sites on peat and soil and that the binding affinity of Cu^{2+} or DZ for both adsorbents was similar. The presence of increased Cu^{2+} concentrations resulting in decreased DZ sorption indicated that Cu^{2+} effectively competed with DZ for these same sorption sites and, hence, suppressed the sorption of DZ.

The Freundlich parameters (Table 1) suggest that the sorption isotherm of Me on peat is practically linear ($n = 1.008$), whereas the sorption of Me onto soil is nonlinear ($n = 0.764$). With increasing concentrations of Cu^{2+} , n values for the sorption of Me on both peat and soil gradually decreased. Peat has high organic matter content and is a better adsorbent for Me than soil, consistent with the sorption of ethametsulfuron-methyl on organic matter amended soil (21). The sorption isotherms of DZ on peat and soil are nonlinear, with n values 0.423 and 0.460. Soil has a high clay content and is also an effective adsorbent for DZ, a finding supported by Rytwo et al. (22), who found that the sorption of monovalent cationic DZ was almost complete when the added DZ was less than or equal to the CEC of montmorillonite.

Figure 1 also shows the sorption isotherms of Me and DZ at different ionic strengths (0.001, 0.01, and 0.1 M NaNO_3). The results suggested that ionic strength has little influence on the sorption of Me. In contrast, the increase of ionic strength decreases the sorption of DZ markedly, which indicated that a portion of DZ was sorbed on peat and soil through cation exchange.

The adsorption isotherms of Cu^{2+} with or without Me or DZ are shown in Figure 2. Significantly more Cu^{2+} was adsorbed onto peat than onto soil, mainly because of the high organic matter content and higher cation exchange capacity of peat. Low concentrations of Me (0.05 mM) had little effect on the adsorption of Cu^{2+} on peat and soil (data

FIGURE 4. FTIR spectra of peat, Me, DZ; and Cu^{2+} -, Me-, and DZ-sorbed peat in the range of 3000–3700 cm^{-1} (A); and peat (a), Me-sorbed peat (b), DZ-sorbed peat (c), Me (d), and DZ (f) in the range of 1000–2000 cm^{-1} (B). The sorbed amounts of Cu^{2+} , Me, and DZ on peat were 0.37, 0.03, and 0.15 mM g^{-1} , respectively.

not shown), but 0.5 mM Me decreased the adsorption of Cu^{2+} significantly. DZ (0.8 mM) strongly suppressed the adsorption of Cu^{2+} by $\sim 15\%$ for peat and by $\sim 20\%$ for soil.

Mechanisms of Cu^{2+} Enhancement Effect on the Adsorption of Me. Since Me is a weak acid with a pK_a of 3.3, the electrostatic properties of peat or soil could also affect the sorption of Me. As the solution pH increased, the percentage of Me in anionic forms increased, and the surface potential of peat and soil became more negative. Thus, the repulsion force between anionic Me and the soil (or peat) surface increased, decreasing the sorption of Me (Figure S2 of the Supporting Information).

A number of the possible mechanisms that may be responsible for enhanced adsorption of Me in the presence of Cu^{2+} are discussed below:

(i) Surface complex formation of Cu^{2+} on soil or peat changes the properties of peat and soil, which further affects the sorption of anionic Me on the negatively charged surface of peat and soil. The ζ -potential of peat and soil were measured as a function of pH at different Cu^{2+} concentrations adsorbed (Figure 3). As expected, the ζ -potential was more negative with increasing solution pH for both adsorbents. This is because increasing the pH to greater than the point of zero charge in soil and peat systems increases negative surface charge, that is, the ζ -potential becomes more negative (Figure 3). The surface charge has a marked influence on the sorption of cations and anions from the solution phase. Increasing negative surface charge decreases the adsorption of anionic Me and increases the adsorption of Cu^{2+} . In turn, when Cu^{2+} was adsorbed on soil and peat, the ζ -potential is less negative; thus, more Me was adsorbed on soil and peat.

