Effects of Copper, Lead, and Cadmium on the Sorption of 2,4,6-Trichlorophenol Onto and Desorption from Wheat Ash and Two Commercial Humic Acids

YU-SHENG WANG, † XIAO-QUAN SHAN,*,† MU-HUA FENG,*,† GUANG-CAI CHEN,†,§ ZHI-GUO PEL,† BEI WEN,† TAO LIU,† YA-NING XIE,*,† AND GARY OWENS†‡

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, PO Box 2871, Beijing 100085, China, State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, 73 East Beijing Road, Nanjing 210008, China, Research Institute of Subtropical Forestry, Chinese Academy of Forestry, Fuyang, Zhejiang 311400, China, Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China, and Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia

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The effects of copper (Cu²⁺), lead (Pb²⁺), and cadmium (Cd²⁺) on the sorption of 2,4,6-trichlorophenol (TCP) to and desorption from wheat ash and two commercial humic acids were studied. Copper and Pb²⁺ diminished the sorption of TCP onto all adsorbents, and made desorption of TCP less hysteretic from ash and German humic acids (GeHA), but more hysteretic from Tianjin humic acids (TJHA). Cadmium had little effect on TCP sorption and desorption. Fourier-transform infra red (FTIR) and X-ray absorption spectroscopy (XAS) in conjunction with fluorescence quenching studies provided insights into the mechanisms of TCP sorption and desorption as affected by Cu²⁺ and Pb²⁺, indicating that complexation of Cu²⁺ and Pb²⁺ was likely via carboxylic, hydroxyl and phenolic groups of ash, TJHA and GeHA, and that these same functional groups also reacted with TCP during sorption. In contrast, Cd, a “soft acid”, had no effect on the adsorption of TCP. Hydration shells of dense water around adsorbed Cu²⁺ and Pb²⁺ ions may also compete with TCP for available surface area. Fluorescence quenching of pyrene verified that for TJHA, Cu²⁺ and Pb²⁺ promoted the formation of supramolecular associations with interior hydrophobic regions separated from aqueous surroundings by exterior hydrophilic layers.

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Introduction

Black carbon (BC) is a byproduct of the incomplete combustion of fossil fuels, biomass, and detrital organic matter (1). Recently the role of BC in soils and sediments has become of interest because of the potential for BC to contribute to the adsorption of neutral organic contaminants (NOCs) more significantly than the well-known contaminant partition with soil/sediment organic matter (SOM). Adsorption of NOCs by BC is nonlinear and generally exceeds absorption by humic acids (HA) by a factor of 10–100 where the BC adsorption domain consists primarily of surface adsorption on BC with some additional solute partition with SOM (2).

While the burning of crop residues in the field is forbidden in many European countries because of detrimental effects on soil structure and soil microorganisms, as well as decreased fertility and an increasing potential for soil erosion it remains a common postharvest practice in many non-European countries. Particulate matter (ash or char) resulting from crop residue burning significantly contributes to the high levels of BC in agricultural soils (3). Wheat and rice ash and ash-amended soils have been previously used for the adsorption of diuron and benzonitrile, where nonlinear adsorption isotherms were observed for wheat and rice ash, suggestive of surface adsorption. For ash-amended soils the adsorption of these two NOCs and the adsorption nonlinearity increased with increasing ash content (4–6). Chars resulting from the pyrolysis of wheat residue between 300 and 600 °C were also used to adsorb benzene and nitrobenzene (7). While NOC sorption by high-temperature chars occurred almost exclusively on the carbonized surfaces, adsorption by low-temperature chars resulted from a combination of surface adsorption and a smaller concurrent partition into the residual organic matter phase (7).

