SORPTION OF *p*-NITROPHENOL ON TWO CHINESE SOILS AS AFFECTED BY COPPERZHI-GUO PEI,[†] XIAO-QUAN SHAN,^{*†} TAO LIU,[‡] YA-NING XIE,[‡] BEI WEN,[†] SHUZHEN ZHANG,[†] andSHAHAMAT U. KHAN[§][†]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China[‡]Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China[§]Department of Chemistry and Biochemistry, MSN 3E2, George Mason University, 4400 University Drive, Fairfax, Virginia 22030-4444, USA

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Abstract—Heavy metals and organic contaminants often coexist in soils. However, very little information is available regarding the effect of metals on the sorption of organic contaminants onto soils and/or of organic contaminants on metal sorption. In the present study, the effect of Cu on the sorption of *p*-nitrophenol on two Chinese soils was investigated using a batch-equilibration method for three conditions: Copper and *p*-nitrophenol were sorbed simultaneously, either Cu or *p*-nitrophenol was sorbed previously, or the soil colloidal phase was removed in part previously. The results suggested that Cu suppressed the sorption of *p*-nitrophenol on soils, whereas *p*-nitrophenol had little effect on Cu sorption because of the higher affinity of Cu for soils. Mechanisms of the Cu suppression effect were suggested by the results. First, large hydrated Cu occupy the siloxane surface of soils and prevent nonspecific interaction between *p*-nitrophenol and soils. Second, the soil colloidal phase is an effective adsorbent of *p*-nitrophenol; thus, more *p*-nitrophenol is retained in the aqueous phase. In addition, the aggregation of the colloidal particles may occur, which blocks soil pores, thereby decreasing the sorption of *p*-nitrophenol on the solid soil phase. Third, x-ray absorption spectroscopy revealed that Cu forms inner-sphere complexes with the carboxyl and hydroxyl functional moieties of the soil particles (clay minerals and organic matter). Fourier-transform infrared spectroscopy study indicated that these groups also react with *p*-nitrophenol through H-bond formation. These results suggested that Cu and *p*-nitrophenol have common sorption sites, at least in the soil organic matter domain, which is partially responsible for the observed overall Cu suppression effect.

Keywords—Sorption *p*-Nitrophenol Copper Soil

INTRODUCTION

The fate, mobility, and bioavailability of both organic and inorganic environmental pollutants in soil are affected by sorption process. *p*-Nitrophenol, one of the most widely used organic compounds, poses a potential threat to human health. It occurs in soil as a degradation product of organophosphorous pesticides, such as parathion, and may be bioavailable to crops used for human consumption. The mechanism of adsorption of *p*-nitrophenol by soil presumably involves H-bond formation between the phenolic hydroxyl and the H-bonding sites of soil organic matter and clay surfaces [1]. Zhu et al. [2] as well as Zhu and Chen [3] studied the sorption of *p*-nitrophenol, phenol, and aniline to a synthesized dual-cation and anion-cation organobentonite. Those authors suggested that the sorption of organic compounds to dual-cation organobentonite was dominated by adsorption at low concentrations and by partitioning at high concentrations. Saltzman and Yariv [4] investigated the adsorption of phenol and *p*-nitrophenol by montmorillonite and found that phenol could compete with water molecules to act as a proton donor or acceptor on clay minerals. The tendency for phenol to act as a proton donor was increased in the presence of a nitro group. It also was found that the hydroxyl group of 2,4-dichlorophenol permitted orientational interactions with the sorbent [5]. The high sorption of dinitrophenol by smectite was attributed to site-specific interac-

tions with exchangeable cations and nonspecific Van der Waals interactions with the siloxane surface of clay minerals [6]. The larger size of highly hydrated cations inhibited site-specific adsorption and decreased exposure of the siloxane surfaces for dinitrophenol [6].

Copper is important for most life forms as a micronutrient, but it can be toxic at high concentrations. Copper is retained in soils through exchange and specific adsorption mechanisms. However, Cu also has a high affinity for soluble organic ligands. With increasing Cu concentration, specific sites become saturated, and exchange sites are filled. Copper in a diffusion association or an outer-sphere complex is surrounded by waters of hydration and is not directly bonded to the soil surface [7]. Flogeac et al. [8] observed that Cu adsorbed on soils tends to form inner-sphere complexes, in which Cu is coordinated with hydroxyl functional moieties from soil particles (clay minerals and organic matter).

Several studies have been reported in the literature regarding the adsorption of metals or hydrophobic organic chemicals (HOCs) onto soils. However, under field conditions, both metals and HOCs may coexist. Very little information is available regarding the effect of metal on the adsorption of HOCs onto soils. Similarly, not much is known concerning the effect of HOCs on metal adsorption [9–12]. Analysis of Fourier-transform infrared spectra data indicated that Cu²⁺ diminished the adsorption of propisochlor on humic acids. Xu et al. [12] suggested that Cu competed with propisochlor for the adsorption sites of humic acid. The addition of Cu also may alter the

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physicochemical properties of soils, which may further affect *p*-nitrophenol adsorption. Soil colloidal particles, such as iron and manganese oxides, clay minerals, and dissolved organic matter, form a colloidal phase [13–15]. The colloidal phase has a greater surface area and is capable of retaining the compounds of interest in solution [16]. The adsorption of atrazine and linuron on natural colloids was 10- to 35-fold greater than that on soils and sediments [17]. The colloidal phase enhanced the water solubility of four chlorophenols [18] and facilitated the transport of contaminants [19].