(ii) Cationic Cu^{2+} and anionic Me are likely to form stable complexes, and these complexes may facilitate the sorption of Me. A copper-ion-selective electrode was used to analyze free Cu^{2+} ion in the equilibrium solution in the absence and presence of Me (Figure S3). The results showed that an

increase in Me concentration in the equilibrium solution resulted in a corresponding decrease in the free Cu^{2+} ion concentration. This was strongly suggestive of the formation of Cu–Me complexes in the equilibrium solution phase. The stronger donor site of Me may be the N atom of the deprotonated sulfonamide group in the ureic bridge, which is an effective target of Cu–Me complexes. Another N atom may be from a triazine ring ortho-N. This finding was supported by Calamai et al. (23), who indicated that Cu^{2+} could coordinate 2N atoms of sulfonylurea herbicide rimsulfuron to form a 6-membered ring chelate, which permitted rimsulfuron to be highly sorbed on smectite. When compared with anionic Me, the Cu–Me complex is less negatively charged, which decreases the repulsive electrostatic forces between Me and the negatively charged peat and soil surface, facilitating the sorption of Me.

To reveal the sorption sites of anionic Me, a FTIR study was performed. Figure 4A shows the FTIR spectra of peat, Me, and Me-sorbed peat in the frequency range of 3000–3700 cm^{-1} . The broad bands at 3407 cm^{-1} are dominated by $-\text{OH}$ or $-\text{COOH}$ stretching vibrations of peat. Me has no absorption at $\sim 3407 \text{ cm}^{-1}$, but it does have several small absorption peaks in the range of 2800–3200 cm^{-1} . When Me was sorbed on peat, the absorption of peat at 3407 was shifted to 3396 cm^{-1} , suggesting the interaction between Me and peat. As shown in the spectra of Me (Figure 4B, d), the bands at 1363 and 1175 cm^{-1} are assigned to an asym- and sym-stretching vibration of $\text{S}=\text{O}$ in a sulfonamide bridge and the two bands at 1728 and 1705 cm^{-1} are attributed to stretching vibrations of two carbonyl groups belonging to the bound ester molecule and to the sulfonamide bridge, respectively (24). When compared with the spectra of Me-sorbed peat (Figure 4B, b-a), the peaks at 1363 and 1175 cm^{-1} , corresponding to the asym- and sym-stretching vibration of $\text{S}=\text{O}$ in a sulfonamide bridge, shift to 1349 and 1170 cm^{-1} , respectively, when Me was sorbed on peat. The shift of carbonyl groups' stretching

vibration was from 1728 and 1705 cm^{-1} to 1735 cm^{-1} . Considering the high electronegativity of the O atom within the S=O or C=O groups and the presence of the H atom from the O–H bond of peat, it was assumed that hydrogen bonding is the most probable reaction mode between Me and peat. This finding was supported by Si et al. (21), who indicated that multifunctional hydrogen bonds between sulfonylurea herbicides and organic matter were the major sorption mechanism.

Mechanisms for Cu^{2+} Suppression of the Adsorption of Cationic DZ. As indicated above, the formation of surface complexes of cupric ions made the surface of both peat and soil less negative (Figure 3), which subsequently has a lower affinity for the sorption of DZ through cation exchange.

It was found that DZ can also interact with neutral sorption sites (–OH or –COOH groups) on peat and soil. Figure 4A shows the FTIR spectra of peat, DZ, and DZ-sorbed peat in the frequency range of 3000–3700 cm^{-1} . As mentioned above, the broad bands at 3407 cm^{-1} are dominated by –OH or –COOH stretching vibrations of peat. DZ has an absorbance at $\sim 3432 \text{ cm}^{-1}$. When DZ was sorbed, the broad peak of peat shifted from 3407 to 3389 cm^{-1} , suggesting –OH and –COOH were responsible for DZ sorption. This result is consistent with Rytwo et al. (25), who studied the adsorption of the divalent organic cationic paraquat, diquat, and methyl green and monovalent cationic methylene blue (MB) on sepiolite. Their results indicated that only adsorbed MB caused a red shift of the Si–OH vibration, suggesting an interaction between MB and neutral Si–OH.

Figure 4B shows the FTIR spectra of DZ in the frequency range of 1000–2000 cm^{-1} , where the absorbance at 1565 and 1487 cm^{-1} is commonly attributed to a stretching vibration of the benzene ring C=C bond, and the peak at 1394 cm^{-1} is attributed to the bending vibration of –CH₃. The band at 1435 cm^{-1} is attributed to the stretching vibration of heterocyclic nitrogen, and the absorption peaks in the range of 1210–1240 cm^{-1} are assigned to the asym-stretching vibration of C–N. When DZ is sorbed onto peat, the absorption peaks of the benzene ring and –CH₃ of DZ exhibited no shift, but the absorption peaks of the asym-stretching vibration of C–N disappeared, and the stretching vibration of heterocyclic nitrogen in DZ shifted from 1435 to 1429 cm^{-1} due to interaction between the –OH or –COOH groups of peat and the heterocyclic nitrogen of DZ.