Humic acid (HA) is defined as the alkaline soluble (acid insoluble) fraction of humic substances and is often a considerable component of SOM. The overall properties of HA are the result of interactions of a polydisperse mixture of aliphatic, aromatic, carbohydrate, and amino containing components. Conceptually, these components form dynamic associations stabilized by hydrophobic interactions and hydrogen bonds and these associations are capable of organizing into micellar structures in suitable aqueous environment (8). Like BCs, HAs are also capable of retaining NOCs and heavy metals. However, the exact mechanism responsible for NOC adsorption by HA remains a controversial issue. Recent studies have revealed that aliphatic-rich SOM exhibited high sorption capacities for NOCs (9), which contradicted the mainstream idea that high sorption was principally correlated with the aromatic carbon content of SOM. However, this apparent contradiction can be explained by polarity differences of SOM since a negative relationship was obtained between the sorption capacity for NOCs and the polarity of HA (10). Humic acid has also been fractionated into different molecular size components and the variation of hexafluorobenzene adsorption with different size fractions proved that the interactions of HA and NOCs were not simple partitioning processes (11).

Due to widespread land application of biosolid wastes and fertilizers, as well as extensive irrigation with reclaimed wastewater in semiariad and arid zones NOCs and heavy metals often coexist in soils. To our knowledge there are currently no systematic studies on the effects of metal ions on both the sorption and desorption of NOCs onto and from BC and HA in the literature, with the exception of one which studied the suppression effect of Cu on the sorption of 2,4-
dichlorophenol, 1,2-dichlorobenzene, and naphthalene on wood charcoal (12). No studies have considered the mechanism of the interaction between metals, NOCs, and NOC adsorbents. In this work we selected Cu$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$, as three examples of toxic metals that commonly exist at elevated levels in the contaminated soil environment (13) and TCP as a typical example of an organic contaminant listed as a priority pollutant by the U. S. Environmental Protection Agency. Copper, Pb$^{2+}$, Cd$^{2+}$, and TCP may occur together in contaminated soils, particularly in proximity to wood preservation facilities, where TCP was used as biocides (14). While extensive individual studies on the sorption of either organic contaminants or metals to humic substances have previously been conducted, there is limited information on the mutual effects these two types of contaminants have on sorption (12, 15, 16) or the mechanisms involved.

The specific aims of this study were (i) to examine how Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ affected the sorption of TCP onto and desorption from wheat ash and HA; and (ii) to elucidate the relevant mechanisms using FTIR, $^{13}$C NMR, XAS, and fluorescence quenching studies.

**Experimental Section**

**Materials.** TCP was purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI) with a purity >98%. TCP has a $pK_a$ of 6.15, $log K_{ow}$ of 3.72, and solubility ($S_w$) of 434 mg L$^{-1}$. Heavy metals were used as their reagent grade nitrate salts. Wheat straw ash was obtained and treated using the method of Yang et al. (4). Two commercial humic acids, TJHA (Tianjin Chemical Factory, Tianjin, China), and GeHA (MP Biomedicals Inc., Germany) were purified following the method of the International Humic Substances Society (IHSS) (17).

**Sorption and Desorption Experiments.** Batch methods for adsorption, desorption and corresponding data analysis were described previously (18). Briefly, BC or HA (10 mg) was mixed with 25 mL of TCP solution in 0.01 M NaNO$_3$ as the background electrolyte and 0.1 g L$^{-1}$ Na$_2$S as a biocide. For all sorption experiments, aliquots of supernatant (15 mL) were withdrawn, the same volume of background desorption solution added to replenish the sample, and the suspensions were shaken for an additional one week, centrifuged, and the concentrations of metals and TCP again analyzed. This procedure was repeated through at least three cycles. Adsorption fine structure (EXAFS) spectra of Cu$^{2+}$ adsorbed ash and HA and their reference compounds were measured using the Brunauere-Emmett-Teller (BET) method. All three adsorbents have large BET surface areas. In SI Table S1. All three adsorbents have large BET surface areas. The C content of the adsorbents revealed that ash and TJHA comprised the dominant nonpolar aromatic carbons, while GeHA contained high aliphatic carbon content and more polar functional groups such as carboxyls.