Based on separate studies concerning the adsorption of metals and HOCs, it has been generally believed that metals and HOCs are preferentially adsorbed at different sites. This would indicate that metals and HOCs follow different adsorption mechanisms. The retention of cationic metals by soil is dependent on soil pH, redox potential, surface area, cation-exchange capacity, organic matter content, and carbonate content [7]. Soil organic matter is the principle factor controlling sorption of HOCs. The sorption of HOCs from water to soils containing relatively high amounts of organic matter is attributed primarily to partitioning into the soil organic fraction [20]. Soil organic matter consists of amorphous organic matter and carbonaceous geosorbents. The sorption of HOCs onto amorphous organic matter shows linear and noncompetitive adsorption, and the sorption of HOCs onto the carbonaceous geosorbent shows nonlinear and extensive competitive adsorption [21]. In view of the foregoing, it appears that the adsorption of metal and HOCs onto soil will not interfere with each other. However, to our knowledge, the literature lacks any convincing evidence supporting such speculation.

In the present study, Cu and *p*-nitrophenol were chosen as representatives of metals and HOCs, respectively. We studied the effect of Cu on adsorption of *p*-nitrophenol, and vice versa, under three conditions: Copper and *p*-nitrophenol were sorbed simultaneously, either Cu or *p*-nitrophenol was sorbed previously, or the soil colloidal phase was removed in part previously. To obtain direct evidence for any such effects, a combination of macroscopic description and microspectroscopic studies, including Fourier-transform infrared spectroscopy (FTIR), x-ray absorption near-edge spectroscopy (XANES), and extended x-ray absorption fine-structure spectroscopy (EXAFS), were used. The relevant mechanisms and the role of the colloidal phase on sorption also are discussed.

MATERIALS AND METHODS

Soil characteristics

The soils used in the present study were collected from Yingtan County of Jiangxi Province (southern China) and Keshan County of Heilongjiang Province (northern China). They represent two typical Chinese soils with various physicochemical characteristics (Table 1). Soil samples were air-dried, ground, and screened through a 1-mm, nylon-fiber sieve to remove stones, plant roots, and other large particles and then stored in plastic bags. The soil suspension pH was measured at a soil to water ratio of 1:1 (w/v). Organic carbon content was determined by the Walkley–Black method [22]. The cation-exchange capacity was determined according to the procedure described by Rhoades [23]. The dissolved organic carbon concentrations of soils were measured with a fully automated total organic carbon analyzer (Phoenix 8000; Tekmar-Dohrmann Company, Cincinnati, OH, USA). Amorphous iron, aluminum, and manganese oxides were determined by ammonium oxalate extraction methods [24]. Crystalline iron, alu-

Table 1. Characteristics of Jiangxi soil (Yingtan County, Jiangxi Province, China) and Heilongjiang soils (Keshan County, Heilongjiang Province, China)^a

	Jiangxi soil	Heilongjiang soil
Sand (%)	22.8	9.8
Silt (%)	26.9	62.8
Clay (%)	49.4	27.4
pH	5.3	7.3
CEC (cmol/kg)	14.7	32.7
Organic matter (%)	0.7	6.9
Fe (%)		
Crystalline	1.6	1.4
Amorphous	0.24	0.47
Al (%)		
Crystalline	1.36	1.58
Amorphous	0.27	0.34
Mn (mg/kg)	40.0	326
DOC (mg/kg)	226	891
BET Surface area (m ² /g)	31.7	19.4

^a BET = Brunauer–Emmet–Teller; CEC = cation-exchange capacity; DOC = dissolved organic carbon.

minum, and manganese oxides were determined by the oxalate–ascorbic acid extraction method described by Shuman [25].

Nitrogen-specific surface area and pore characteristics of soils were estimated using an accelerated surface area and porosimetry system (ASAP 2000; Micromeritics Company, Norcross, GA, USA) and applying the Brunauer–Emmet–Teller equation to sorption of N₂ at 77 K.

Reagents

p-Nitrophenol (*p*-NO₂-C₆H₄-OH; purity, 97%) was purchased from Beijing Xingjin Company (Beijing, China) and used as received without further purification. Its solubility in water is 13,700 mg/L at pH 5.0, and its pK_a is 7.15 [26]. The Cu(NO₃)₂·3H₂O, NaNO₃, NaOH, and HNO₃ were of guaranteed reagent grade. Methanol was of high-performance liquid chromatography (HPLC) grade.

Effect of Cu on adsorption of *p*-nitrophenol

p-Nitrophenol was dissolved in 0.01 M NaNO₃ and 0.10 g/L NaNO₃ solution. The batch-equilibration adsorption experiments were carried out in triplicate by mixing 0.40 g of soil with 20 ml of 0.01 M NaNO₃ solution containing various concentrations of *p*-nitrophenol (0.10–3.0 mg/ml) and Cu (0.10, 0.50, and 2.0 mM) in 50-ml glass centrifuge tubes sealed with Teflon®-lined screw caps (Sanhe Company, Haimen, China). The pH of the *p*-nitrophenol–soil suspension was adjusted to 5.0 by addition of 0.1 M HNO₃ or 0.1 M NaOH. The pH of 5.0 (two pH units lower than the pK_a [7.15] of *p*-nitrophenol) was selected so that *p*-nitrophenol was present in neutral form. In all cases, the pH of the equilibrium solutions for simultaneous and successive adsorption was maintained at 5.0 ± 0.2 (mean ± standard deviation throughout). The suspension was rotated continuously for 24 h at room temperature (23 ± 1°C). After centrifugation at 1,667 *g* for 20 min, *p*-nitrophenol and Cu in the supernatant were determined by HPLC and inductively coupled plasma–mass spectrometry (ICP-MS), respectively.

Effect of Cu on adsorption of p-nitrophenol when either p-nitrophenol or Cu was adsorbed previously

The procedure outlined above for simultaneous adsorption of both adsorbates was followed. The only exception was that either Cu or *p*-nitrophenol was adsorbed previously on soil for 24 h, and then the suspension was shaken for another 24 h after the solution containing various concentrations of *p*-nitrophenol or Cu was added.