As shown in Figure 4A, the adsorption of Cu^{2+} shifts the broad peak of peat from 3407 to 3415 cm^{-1} , suggesting –OH and –COOH were responsible for Cu^{2+} adsorption (26). Cu^{2+} is a heavy metal with high electronegativity (1.9) and may form outer- and inner-sphere complexes on the soil surface. When an inner-sphere complex is formed, Cu^{2+} is bound directly to the peat and soil surface, and the surrounded water molecules are partially displaced by –OH groups of soil minerals and organic matter (27) and by –COOH groups of soil organic matter (28). On the basis of the FTIR data of DZ and Cu^{2+} , it appears that competitive sorption between DZ and Cu^{2+} for the same sorption sites is occurring, and this is responsible for the observed mutual suppression of sorption of both DZ and Cu^{2+} .

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Supporting Information Available

The Supporting Information includes data for the properties of peat and soil (Table S1), structures and properties of Me and DZ (Table S2), sorption isotherms of DZ obtained when either DZ or Cu^{2+} had previously been sorbed (Figure S1), the effect of pH on the sorption of Me and DZ (Figure S2), and free Cu^{2+} ion concentrations in solution under different

concentrations of Me (Figure S3). This information is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Strawn, D. G.; Sparks, D. L. The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite. *J. Colloid Interface Sci.* **1999**, *216*, 257–269.
- (2) Sander, M.; Lu, Y. F.; Pignatello, J. J. Conditioning-annealing studies of natural organic matter solids linking irreversible sorption to irreversible structural expansion. *Environ. Sci. Technol.* **2006**, *40*, 170–178.
- (3) National Research Council. *Alternatives for Ground Water Cleanup*; National Academy Press: Washington, DC, 1994.
- (4) Xiao, L.; Qu, X. L.; Zhu, D. Q. Biosorption of nonpolar hydrophobic organic compounds to *Escherichia coli* facilitated by metal and proton surface binding. *Environ. Sci. Technol.* **2007**, *41*, 2750–2755.
- (5) Wang, X. L.; Yang, K.; Tao, S.; Xing, B. S. Sorption of aromatic organic contaminants by biopolymers: effects of pH, copper (II) complexation, and cellulose coating. *Environ. Sci. Technol.* **2007**, *41*, 185–191.
- (6) Aksu, Z.; Akpınar, D. Modelling of simultaneous biosorption of phenol and nickel (II) onto dried aerobic activated sludge. *Sep. Purif. Technol.* **2000**, *21*, 87–99.
- (7) Aksu, Z.; Akpınar, D. Competitive biosorption of phenol and chromium (VI) from binary mixtures onto dried anaerobic activated sludge. *Biochem. Eng. J.* **2001**, *7*, 183–193.
- (8) Xu, Z.; Huang, M.; Gu, Q.; Wang, Y.; Cao, Y.; Du, X.; Xu, D.; Huang, Q.; Li, F. Competitive sorption behavior of copper (II) and herbicide Propisochlor on humic acids. *J. Colloid Interface Sci.* **2005**, *287*, 422–427.
- (9) 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.
- (10) Morillo, E.; Undabeytia, T.; Maqueda, C.; Ramos, A. The effect of dissolved glyphosate upon the sorption of copper by three selected soils. *Chemosphere* **2002**, *47*, 747–752.
- (11) Arias, M.; Paradelo, M.; López, E.; Simal-Gándara, J. Influence of pH and soil copper on adsorption of metalaxyl and penconazole by the surface layer of vineyard soils. *J. Agric. Food Chem.* **2006**, *54*, 8155–8162.
- (12) Maqueda, C.; Undabeytia, T.; Morillo, E. Retention and release of copper on montmorillonite as affected by the presence of a pesticide. *J. Agric. Food Chem.* **1998**, *46*, 1200–1204.
- (13) Undabeytia, T.; Nir, S.; Polubesova, T.; Rytwo, G.; Morillo, E.; Maqueda, C. Adsorption–desorption of chlordimeform on montmorillonite: effect of clay aggregation and competitive adsorption with cadmium. *Environ. Sci. Technol.* **1999**, *33*, 864–869.
- (14) Pateiro-Moure, M.; Pérez-Novo, C.; Arias-Estévez, M.; López-Periago, E.; Martínez-Carballo, E.; Simal-Gándara, J. Influence of copper on the adsorption and desorption of paraquat, diquat, and difenzoquat in vineyard acid soils. *J. Agric. Food Chem.* **2007**, *55*, 6219–6226.
- (15) Pei, Z. G.; Shan, X. Q.; Wen, B.; Zhang, S. Z.; Liu, T.; Xie, Y. N.; Wen, B.; Zhang, S. Z.; Khan, S. U. Sorption of *p*-nitrophenol on two Chinese soils as affected by copper. *Environ. Toxicol. Chem.* **2006**, *25*, 2584–2592.
- (16) Pei, Z. G.; Shan, X. Q.; Wen, B.; Zhang, S. Z.; Liu, T.; Xie, Y. N.; Wen, B.; Zhang, S. Z.; Khan, S. U. Effect of lead on the sorption of 2,4,6-trichlorophenol on soil and peat. *Environ. Pollut.* **2007**, *147*, 764–770.
- (17) Wang, H. Z.; Liu, X. M.; Wu, J. J.; Huang, P. M.; Xu, J. M.; Tang, C. X. Impact of soil moisture on metsulfuron-methyl residues in Chinese paddy soils. *Geoderma* **2007**, *142*, 325–333.
- (18) Muchuweti, M.; Birkett, J. W.; Chinyanga, E.; Zvauya, R.; Scrimshaw, M. D.; Lester, J. N. Heavy metal content of vegetables irrigated with mixture of wastewater and sewage sludge in Zimbabwe: implications for human health. *Agric. Ecosyst. Environ.* **2006**, *112*, 41–48.
- (19) Nelson, D.; Sommers, L. In *Methods of Soil Analysis; Part 3, Chemical Methods*; Soil Science Society Book Series; American Society of Agronomy: Madison, WI, 1996; Vol. 5, pp 961–1010.
- (20) Sumner, M.; Miller, W. In *Methods of Soil Analysis; Part 3, Chemical Methods*; Soil Science Society Book Series; American Society of Agronomy: Madison, WI, 1996; Vol. 5, pp 1201–1230.
- (21) Si, Y. B.; Zhang, J.; Wang, S. Q.; Zhang, L. G.; Zhou, D. M. Influence of organic amendment on the adsorption and leaching of ethametsulfuron-methyl in acidic soils in China. *Geoderma* **2006**, *130*, 66–76.