**Characterization.** Ash and HA were subjected to cross-polarization and magic angle spinning (CP-MAS)$^{13}$C NMR analysis with a Bruker Advance 400 MHz NMR spectrometer. Nitrogen specific surface area (SSA) of wheat ash and HA were measured using the Brunauere-Emmett-Teller (BET) equation for sorption of N$_2$ at 77 K. FTIR spectra were obtained using a Perkin-Elmer GX2000 FTIR spectrometer. The X-ray adsorption near-edge structure (XANES) and extended X-ray adsorption fine structure (EXAFS) spectra of Cu$^{2+}$- and Pb$^{2+}$-adsorbed ash and HA and their reference compounds were collected at the Beijing Synchrotron Radiation Facility (BSRF). The details of NMR, FTIR, and XAS characterizations are described in the Supporting Information (SI).

**Fluorescence Quenching Experiment.** As detailed in the SI, the method of Ndou and von Wandruszka (19) was used.

**Results and Discussion**

$^{13}$C NMR Spectra and Elemental Composition of Adsorbents. The $^{13}$C NMR spectra of ash, TJHA, and GeHA are shown in Figure 1. The dominant peak in the spectra of ash at 130 ppm is attributable to natural aromatic carbon, consistent with the NMR spectra of crop derived chars (7), whereas the NMR spectra of GeHA was similar to that of HA isolated from soil (20). Ash and TJHA both have low aliphatic carbon content (0–110 ppm). In contrast, GeHA had a much higher paraffinic carbon (0–50 ppm), methoxyl and other oxygen-substituted aliphatic carbon (50–110 ppm) contents. In the carboxylic carbon region (165–110 ppm), the intensities of the paraffinic carbon of GeHA were higher than that of ash and TJHA. A comparison of the $^{13}$C NMR spectra of the three adsorbents revealed that ash and TJHA comprised the dominant nonpolar aromatic carbons, while GeHA contained high aliphatic carbon content and more polar functional groups such as carboxyls.

The elemental analyses of ash, TJHA, and GeHA are shown in SI Table S1. All three adsorbents have large BET surface areas (especially for ash), high organic carbon (OC), and low H, O, and N contents. The C content of the adsorbents decreases in the order ash > TJHA > GeHA, whereas the H and O contents, H/C and O/C atomic ratios are in the reverse order. Using the ratio of (N + O)/C or O/C as an index of organic matter polarity, the polarity and hydrophilicity followed the order ash < TJHA < GeHA. The H/C, O/C and (N + O)/C atomic ratios of 0.40, and 0.18 of ash are comparable with a H/C of 0.55, and an O/C of 0.29 for crop residue-derived chars prepared under oxygen-limited conditions for 6 h at 300 °C (7). For TJHA and GeHA, the H/C, O/C,
and (N + O)/C ratios ranged from 0.71 to 0.91, 0.40 to 0.62, and 0.40 to 0.64, respectively, and were similar to the ratios for HA isolated from soil (20). Since the molar O/C ratio should partially be an indicator of hydrophilicity, the value of 0.18 for the O/C ratio of ash indicates that ash is hydrophilic and should facilitate the formation of water clusters on the ash surface.

Adsortion Isotherms. Preliminary experiments indicated that sorption of TCP was approximately constant over the pH range 3–5 and decreased above pH 5 as TCP became more ionized (data not shown). Thus in order to prevent TCP from being deprotonated, and Cu$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$ from being hydrolyzed or from participating in the formation of unexpected complexes with TCP, the pH was maintained at 4.5. Moreover, this pH was consistent with the soil pH of red loams in southern China and thus the insights gained regarding TCP adsorption could potentially be applicable to a wide variety of Chinese soils.

The adsorption isotherms of TCP in the absence and presence of Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ were nonlinear (Figure 2). The Freundlich model ($q_p = K_p C^\alpha$), where $K_p$ is the Freundlich affinity coefficient (mg/g)/(mg/L)$^\alpha$), and $N$ is the Freundlich exponential coefficient) fit the experimental data for sorption isotherms well (SI Table S2).