Adsorption isotherms of Cu, Pb, Cd, and Mg in the absence or presence of p-nitrophenol

Soil (0.40-g portions) was immersed in 10 ml of background electrolyte (0.01 M NaNO₃) solution in 50-ml centrifuge tubes and stirred for 4 h, which was equal to the hydration time of the soil. After this pre-equilibration step, Cu, Pb, Cd, or Mg was added individually in the presence of *p*-nitrophenol. For the control sample, no *p*-nitrophenol was added. The initial concentrations of metals were 0.10 to 4.0 mM, and the initial concentration of *p*-nitrophenol was 2.0 mg/ml. The pH of all sorbate solutions was adjusted to 5.0. The final volume of the equilibrium solution was adjusted to 20 ml. The adsorption equilibration time was 24 h. After reaching equilibrium, the suspension was centrifuged at 1,667 *g* for 20 min to separate the liquid and solid phases, and then Cu, Pb, Cd, and Mg levels in the supernatants were determined by ICP-MS. The adsorption experiments were carried out in triplicate. The adsorption isotherms of the metals in the presence of *p*-nitrophenol were compared with those in the absence of *p*-nitrophenol.

Effect of soil colloidal phase on adsorption of p-nitrophenol

The soil colloidal phase was removed in part by shaking 0.40 g of soil with 20 ml of 0 to 2.0 mM Cu for 24 h. After reaching equilibrium, the suspension was centrifuged at 1,667 *g* for 20 min, the supernatant filtrated through a 0.45- μ m polycarbonate filter, and the concentration of dissolved organic carbon in the filtrate measured with a fully automated total organic carbon analyzer (Phoenix 8000). The soil residue remaining on the filter paper was combined with the soil in the centrifuge tube by rinsing the filter paper with a suitable volume of 0.01 M NaNO₃ solution. The combined soil and colloids were used as a new sorbent for adsorption of *p*-nitrophenol. The amount of electrolyte solution remaining in the solid soil phase and used to rinse the filter paper was calculated gravimetrically and employed to correct the solution phase of the next adsorption experiment. The adsorption of *p*-nitrophenol onto nontreated and treated soils was compared.

Fourier-transform infrared measurements

Infrared spectra were obtained using a NEXUS 670 FTIR spectroscope (Thermo Nicolet Company, Madison, WI, USA) equipped with deuterated triglycine and mercury-cadmium-telluride detectors (Thermo Nicolet Company), a potassium bromide (KBr) beam splitter (Thermo Nicolet Company), and a sample bench purged with dry air. The resolution for FTIR spectroscopy was 2.0 cm⁻¹, and a total of 64 scans were collected for each spectrum. The samples prepared from the soil suspensions were filtered with a 0.45- μ m hydrophilic polyethersulfone membrane and then freeze-dried overnight. The FTIR spectroscopy for pellets of a mixture of 5.0 mg of soil and 100 mg of dried KBr pressed under reduced pressure were recorded.

X-ray absorption measurements and data analyses

The x-ray absorption spectra at Cu K-edges were recorded at a wiggler beamline and EXAFS end station of the Beijing Synchrotron Radiation Facility (China) using a homemade Si(111) double-crystal monochromator. During the experiment, the storage ring was operated at 2.2 GeV, with a beam current of approximately 80 mA. To suppress the unwanted high-order harmonics, the parallelism of the two crystals in the monochromator was adjusted to mistune the incident beam by 30%. The incident beam intensities were monitored and recorded using a nitrogen gas-flow ionization chamber. The fluorescence signals were measured using a Lytle-type fluorescence detector (EXAFS Company, Pioche, NV, USA) with filter (EXAFS Materials, Danville, CA, USA). Absorption data were collected in an energy range from 8,920 to 9,080 eV, covering the K-edge absorption of Cu atoms. Three scans were made and averaged for both the adsorbed soil samples and the chemical standards.

The code WinXAS 2.1 [27] was used for data analysis. The midpoint of the absorption jump was chosen as the energy threshold. The pre-edge absorption background was fitted and subtracted using the Victoreen formula. The postedge absorption backgrounds were fitted using the spline function and subtracted from the absorption spectra. The EXAFS functions were normalized using the absorption edge jump and Fourier-transformed to *R*-space with *k*³-weighting over the range from 2.2 to 8.5 Å. The fit was performed in *k*-space with a model of one shell, where the coordination number (*N*), atomic distance (*R*), energy offset (*E*₀), and Debye-Waller factor (σ^2) were allowed to float freely. Phase shifts and backscattering amplitudes were obtained from the theoretical calculation using FEFF 6.0 [28] and fit with the reference compound, Cu(OH)₂.

Determination of Cu and p-nitrophenol

The concentrations of *p*-nitrophenol were determined by HPLC (Agilent Technologies, Wilmington, CT, USA) with a diode-array detector at the maximum adsorption wavelength of 317 nm and a polar reversed-phase C18 column (length, 15 cm; inner diameter, 4.6 mm). Isocratic elution was performed at a flow rate of 0.7 ml/min using the mobile-phase methanol: water (60:40). Soil plus soil background electrolyte solution without adsorbates were used as a control. Under the HPLC conditions described, *p*-nitrophenol showed a single peak at the retention time of 6.5 min. The concentrations of Cu, Pb, Cd, and Mg were determined by ICP-MS (Plasma Quad3; Fisons Instruments, Manchester, UK). The amounts of *p*-nitrophenol and metals adsorbed were calculated from the differences between the initial and final equilibrium concentrations. The recoveries of *p*-nitrophenol and metals without soil under the experimental conditions described for adsorption were greater than 98%.

