

Submicron Distribution and Association of Copper and Organic Carbon in A Contaminated Soil Using Scanning Transmission X-ray Microspectroscopy

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Copper (Cu), as one of the typical heavy metals, is frequently concentrated in soils as a result of mining and smelting activities^[1, 2]. Since the mobility and bioavailability of Cu in soils depends greatly on its chemical speciation, molecular-level understanding the distribution and association of Cu with soil components is important for the prediction of Cu fate. Cu was predominantly associated with soil organic carbon (SOC) in contaminated agricultural soils^[3, 4]. Since the heterogeneity of functional C domains of SOC occurred at the sub-micron spatial scale in soils^[5], this probably influence Cu distribution at the similar spatial scales due to the high affinity of Cu to functional C-domains of SOC, such as carboxylic-C, aromatic-C etc^[6, 7]. However, the submicron distribution and association of Cu with various functional C domains of the SOC in contaminated soils has been little reported. Scanning transmission X-ray microspectroscopy (STXM) could probe the distribution of various C-domains of SOC and Cu at submicron spatial scale^[8, 9], which facilitates investigating the association of SOC and Cu in heterogeneous soils. Therefore, the objectives of this study is to characterize the speciation, distribution and association of Cu and functional C-domains of SOC in a contaminated agricultural soil clay fraction using multiple synchrotron-based EXAFS and STXM.

In the Cu K-edge bulk EXAFS spectra (**Figure 1**), the resolved minor shoulder from 5 to 6 Å⁻¹ in the sample spectra was aligned with that of Cu adsorbed on humic acid, indicating the presence of organic Cu species. Karlsson et al., also interpreted this shoulder peak as an indicator of organic Cu species in soils.^[10] Furthermore, LCF results exhibited that the three major Cu species were organic Cu, Cu associated with Fe hydroxide (Cu-Geo) and Cu₂O. Organic Cu, accounting for 62.4% of the total Cu content, was predominant over Cu-Geo (~ 28%) and Cu₂O (~ 10%) in the soil. These results agreed with the dominance of organic Cu species in the agricultural soils using Cu K-edge EXAFS analysis^[3, 4]. Furthermore, STXM results exhibited the heterogeneous distribution of Cu, C and various C functional groups including aromatic-C, aliphatic-C and carboxylic-C at the submicron scale (**Figure 2**). The observed overlapping of hot Cu spots 1 and 2 with C hot spots 3 and 4, respectively, indicated the predominant association of Cu with SOC, in consistent with the bulk Cu EXAFS analysis (Figure 1). Further deconvolution of C speciation revealed SOC at spots 3 and 4 dominated as aromatic-C and carboxylic-C rather than aliphatic-C (spot 5). Generally, aromatic-C enriched SOC fraction could originate from undegradable plant residuals and black carbon^[11]; while aliphatic-C enriched SOM fraction was regarded as microbial origin^[5]. Therefore, Cu was preferentially associated with aromatic-C enriched SOM, which agreed with model systems studies^[7, 12]. This study firstly revealed the contrast roles of different C functional domains of SOC on Cu immobilization in the contaminated soil using EXAFS and STXM analysis, which benefit further application of aromatic-enriched biomaterials in the remediation of contaminated soils by Cu and other heavy metals.

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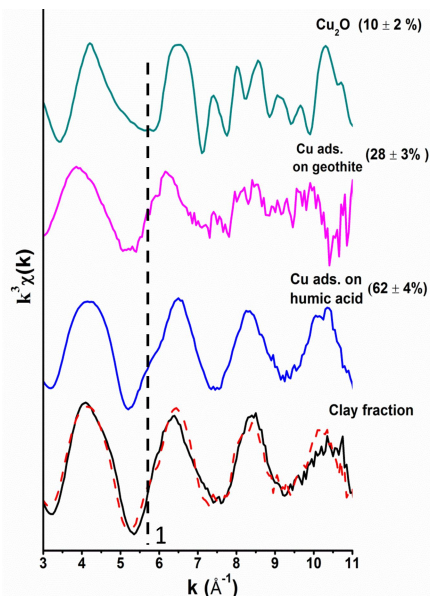


Figure 1. Characterization and quantification of Cu speciation in the clay fraction of the contaminated soil using fingerprint and linear combination fitting analysis. Peak of interested was labeled as 1, the dashed red line is the fitting spectrum and the black solid line is experimental spectrum; the R factor and reduced chi-square for the fitting were 0.1073 and 0.6093, respectively.

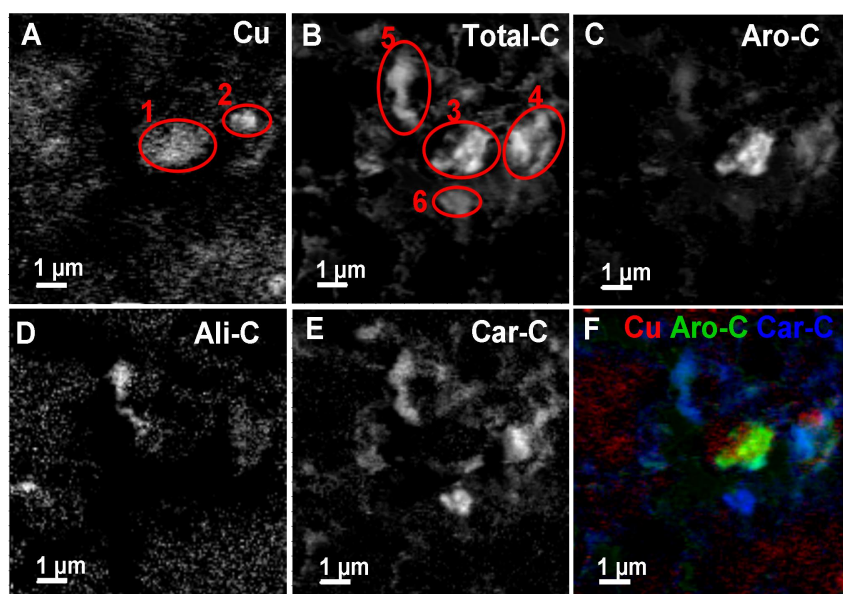


Figure 2 Submicro-scale distribution of Cu and different organic C in the investigated soil clay fraction determined by STXM. A, Total Cu (subtraction of energy region at 926.3 – 927.3 eV from 931 – 932 eV). B, Total carbon (subtraction of energy region at 280 – 282 eV from 290 – 292 eV). C Aromatic-C (Aro-C, subtraction of energy region at 280 – 282 eV from 284.5 – 286 eV). D, Aliphatic-C (Ali-C, subtraction of energy region at 284.5 – 286 eV from 287.3 – 287.8 eV). E, Carboxylic-C (Car-C, subtraction of energy region at 284.5 – 286 eV from 288 – 289 eV). F, Overlapping of Cu, Aro-C and Car-C in the investigated soil clay fraction assemblies. Spots of interested are labeled as 1 to 6.