The properties of ash and HA govern the sorption of TCP. The main difference is that the surface area of ash is one magnitude of order higher compared to TJHA and GeHA. Ash also has an increased degree of carbonization, i.e., lower H/C, O/C, (N + O)/C ratios and a much higher sorption capacity for TCP compared to TJHA or GeHA irrespective of the presence of Cu$^{2+}$, Pb$^{2+}$ or Cd$^{2+}$. Surface adsorption is probably the dominant mechanism. GeHA is more aliphatic-rich than TJHA and has a higher adsorption capacity compared to TJHA (Figure 2). This finding was consistent with Simpson et al. (9), but contradicted the hypothesis that low polarity HA would have a higher sorption capacity for TCP onto GeHA suggested that partition may be a more important sorption mechanism. In short, the nonlinear sorption of TCP to TJHA and GeHA suggested that the interactions of HA and TCP cannot be strictly viewed as simple partitioning process (11).

**Effects of Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ on the Sorption of TCP.** The effects of Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ on the adsorption of TCP onto ash, TJHA, and GeHA (Figure 2) indicated that Cu$^{2+}$ and Pb$^{2+}$ decreased the sorption of TCP, whereas Cd$^{2+}$ had little effect on the adsorption of TCP. The suppression effects of Cu$^{2+}$ and Pb$^{2+}$ were generally more pronounced with increasing concentrations of Cu$^{2+}$ and Pb$^{2+}$ (SI Figure S2). Ash and HA are highly effective adsorbents for Cd$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ and TCP (12, 22, 23). In order to elucidate the relevant mechanisms of the suppression effects of Cu$^{2+}$ and Pb$^{2+}$ on the adsorption of TCP, FTIR, and XAS spectroscopic techniques were used to verify whether Cu$^{2+}$ and Pb$^{2+}$ form outer- and/or inner-sphere complexes on the surfaces via carboxylic, carbonyl, and hydroxyl groups and whether both metals and TCP have the same binding sites.

The FTIR spectra of the adsorbents without added TCP (spectra a), TCP alone (spectra b) and TCP adsorbed-adsorbent (spectra c) are shown in Figure 3. In the absence of TCP all three adsorbents had peaks attributable to carboxylate/carbonyl (C=O) stretching at 1707 and 1605 cm$^{-1}$, 1709 and 1605 cm$^{-1}$, and 1712 and 1605 cm$^{-1}$ for ash, TJHA, and GeHA, respectively (spectra a). Additional peaks attributable to phenolic—OH deformations occurred at 1384, 1376, and 1377 cm$^{-1}$ for ash, TJHA, and GeHA, respectively (spectra a), while only ash had a significant peak at 1261 cm$^{-1}$ (spectra a) corresponding to aromatic CO- and phenolic—OH stretchings. The FTIR spectra of TCP alone (spectra b) contained peaks attributable to phenolic—OH deformations (1396 cm$^{-1}$), C=O stretching of the TCP phenyl ring (1475 cm$^{-1}$), O—H bending and deformation vibrations (1319 and 1219 cm$^{-1}$), and C—O stretching (1282 cm$^{-1}$). The main peaks attributable to TCP also appeared in the spectra of TCP adsorbed ash and HA with slight spectral shifts (spectra c), indicating that TCP was successfully adsorbed to those adsorbents. In order to confirm whether TCP was adsorbed onto the adsorbents, difference spectra were obtained by subtracting spectra (a) or (b) from spectra (c), to give spectra (c—a) and (c—b), respectively. The difference spectra indicated that the C—O stretching vibration of TCP shifted from 1282 cm$^{-1}$ in spectra b, to 1276, 1276, and 1274 cm$^{-1}$ in spectra c—a, for TCP adsorbed-ash, -TJHA, and -GeHA, respectively, which was attributable to hydrogen-bonding and indicative of TCP adsorption. The shifts of O—H bending and deformation vibrations from 1319 and 1219 cm$^{-1}$ (spectra b) to 1311 and 1230 cm$^{-1}$ for TCP adsorbed-ash, 1321, and 1226 cm$^{-1}$ for TCP adsorbed-TJHA, and 1315 and 1224 cm$^{-1}$ for TCP adsorbed-GeHA (spectra (c—a)) were also ascribed to the formations of complexes between the hydroxyl group of TCP and the adsorbents. After TCP was adsorbed the peaks