RESULTS AND DISCUSSION

Effect of Cu on adsorption of p-nitrophenol

The effect of Cu on the adsorption of *p*-nitrophenol was evaluated when both adsorbates were adsorbed on Heilongjiang and Jiangxi soils simultaneously. The results are shown in Figure 1a and b. The adsorbed amount of *p*-nitrophenol on the two soils decreased with increasing Cu concentration from 0 to 2.0 mM, suggesting that Cu decreased the adsorption of *p*-nitrophenol. For the Jiangxi soil, no adsorption of *p*-nitro-

Fig. 1. Adsorption isotherms of *p*-nitrophenol on Heilongjiang soil (northern China; a, c, and e) and Jiangxi soil (southern China; b, d, and f) when *p*-nitrophenol and Cu were adsorbed simultaneously (a and b) and when *p*-nitrophenol (c and d) or Cu (e and f) was previously adsorbed: 0.40 g of soil and 20 ml of 0.01 M NaNO₃ containing no Cu (■), 0.10 mM Cu (▼), 0.50 mM Cu (●), or 2.0 mM Cu (▲).

phenol was observed when Cu concentration was greater than 0.50 mM. In contrast, Cu had a smaller suppression effect on the adsorption of *p*-nitrophenol on the Heilongjiang soil. Compared with the Heilongjiang soil, the Jiangxi soil adsorbed more *p*-nitrophenol when Cu was absent. As shown in Table 1, Jiangxi soil had greater surface area and clay content, thereby indicating that this soil provided more adsorption sites for *p*-nitrophenol [29]. According to Karickhoff [30], when the ratio of clay minerals to organic matter is sufficiently high (i.e., >10–30), soil clay minerals are considered to be especially important to the adsorption of polar organic compounds.

p-Nitrophenol adsorption isotherms in the presence of Cu can be described by the Freundlich adsorption equation:

$$Q = K_f C^n$$

where Q and C are the soil-phase (mg/g) and liquid-phase (mg/ml) equilibrium concentrations, respectively; n (dimensionless) is a constant of the isotherm curvature; and K_f [(mg/g)/(mg/ml) ^{n}] is the Freundlich adsorption coefficient, an index of the sorption capacity of the soils. The Freundlich adsorption coefficients are listed in Table 2. To determine the Cu remaining in the solid phase, the concentration of Cu in the supernatant solution also was determined simultaneously. However, the adsorbed Cu on the solid-phase soil varied only slightly. Obviously, Cu adsorption was independent of the presence of *p*-nitrophenol.

To determine the effect of Cu on the adsorption of *p*-nitrophenol onto soil that had previously adsorbed *p*-nitrophenol, a series of experiments was conducted. First, the two soils were equilibrated with *p*-nitrophenol for 24 h, and then a certain amount of Cu solution was added to the equilibrated suspension to make the initial Cu concentrations 0.10, 0.50, and 2.0 mM, respectively. The suspension was further equilibrated for an additional 24 h (Fig. 1c and d). The results indicated that the suppression effect of Cu on *p*-nitrophenol adsorption was quite similar to that when both adsorbates were adsorbed simultaneously. Table 2 shows the Freundlich parameters of *p*-nitrophenol adsorption isotherms when *p*-nitrophenol was adsorbed previously on soils. This observation may result from the fact that Cu, with its positive charge, has a stronger adsorption affinity than *p*-nitrophenol for the adsorption sites of the soils. Figure 1e and f shows the adsorption isotherms of *p*-nitrophenol when Cu was previously adsorbed on soils. In this case, Cu had an effect on *p*-nitrophenol adsorption similar to that when the two adsorbates were adsorbed simultaneously. The differences in K_f (Table 2) support these observations.

Effect of *p*-nitrophenol on adsorption of Cu, Pb, Cd, and Mg

Figure 2 shows the adsorption isotherms of Cu, Pb, Cd, and Mg in the absence and presence of 2.0 mg/ml of *p*-nitrophenol. In the absence of *p*-nitrophenol, more Cu, Pb, Cd, and Mg were adsorbed onto the Heilongjiang soil than onto the Jiangxi soil, mainly because of the relatively higher pH, cation-exchange capacity, and organic matter content of the Heilongjiang soil [7]. The adsorption capacity of the four metal cations followed the descending order of Pb ≥ Cu > Cd > Mg. However, the presence of *p*-nitrophenol showed a different effect on the adsorption of metal cations. For metals with a relatively high affinity for soils (e.g., Pb, Cu, and Cd), *p*-nitrophenol had little effect on their adsorption. By contrast, adsorption of Mg

Table 2. Freundlich constants (K_f and n) and correlation coefficients (r) of *p*-nitrophenol sorption onto Jiangxi soil (Yingtian County, Jiangxi Province, China) and Heilongjiang soils (Keshan County, Heilongjiang Province, China; $n = 3$)

Soil	Cu (mM)	K_f^a	n^a	r^a	K_f^b	n^b	r^b	K_f^c	n^c	r^c
Heilongjiang	0	11.5	0.856	0.99	11.5	0.856	0.97	11.5	0.856	0.97
	0.10	7.24	0.722	0.98	4.73	1.05	0.98	6.43	0.684	0.96
	0.50	4.60	0.478	0.95	3.94	0.704	0.96	2.97	0.781	0.98
	2.0	2.94	0.598	0.83	2.15	0.771	0.95	1.13	1.04	0.95
Jiangxi	0	17.4	1.02	0.99	17.4	1.02	0.99	17.1	1.26	0.99
	0.10	8.72	0.360	0.82	3.51	0.823	0.99	6.91	0.632	0.97
	0.50	— ^d	—	—	—	—	—	—	—	—
	2.0	—	—	—	—	—	—	—	—	—

^a Copper and *p*-nitrophenol were adsorbed simultaneously.

^b *p*-Nitrophenol was previously adsorbed.

^c Copper was previously adsorbed.

^d — = near zero.

Fig. 2. Adsorption isotherms of Cu, Pb, Cd, and Mg on (a) Heilongjiang soil (northern China) and (b) Jiangxi soil (southern China): 0.40 g soil and 20 ml 0.01 M NaNO₃ solution containing (■) no *p*-nitrophenol or (●) 2.0 mg/ml of *p*-nitrophenol.

was decreased in the presence of *p*-nitrophenol for both soils, mainly because of the weak electrostatic interaction between Mg and soils.