- (22) Rytwo, G.; Tavasi, M.; Afuta, S.; Nir, S. Adsorption of difenzoquat on montmorillonite: model calculations and increase in hydrophobicity. *Appl. Clay Sci.* **2004**, *24*, 149–157.
- (23) Calamai, L.; Pantani, O.; Pusino, A.; Gessa, C.; Fusi, P. Interaction of rimsulfuron with smectites. *Clays Clay Miner.* **1997**, *45*, 23–27.
- (24) Pantani, O.; Pusino, A.; Calamai, L.; Gessa, C.; Fusi, P. Adsorption and degradation of rimsulfuron on Al hectorite. *J. Agric. Food Chem.* **1996**, *44*, 617–621.
- (25) Rytwo, G.; Tropp, D.; Serban, C. Adsorption of diquat, paraquat and methyl green on sepiolite: experimental results and model calculations. *Appl. Clay Sci.* **2002**, *20*, 273–282.
- (26) Alvarez-Puebla, R. A.; Valenzuela-Calahorra, C.; Garrido, J. J. Retention of Co(II), Ni(II), and Cu(II) on a purified brown humic acid. Modeling and characterization of the sorption process. *Langmuir* **2004**, *20*, 3657–3664.
- (27) Flögeac, K.; Guillon, E.; Aplincourt, M. Surface complexation of copper (II) on soil particles: EPR and XAFS studies. *Environ. Sci. Technol.* **2004**, *38*, 3098–3103.
- (28) Xia, K.; Bleam, W.; Helmke, P. A. Studies of the nature of Cu²⁺ and Pb²⁺ binding sites in soil humic substances using X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **1997**, *61*, 2211–2221.

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