![FIGURE 2. Effects of Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ on the sorption of TCP to wheat ash, TJHA, and GeHA containing (■) no metals, (○) 0.1 mM Cd, (▲) 0.1 mM Cu, and (▼) 0.1 mM Pb (n = 3).](image-url)
at 1605 and 1707 cm\(^{-1}\) for ash, 1605, and 1709 cm\(^{-1}\) for TJHA, and 1605 and 1712 cm\(^{-1}\) for GeHA (spectra a) were shifted to 1588 and 1701 cm\(^{-1}\) for TCP-adsorbed ash, 1597 and 1702 cm\(^{-1}\) for TCP-adsorbed TJHA, and 1592 and 1706 cm\(^{-1}\) for TCP-adsorbed GeHA (spectrum (c–b)), indicating that the carboxyl groups of the adsorbents were participating in the adsorption reaction. A shift from 1261 cm\(^{-1}\) for ash (spectrum a) to 1255 cm\(^{-1}\) (spectrum (c–b)) suggested that the \(-\)OH groups of ash were also participating in the adsorption reaction.

XAS is an alternative technique that can be used to provide information on the metal complexes formed with soil organic matter (SOM) and has previously shown that Cu is mainly adsorbed on SOM via bidentate inner-sphere coordination with carboxyl or amine ligands (24). While numerous XAS studies of Pb adsorption to soil minerals exist (25–27), little information was available on the adsorption of Pb onto SOM. Cadmium formed a variety of complexes being 4-coordinate with thiols, and 4- and 6-coordinate with O/N ligands (28). The speciation of Cu, Pb, and Cd in wheat ash had not been previously studied using XAS and it was therefore of interest to compare the adsorption sites of these metals in wheat ash and humic acids determined using XAS in combination with FTIR to identify whether these metals and TCP shared common adsorption sites. Such comparisons help to elucidate the mechanisms of interactions between Cu, Pb, Cd, and TCP in ash and humic acids.

The coordination environments of Cu\(^{2+}\) and Pb\(^{2+}\) in their adsorbed-ash, -TJHA, and reference complexes (Cu(CH\(_2\)COO)\(_2\), Pb(CH\(_2\)COO)\(_2\), Cu(NO\(_3\))\(_2\), Pb(NO\(_3\))\(_2\), and PbO) are shown in SI Figures S3, S4, and Table S3 (since the XAS spectra of Cu and Pb adsorbed-TJHA and -GeHA are the same only the XAS spectra of adsorbed-TJHA are given). No XAS study was performed for Cd\(^{2+}\) because of energy limitations in the Beijing Synchrotron Radiation Laboratory. Analysis of the XANES and EXAFS data on Cu and Pb adsorbed-ash, -TJHA and -GeHA strongly resembles that of Cu(CH\(_2\)COO)\(_2\) and Pb(CH\(_2\)COO)\(_2\). Copper was coordinated with four equatorial oxygen atoms and two axial oxygen atoms via carboxyl, phenolic and hydroxyl groups. The average Cu–O\(_{eq}\) and average Cu–O\(_{ax}\) bond lengths were 1.96–1.97 Å, and 2.24–2.25 Å, respectively. The decreased intensities of \(\alpha\) peak (SI Figure S3), which is influenced by the degree of bond covalency and local structural disorder (29), and the shorter axial Cu–O bond length in Cu–HA and Cu–ash complexes than that of Cu(CH\(_2\)COO)\(_2\) (SI Table S3), indicated that the adsorbed Cu was present in a disordered geometry of an inner-sphere complex (30). The formation of the inner-sphere complex of Cu through carboxyl, phenolic, and hydroxyl groups leads to smaller, denser, and more rigid molecules or molecular configurations (31, 32). The adsorbed Cu on HA changed its surface functionalities and spatial arrangement of hydrophobic domains, thus decreasing TCP sorption to HA. For Pb, the positions of the RSF (radial structural function) peaks at 1.8 Å indicated that Pb was coordinated to oxygen atoms in all samples; the second RSF peaks at 3.7 Å may be attributed to the coordination of carbon atoms (SI Figure S4) (33). The results indicated that Pb\(^{2+}\) was coordinated with two oxygen atoms via carboxyl, phenolic, and hydroxyl groups, where the average Pb–O bond lengths were 2.38 Å. The shorter Pb–O bond distances for adsorbed Pb compared to Pb\(^{2+}\) (aq) (SI Table S3) are consistent with Pb–O bond distances of inner-sphere complexes (27, 34).