In view of the foregoing, it may be concluded that Cu had a significant suppression effect on the adsorption of *p*-nitrophenol, whereas *p*-nitrophenol had little effect on the adsorption of Cu. The relevant mechanisms involved in the observed suppression effect by Cu on the adsorption of *p*-nitrophenol are discussed in the following sections.

Possible formation of Cu-*p*-nitrophenol complexes

The maximum ultraviolet-visible absorption intensity for most phenols is at approximately 270 nm, whereas for uncomplexed Cu, it is at approximately 700 nm. For a charge-transfer complex, the precise wavelength of ultraviolet-visible absorption has not been determined, but the maximum intensity of absorption is at approximately 500 nm. To clarify whether Cu and *p*-nitrophenol form Cu-*p*-nitrophenol complexes in soil suspension and whether the complex formation is responsible for the observed apparent suppression effect of Cu, the possible formation of Cu-*p*-nitrophenol complex in the equilibrium solution was studied using the methods developed by Oess et al. [31]. The supernatants, which were separated from the suspension after equilibrium, were scanned from 200 to 800 nm. Our results indicated that no change occurred in the ultraviolet-visible absorption intensity at approximately 500 nm for absorption of *p*-nitrophenol in the

Fig. 3. Adsorption isotherms of *p*-nitrophenol on (a) Heilongjiang soil (northern China) and (b) Jiangxi soil (southern China): 0.40 g soil and 20 ml 0.01 M NaNO₃ solution containing (■) no metal cation, (●) 0.50 mM Mg, (▲) 0.50 mM Cd, (▼) 0.50 mM Pb, or (◆) 0.50 mM Cu.

presence or absence of Cu. Based on these observations, it appears that the formation of Cu-*p*-nitrophenol complexes in the equilibrium solution is unlikely, and that this cannot account for the observed suppression effect of Cu on the adsorption of *p*-nitrophenol.

Effects of different hydrated metal cations on *p*-nitrophenol adsorption

To elucidate the mechanisms of how Cu affects the adsorption of *p*-nitrophenol, several metal cations were chosen as probes to study their effects on the adsorption of *p*-nitrophenol. Figure 3 demonstrates that the nature of the metal cations adsorbed onto the soils had different effects on the adsorption of *p*-nitrophenol. The heavy metals Cu, Pb, and Cd diminished the adsorption of *p*-nitrophenol on soils significantly; Cu exhibited the largest suppression effect and Mg the least. The reasons for this may be because Mg generally is adsorbed on soil through electrostatic attractions and forms an outer-sphere complex [32]. As a result, the weak interaction between Mg and soil surface had an insignificant effect on the adsorption of *p*-nitrophenol. Metals diminished the adsorption of *p*-nitrophenol on soils following the order Cu > Pb > Cd > Mg, and this order is consistent with their electronegativity order: Cu (1.9) > Pb (1.8) > Cd (1.7) > Mg (1.2). The results suggested that the large electronegativity of certain metals tends to easily dissociate H from the functional groups of soil organic matter and water molecules [33]. Furthermore, heavy metals have high hydration enthalpies, with Cu²⁺ having an enthalpy of 2,100 kJmol⁻¹, Cd²⁺ an enthalpy of 1,807 kJ/mol, and Pb²⁺ an enthalpy of 1,481 kJmol⁻¹. Various studies have

suggested that nitroaromatic compounds adsorb primarily at the siloxane surface of minerals exhibiting a permanent negative charge because of isomorphic substitution. This concept is particularly true for soils with high clay content, such as the Jiangxi soil, which has an organic matter content of only 0.7%. For relatively weakly hydrated exchangeable cations (e.g., Mg), the combined size of the cations and associated water molecules did not occupy all the available space, and greater sorption of *p*-nitrophenol occurred. For Cu, with a larger enthalpy of hydration, minimal sorption of *p*-nitrophenol occurred, because the available siloxane surface of soils was small, thus diminishing the adsorption of *p*-nitrophenol through nonspecific van der Waals interactions with the siloxane surface. This speculation is supported by the observations of Johnston et al. [6].

Considering the K_{ow} of 93 for *p*-nitrophenol and 6.9% organic matter content of the Heilongjiang soil, it appears that partitioning of *p*-nitrophenol to organic matter also contributes to the overall sorption in addition to the soil surface adsorption. However, Cu has a high affinity for organic matter and tends to form inner-sphere complexes with soil particles at the siloxane surfaces and with the carboxyl and hydroxyl groups of organic matter; *p*-nitrophenol also can react with these groups through H-bonding [1]. The effect of Cu on sorption of *p*-nitrophenol in this domain will be discussed below.

Effect of soil colloidal phase on the adsorption of *p*-nitrophenol

The changes in soil physicochemical properties as affected by Cu also may be a reason for the observed decrease in the adsorption of *p*-nitrophenol. Figure 4 shows the adsorption isotherms of *p*-nitrophenol onto the Heilongjiang and Jiangxi soils before and after removal of the colloidal phase as described earlier. The adsorbed amount of *p*-nitrophenol on the newly treated Heilongjiang soil with 0 or 0.10 mM Cu was much higher than that on the nontreated soil. However, this difference was relatively small when the Heilongjiang soil was pretreated with 0.50 or 2.0 mM Cu. In contrast, the differences were small in the adsorption of *p*-nitrophenol onto the newly treated and nontreated Jiangxi soil.

We attribute the observed effect of the colloidal phase on the adsorption of *p*-nitrophenol to two aspects. First, pre-equilibration of the soils with Cu partially removed the colloidal phase. Thus, less colloidal phase remained in the equilibrium solution. This resulted in less *p*-nitrophenol in the liquid phase, thereby increasing the adsorbed amount of *p*-nitrophenol onto soil. This is consistent with the observations of Angelo and Reddy [18], who found that the colloidal phase could enhance the water solubility of chlorophenols. Second, the colloidal phase in the solution phase can aggregate in the presence of Cu, thereby altering the physicochemical properties of soils. Table 3 shows the decrease of dissolved organic carbon content in the supernatants with increasing Cu concentrations used in the pretreatment experiments, especially for the Heilongjiang soil [34]. These results suggested that aggregation of soil colloids may occur in the Heilongjiang soil, which might decrease the soil pore size. The average pore sizes of the Heilongjiang and Jiangxi soils were 129.8 and 95.8 Å, respectively, when soil was treated with 0.01 M NaNO₃. When the Heilongjiang and Jiangxi soils were pretreated with 2.0 mM Cu solution, the average pore sizes of the two soils were 66.5 and 98.7 Å, respectively. For the Jiangxi soil, only an insignificant change was observed in the average pore size because of its low col-

Fig. 4. Comparison of adsorption isotherms of *p*-nitrophenol between the (●) nonpretreated Heilongjiang (northern China) and Jiangxi soils (southern China) and (■) pretreated soils with (a) 20 ml of 0.01 NaNO₃, (b) 20 ml of 0.01 NaNO₃ plus 0.10 mM Cu, (c) 20 ml of 0.01 NaNO₃ plus 0.50 mM Cu, or (d) 20 ml of 0.01 NaNO₃ plus 2.0 mM Cu.

loidal-phase content. However, for the Heilongjiang soil, the considerable decrease in the average pore size suggested that the coagulated colloids blocked soil pores. Xing and Pignatello [5] speculated that subnanometer pores of organic matter contributed significantly to the competition and nonlinearity of organic pollutants. If soils have subnanometer pores, the change in their sizes will affect the hole-filling process of *p*-nitrophenol [5]. For the Heilongjiang soil, the adsorbed amount of *p*-nitrophenol on pretreated soil was higher than that on

Table 3. Concentration of dissolved organic carbon (DOC) partially extracted from Jiangxi soil (Yingtan County, Jiangxi Province, China) and Heilongjiang soils (Keshan County, Heilongjiang Province, China) with 20 ml of 0.01 M NaNO₃ containing various concentrations of copper ($n = 3$)

Soils	Concentrations of Cu (mM)	DOC in soil solution (mg/L)
Heilongjiang	0	16.8
	0.10	14.3
	0.50	8.25
	2.0	5.38
Jiangxi	0	4.31
	0.10	4.20
	0.50	4.56
	2.0	2.92

Fig. 5. Fourier-transform infrared spectra: (a) Heilongjiang soil (northern China), (b) Heilongjiang soil plus *p*-nitrophenol, (c) spectrum of **b** minus **a**, and (d) *p*-nitrophenol.

nontreated soil because of a lower colloidal-phase content in the solution of the pretreated soil. With increasing Cu concentrations for the pretreatment, the differences in colloidal-phase content between the pretreated and nontreated soils diminished. Thus, the differences in the adsorption of *p*-nitrophenol between the pretreated and nontreated Heilongjiang soil also were decreased. However, for the Jiangxi soil, the colloidal phase removal had little effect on the adsorption of *p*-nitrophenol because of its low colloidal content. To verify our hypotheses further, a better coagulant Al^{3+} was used. The result is described by a constant distribution coefficient. The equation is expressed as follows:

$$K_d = Q/C$$

where Q and C are the soil-phase (mg/g) and liquid-phase (mg/ml) equilibrium concentrations, respectively. The effect of 2.0 mM Al^{3+} on the *p*-nitrophenol adsorption is reflected by the diminishing K_d values from 10.9 to 6.7 for the Heilongjiang soil. However, compared with Al^{3+} , 2.0 mM Cu^{2+} decreased the K_d values from 10.9 to 3.6. This comparison suggested that the aggregation effect may have been responsible, in part, for the decrease of *p*-nitrophenol adsorption.

Analysis of FTIR spectra

The FTIR spectra of the Heilongjiang soil, soil plus *p*-nitrophenol, and *p*-nitrophenol are shown in Figure 5. Figure 5a is the spectra of the Heilongjiang soil. The band at 1,400 to 1,300 cm^{-1} can be attributed to COO^- antisymmetric stretching, C-O stretching, and O-H deformation. Figure 5b is the spectra of soil with adsorbed *p*-nitrophenol. The weak band at 1,385 cm^{-1} can be attributed to the -OH deformation of *p*-nitrophenol. It is observed at 1,381 cm^{-1} in KBr disks (standard *p*-nitrophenol) and at 1,385 cm^{-1} in the sample of soil plus *p*-nitrophenol. The shift of this peak indicates the presence of H-bonding between *p*-nitrophenol and hydroxyl functional moieties of the soil particles (clay minerals and organic matter) [4]. Because of the presence of soil -OH, much of the spectral information for *p*-nitrophenol, such as the C-O stretching band, is overlaid. Figure 5c shows the spectra of soil plus *p*-nitrophenol when soil is used as a background. When *p*-nitrophenol was adsorbed on soil, the $\nu_{\text{symmetry}}(\text{NO})$ band was shifted from 1,344 cm^{-1} (Fig. 5d) to 1,340 cm^{-1} , suggesting that the O atoms of nitro group can also coordinate with soil surface.

Fig. 6. Normalized x-ray absorption near-edge structure spectra of (a) Cu adsorbed on soil, $\text{Cu}(\text{OH})_2$, CuO , and aqueous $\text{Cu}(\text{NO}_3)_2$; (b) first-derivatives of aqueous $\text{Cu}(\text{NO}_3)_2$ and adsorbed Cu on soil; (c) x-ray absorption fine-structure (EXAFS) spectrum (χ function) of adsorbed Cu on soil; (d) Fourier transformation of the EXAFS spectrum; and (e) first-shell fit of the EXAFS function of adsorbed Cu on soil. Experimental first-shell filtered data in 1.22 to 2.09 Å (dotted line) and best fit (solid curve) modeled as Cu-O contributions. Experimental phase and amplitude functions were extracted from EXAFS spectrum of the $\text{Cu}(\text{OH})_2$ reference compound.