Based on the above FTIR and XAS results, the following mechanisms are most likely responsible for the observed suppression effects of Cu\(^{2+}\) and Pb\(^{2+}\) on the adsorption of TCP. Carboxylic, hydroxyl, and phenolic groups of ash, TJHA, and GeHA may be involved in the reaction between TCP and these adsorbents via hydrogen bond formation. However, complexation of Cu\(^{2+}\) and Pb\(^{2+}\) is also likely through these same functional groups and the bond between these metals and those functional groups is much stronger than the hydrogen bonding between TCP and the adsorbents. Therefore, Cu\(^{2+}\) and Pb\(^{2+}\) potentially suppress adsorption of TCP as the metals out compete TCP for available binding sites. Since the metal–adsorbent complex formation is so strong, TCP had little effect on the adsorption of Cu\(^{2+}\) and Pb\(^{2+}\).

Additionally, hydration shells of dense water surrounding adsorbed Cu\(^{2+}\) and Pb\(^{2+}\) ions may intrude into the adjacent surfaces and compete with TCP for available surface area. It is generally recognized that hydration reactions become more important if hydrated metals and adsorbent micropores have comparable sizes (12). As an example, the micropore and mesopore data for ash (SI Figure S7) indicated that micropores of 2.5–15 Å account for 65.6% of cumulative micropore and mesopore volumes. Micropore distribution patterns (inset of SI Figure S7) indicated micropores of 2.5–5, 5–9.9–15, and 15–20 Å account for 33.4, 1.9, 30.2, and 0.1% of the cumulative micropore and mesopore volumes, respectively. While information on the length of Cu\(^{2+}\)–OH\(_2\) bonds was limited (35), the sizes of hydrated Cu\(^{2+}\) ions on ash surfaces would be 4–5 Å, assuming that they are identical to that of the free ions in water (12). In comparison the calculated molecular diameter of TCP is 7.9 Å (36) and thus, both Cu\(^{2+}\) and TCP may enter the micropores and mesopores. With a fraction of the ash surface occupied by hydrated Cu\(^{2+}\) ions, the sorption of TCP consequently decreased due to the presence of hydrated Cu\(^{2+}\) ions.

Since Cd\(^{2+}\) is a “soft acid” (37), it is less efficient in forming complexes with oxygen-containing groups compared to either Cu\(^{2+}\) or Pb\(^{2+}\) and consequently Cd had little effect on TCP adsorption.

**Effects of Cu\(^{2+}\), Pb\(^{2+}\) and Cd\(^{2+}\) on Desorption of TCP.**

Since desorption behavior can provide additional informa-

![Image](Image 106x622 to 502x757)
tion on sorbate-sorbent interactions, desorption of TCP in the absence and presence of Cu and Pb as function of equilibrium TCP concentrations were examined. The sorption ($N_d$) and desorption ($N_u$) isotherm data for wheat ash, TJHA, and GeHA (SI Figure S5) allows the ratio of $N_d/N_u$ defined as the hysteresis index ($H_I$), to be calculated, where the smaller HI corresponds to the greater degree of hysteresis ($H_I$). In all cases desorption of TCP was hysteretic. Desorption increased from low to high TCP solution concentrations and then decreased at the highest concentration as shown by the $N_u$ values (SI Figure S5). This trend of increasing desorption with increasing TCP concentration can be explained by the limited number of sites available for high energy binding. At low TCP concentrations, a large percentage of TCP binds to the high energy sites, resulting in decreased desorption. At high TCP concentrations, more TCP molecules occupy low energy binding sites which can be more readily desorbed. At the highest concentration, TCP molecules overwhelmed the adsorbent system and caused structural swelling of the adsorbents which led to additional binding sites becoming available and reduced $N_d$ on desorption. Desorption of TCP was more difficult from ash than from TJHA and GeHA in the absence of Cu$^{2+}$ and Pb$^{2+}$, especially at low $C_0$ concentration.