Coordination environment of Cu by x-ray absorption spectroscopy

Figure 6a and b shows the normalized XANES spectra of Cu adsorbed on the Heilongjiang soil and the first derivative spectrum. The adsorption edge has two different inflections, as shown in Figure 6b, with the derivative peaks α at approximately 8,986 eV and β at approximately 8,991 eV. An absorption peak before the edge jump in the pre-edge region arises from $1s \rightarrow 3d$ transitions. This peak is sensitive to the presence of a center of symmetry, and its intensity increases with distortion that removes this center of symmetry, thereby allowing the 3d-4p orbital mixing [35]. The splitting of peaks α and β in the first derivative spectrum with an energy gap of approximately 4.5 eV is shown in Figure 6b. This splitting provides an estimate of the (de)stabilization of the $4p_z$ of Cu because of the asymmetric arrangement of the 4p orbital of Cu and neighboring ligands. This energy derivation is closer to that of Cu in a slightly tetragonally distorted octahedral environment [36]. The β -related peak arises from the transition of $1s$ to $4p_x$ and $4p_y$. The derivation of peak α from peak β is closely associated with the degree of bond covalency and the degree of local structural disorder. In Figure 6b, the diminished α peak in comparison with the β peak suggests that soil particles are sterically hindered because of their three-

dimensional structure. When Cu approaches, it cannot bond in the equatorial plane with the same degree of angular overlap as water [8]. The α peak intensity for aqueous $\text{Cu}(\text{NO}_3)_2$ solution was greater than the β peak. In Figure 6b, the diminished α peak in comparison with the β peak suggests that water molecules associated with Cu are partly replaced by soil particles [36].

The k^3 -weighted $\chi(k)$ spectrum of Cu–soil particles and its corresponding radial structural function, derived from Fourier transformation, are presented in Figure 6c and d. The weighted EXAFS spectrum shows oscillations of approximately equal amplitude across the entire k range as well as the amplified noises at high k . The position of the peaks in the radial structural function is an indication of the atomic distances between Cu(II) and ligands in local coordination shells if the phase shift was modified. The strongest peak, which appears between 1.22 and 2.09 Å in Figure 6d, corresponds to the first Cu–O shell.

The first shell of EXAFS function was fit in k -space, which is shown in Figure 6e. The best fit was obtained by adopting a coordination of Cu–6O, indicating that the Cu(II) ion is present in an octahedral geometry (i.e., four O atoms at the equatorial plane and two O atoms at the vertical axial direction). The average Cu–O_{eq} bond length is 1.98 Å, and the Cu–O_{ax} bond length is equal to 2.38 Å. The data are consistent with those obtained from XANES (i.e., a slightly distorted octahedral coordination around Cu in soil particles). The distortion arises from the Jahn–Teller effect of the Cu–O clusters. It therefore is suggested that Cu is adsorbed on soil through an inner-sphere complex in which the water molecules are partly displaced by carboxyl and hydroxyl groups of siloxane surface and soil organic matter.

CONCLUSION

In view of the foregoing study, it can be concluded that Cu diminished the adsorption of *p*-nitrophenol onto soil. However, *p*-nitrophenol had little effect on the adsorption of Cu because of the strong affinity of Cu for soil. The underlying mechanisms of the diminished adsorption of *p*-nitrophenol as affected by Cu were hypothesized as follows: First, it was suggested that the Cu in a diffuse-ion association or an outer-sphere complex is surrounded by waters of hydration. The hydrated Cu ions associate with exchangeable sites of the siloxane surface of soil minerals, thereby suppressing the sorption of *p*-nitrophenol through the Van der Waals force. Second, the soil colloidal phase has a high capacity for adsorption of Cu and *p*-nitrophenol. Thus, more *p*-nitrophenol was retained in the colloidal phase, and the adsorbed *p*-nitrophenol onto the solid soil phase decreased. With the addition of Cu, the colloidal phase also tends to aggregate on the soil surface, thereby overlaying the adsorption sites of *p*-nitrophenol and/or blocking soil pores, resulting in the decrease of *p*-nitrophenol adsorption onto soil. Third, Cu is retained in soils through exchange and specific adsorption mechanism. Copper has a high affinity for soil organic matter, because it provides sites such as carboxylic, phenolics, alcoholic, enolic–OH, and amino groups. The x-ray absorption spectroscopy revealed that Cu formed inner-sphere complexes with the carboxyl and hydroxyl functional moieties of the soil particles (clay minerals and organic matter). The FTIR study verified that these groups also can react with *p*-nitrophenol through H-bond formation. The results suggested that even partial overlapping of adsorption sites

for Cu and *p*-nitrophenol, especially in the soil organic matter domain, can suppress adsorption of *p*-nitrophenol.

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REFERENCES

- Boyd SA. 1982. Adsorption of substituted phenols by soil. *Soil Sci* 134:337–343.
- Zhu LZ, Chen BL, Shen XY. 2000. Sorption of phenol, *p*-nitrophenol, and aniline to dual-cation organobentonites from water. *Environ Sci Technol* 34:468–475.
- Zhu LZ, Chen BL. 2000. Sorption behavior of *p*-nitrophenol on the interface between anion–cation organobentonite and water. *Environ Sci Technol* 34:2997–3002.
- Saltzman S, Yariv S. 1975. Infrared study of the sorption of phenol and *p*-nitrophenol by montmorillonite. *Soil Sci Soc Am Proc* 39:474–479.
- Xing BS, Pignatello JJ. 1998. Competitive sorption between 1,3-dichlorobenzene or 2,4-dichlorophenol and natural aromatic acids in soil organic matter. *Environ Sci Technol* 32:614–619.
- Johnston CT, Sheng G, Teppen BJ, Boyd SA, De Oliveira MF. 2002. Spectroscopic study of dinitrophenol herbicide sorption on smectite. *Environ Sci Technol* 36:5067–5074.
- McLean JE, Eledsoe BE. 1992. Behavior of metals in soils, Ground Water Issue. EPA/540/S-92/018. U.S. Environmental Protection Agency, Washington, DC.
- Flogeac K, Guillon E, Aplincourt M. 2004. Surface complexation of copper(II) on soil particles: ERP and EAFS studies. *Environ Sci Technol* 38:3098–3103.
- Maqueda C, Undabeytia T, Morillo E. 1998. Retention and release of copper on montmorillonite as affected by the presence of a pesticide. *J Agric Food Chem* 46:1200–1204.
- Morillo E, Undabeytia T, Maqueda C, Ramos A. 2000. Glyphosate adsorption on soils of different characteristics: Influence of copper addition. *Chemosphere* 40:103–107.
- Morillo E, Undabeytia T, Maqueda C, Ramos A. 2002. The effect of dissolved glyphosate upon the sorption of copper by three selected soils. *Chemosphere* 47:747–752.
- Xu ZH, Huang MX, Gu QB, Wang Y, Cao YZ, Du XM, Xu DP, Huang Q, Li FS. 2005. Competitive sorption behavior of copper (II) and herbicide propisochlor on humic acids. *J Colloid Interface Sci* 287:422–427.
- Voice TM, Rice CP, Weber WJ Jr. 1983. Effect of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. *Environ Sci Technol* 17:513–518.
- Gschwend PM, Wu S. 1985. On the constancy of sediment–water partition coefficients of hydrophobic organic pollutants. *Environ Sci Technol* 19:90–96.
- Turner A, Rawling MC. 2002. Sorption of benzo[α]pyrene to sediment contaminated by acid mine drainage: Contrasting particle concentration-dependencies in river water and seawater. *Water Res* 36:2011–2019.
- Higgo JJW, Rees LVC. 1986. Adsorption of actinides by marine sediments: Effect of the sediment/seawater ratio on the measured distribution ratio. *Environ Sci Technol* 20:483–490.
- Means JC, Wijayaratne R. 1982. Role of natural colloids in the transport of hydrophobic pollutants. *Science* 215:968–970.
- Angelo ED, Reddy KR. 2003. Effect of aerobic and anaerobic conditions on chlorophenol sorption in wetland soils. *Soil Sci Soc Am J* 67:787–794.
- Honeyman BD. 1999. Colloidal culprits in contamination. *Nature* 397:23–24.
- Chiou CT, Porter PE, Schmedding DW. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environ Sci Technol* 17:227–231.
- Cornelissen G, Gustafsson O, Bucheli TD, Jonker MTO, Koelmans AA, Van Noort PCM. 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ Sci Technol* 39:6881–6895.
- Nelson DW, Sommers LE. 1982. Total carbon, organic carbon, and organic matter. In Page AL, ed, *Methods of Soil Analysis*,

- 2nd ed, *Part 2. Chemical and Microbiological Properties*. American Society of Agronomy, Madison, WI, pp 539–579.
23. Rhoades JD. 1982. Cation-exchange capacity. In Page AL, eds, *Methods of Soil Analysis*, 2nd ed, *Part 2. Chemical and Microbiological Properties*. American Society of Agronomy, Madison, WI, pp 149–158.
24. McKeague JA, Day JH. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can J Soil Sci* 46:13–22.
25. Shuman LM. 1982. Separating soil iron- and manganese-oxide fractions for microelement analysis. *Soil Sci Soc Am J* 46:1099–1102.
26. Boyd SA, Sheng G, Teppen BJ, Johnston CT. 2001. Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. *Environ Sci Technol* 35:4227–4234.
27. Ressler T. 1997. WinXAS: A new software package not only for the analysis of energy-dispersive XAS data. *Journal de Physique IV* 7:C2:269–270.
28. Zabinsky SI, Rehr JJ, Ankudinov A, Albers RC, Eller MJ. 1995. Multiple-scattering calculations of x-ray absorption spectra. *Phys Rev B* 52:2995–3009.
29. Sheng G, Johnston CT, Teppen BJ, Boyd SA. 2001. Potential contributions of smectite clays and organic matter to pesticide retention in soils. *J Agric Food Chem* 49:2899–2907.
30. Karickhoff SW. 1984. Organic pollutant adsorption in aqueous systems. *Journal of Hydraulic Engineering* 110:707–735.
31. Oess A, Cheshire MV, McPhail DB, Stoll S, Alaili ME, Vedy JC. 1999. Elucidation of phenol–Cu interaction mechanisms by potentiometry, ESR, UV absorption spectroscopy, and molecular simulations. *Sci Total Environ* 228:49–58.
32. Scheidegger AM, Sparks DL. 1996. A critical assessment of sorption–desorption mechanisms at the soil mineral/water interface. *Soil Sci* 161:813–831.
33. Hsu PH. 1989. Aluminum oxides and oxyhydroxides. In Dixon JB, Weed SB, eds, *Minerals in Soil Environments*. Soil Science Society of America, Madison, WI, pp 331–378.
34. Oste LA, Temminghoff EJM, Van Riemsdijk WH. 2002. Solid-solution partitioning of organic matter in soils as influenced by an increase in pH or Ca concentration. *Environ Sci Technol* 36:208–214.
35. Hahn JE, Scott RA, Hodgson KO, Doniach S, Desjardin S, Solomon EI. 1982. Observation of an electric quadrupole transition in the x-ray absorption spectrum of a Cu(II) complex. *Chemical Physics Letters* 88:595–597.
36. Alcacio TE, Hesterberg D, Chou JW, Martin JD, Beauchemin S, Sayers DE. 2001. Molecular scale characteristics of Cu(II) bonding in goethite–humate complexes. *Geochim Cosmochim Acta* 65:1355–1366.