The effects of Cu$^{2+}$ and Pb$^{2+}$ on TCP desorption are complicated. For ash and GeHA, the adsorption of Cu$^{2+}$ and Pb$^{2+}$ increased TCP desorption (compare $N_u$ values in SI Figure S5b and c to that in SI Figure S5a). The $N_d$ values of GeHA were larger than that of ash, indicating that TCP desorption from GeHA was comparatively easy. Lead more effectively increased desorption of TCP from ash and GeHA compared to Cu (see SI Figure S5b and c for ash and GeHA). Since adsorption of Cu and Pb increased desorption of TCP from ash and GeHA, this suggested that Cu and Pb binding to high energy sites was forcing TCP adsorption onto low energy sites and consequently making TCP desorption relatively easy.

However, the effects of adsorbed Cu$^{2+}$ and Pb$^{2+}$ on TCP desorption from TJHA were completely different. When Cu$^{2+}$ and Pb$^{2+}$ were adsorbed on TJHA, TCP desorption decreased. This suggested that, compared to ash and GeHA, different adsorption and desorption mechanisms occur for TJHA. While the major form of carbon in ash is BC and surface adsorption is probably the main adsorption mechanism (4), TJHA is a relatively mature humic substance containing supramolecular associations that may be affected by ionic strength, in which intra- or intermolecular organizations produce interior hydrophobic regions separated from the aqueous surroundings by exterior hydrophilic layers (38) and this allows for fundamentally different desorption interactions. In addition, Cu$^{2+}$ and Pb$^{2+}$ can participate in cross-linking which promotes the formation of supramolecular associations. Thus for TJHA, rather than simple surface adsorptions, TCP was sorbed into interior hydrophobic regions and was consequently more difficult to desorb.

In order to verify the interior hydrophobic nature of supramolecular associations of TJHA, a comparison of fluorescence quenching between ash, GeHA, and TJHA was made (Figure 4). In the absence of any metal and in the presence of ash and GeHA the fluorescence of pyrene decreased with increasing concentrations of KBr. This suggested that pyrene was mainly being adsorbed on the surface of ash and/or mainly took place at the exterior surface of GeHA. However, in the presence of TJHA the fluorescence of pyrene remained almost unchanged when KBr concentrations increased, suggesting that for TJHA hydrophilic exterior regions were potentially shielding hydrophobic interior regions from contact with vicinal water molecules, and since pyrene was believed to participate in partitioning and/or adsorption to interior hydrophobic regions this effectively shielded pyrene from quenching interactions with bromide. As was observed with both ash and GeHA, the fluorescence of pyrene also decreased with increasing TJHA concentrations (Figure 4) which was attributable to the “inner filter effect” that results from the absorption of excitation and fluorescence (39).

The observed decrease in pyrene fluorescence with increasing bromide concentration was not due to any salting out effect since the concentration of a pyrene standard (2.0 $\times$ 10$^{-3}$ M) remained unchanged when the KBr concentrations increased from nil to 0.16 M (SI Figure S6), suggesting that the decreased pyrene fluorescence was attributed to the quenching of pyrene fluorescence rather than to the salting out effect. Application of the Ssetschenow equation (40) also predicted <5% reduction in pyrene solubility due to increased salt content which was significantly less than the observed fluorescence quenching.

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**Supporting Information Available**

Details of the characterization procedures for wheat ash and humic acids and data analyses; desorption of TCP from ash, TJHA and GeHA; quenching of pyrene fluorescence. This material is available free of charges via the Internet at http://pubs.acs.org.

**Literature Cited**


