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XAS analysis of copper binding in soils

Wapakorn SIRIWONG[1,*], Penphitcha AMONPATTARATKIT[2], Wantana KLYSUBUN[2]

[1] *Department of Natural Resources and Environment, Faculty of Agriculture, Natural Resources and Environment, Naresuan University, Phitsanulok Province, 65000, Thailand*
[2] *Synchrotron Light Research Institute,111University Ave., Muang, Naknon Ratchasima,30000, Thailand*

[*]**Corresponding author e-mail:** wapakorna@nu.ac.th

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Abstract

Ecological distribution of copper from soil is depended on its bioavailability and mobility. Copper binding on heterogeneous soil composition is a key information for understanding the long-term fate benefiting suitable management practice for copper in the environment. X-ray absorption spectroscopy (XAS) techniques were used to provide microscopic scale information of copper-binding on different soils. Soil samples containing 14.9-56.6% clay and 0.5-3.4% organic matter were studied. Dry-powder soil samples containing approximated 0.3% copper from batch equilibrated equilibrium experiments were analyzed. Copper K-edge spectrum were collected at the Synchrotron light research institute (SLRI), Thailand in X-ray absorption near edge structure (XANES) and Extended x-ray absorption fine structure (EXAFS) spectrum region. Linear combination fit (LCF) analysis of XANES spectrum resulted the phase fraction of copper were copper acetate (55-79%) and copper sulfate (9-46%) in all soils, while, copper hydroxide (24%) was exhibited in siliceous coarse-texture soil. EXAFS analysis using copper acetated model structure found four oxygen surrounded copper atom at 1.91-1.974 Å in the first shell which positioned in the equatorial plane of a Jahn-Teller distorted octahedral without the existing of weak binding of two axial oxygen atom. Carbon atoms presented in the second shell at 2.73-2.91 Å and its coordination number related to soil organic matter content. XANES and EXAFS studied on copper binding in soils result that the predominant copper in soil is in organic matter complex via carboxyl functional group and sulfated ligand. Copper-C binding occurred in local structure which corresponded to soil organic matter content.

1. Introduction

Soil copper is a naturally occurring trace element needed for many enzymatic functions. Copper content is typical range from 8 to 128 mg·kg^{-1} [1] in tropical whereas an intensive fungicide application in contamination vineyard, soil copper content can reach 1,500 mg/kg [2]. Excess soil copper concentration can be an environmental contamination problem since its toxicity to biological system. Sources of soil copper contamination can be fungicide, phosphate fertilizer, sewage sludge and livestock manures. Ecological distribution of copper from soil is depended on its bioavailability and mobility which controlled by the copper speciation on heterogeneous soil compositions. Evaluation of copper speciation had intensively been studied using sequential extraction procedures including Tessier method [3], Kersrten and Forstner [4] and Modified BCR [5], etc. It concluded that copper is generally a limited mobilized element which mostly bound in crystal lattice, organic and oxide fraction [3,6] The main sinks for soil copper are iron and manganese oxides, organic matter, sulfides and carbonates while clay minerals and phosphates are of lesser significance [7]. Important binding mechanisms are chelating and complexation with organic compounds and nonspecific precipitation [1]. Copper is oxidizable by soil sulfur, however, in soil with low sulfur content copper is usually bound with organic matter [8,9]. Sequential extraction procedures had many developed protocols. The results of different procedures are not always comparable due to the lacking in uniformity, moreover, the artifacts from these techniques had been discussed that could be occurred from the many choices of solvent, different extractant orders, process length and solid/liquid ratio [10]. Also, these techniques provide information about copper sorption on soil-water interface in macroscopic aspect.

X-ray Absorption Spectroscopy (XAS) is a challenging technology using synchrotron radiation that is able to unravel the coordination modes of ions to ligands on a surface of single soil composition and bulk soil sample. Extend X-ray absorption fine structure spectroscopy (EXAFS) is an advanced technique permits structure analysis of metal adsorption on soil constitution. Fit parameters including bond distance, coordination number and type of neighbor elements are applicable in describing the local structure of metal on binding site in microscopic aspect. Several studied have been reported on the binding of copper on soil components.

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EXAFS analysis provided microscopic information that copper in most soils is primary associated either with soil organic matter or organic matter coated onto the mineral fraction of soil particles [11-13]. Similar to copper-humic complex which have been reported to range between 2.76-3.16 Å, the coordination of copper with four oxygen or oxygen/nitrogen atoms at a distance between 1.92-1.95 Å in the first shell and with carbon at 2.74-2.81 Å in the second shell was exhibited in a number samples of soil [12,13], copper is complexed to soil organic matter via bidentate inner- sphere coordination with carboxyl or amine ligand and was held in inner-sphere surface complex in an octahedral coordination first-shell oxygen atom. Copper is chelated in five-membered ring rather than carbonate, oxide bound [11-13]. On clay mineral, EXAFS data from copper- sorbed Ca- and K-vermiculite showed that copper is adsorbing on to the edges of vermiculite rather than interlayer either in inner-sphere or outer-sphere complex. Backscattering of Al, Si or Mg was additionally present in a second-shell at a distance of 3.2 Å [14]. XANES techniques applied to estimate the speciation of Cu (II) with soil solid- phase components found that the surface structure of soil composition and their functional groups are major factor in metal sorption [15]. XANES spectrum is applicable in investigating the local atom coordinate surrounding copper sorbed on soils and clay minerals. Peak and shoulder energies determined from the second derivative show that the position of the second shoulder represents multiple scattering and the geometry of the surrounded ligand. Molecular orbital transition in the first derivative spectrum represents metal complex structure, similar to the first- row transition metals, copper exhibit different pattern between octahedral and tetrahedral structure. Octahedral complex shows a small bump in the pre- edge region due to 1s→ 3d transition just before edge jump, the additional obvious shoulder structure in the middle way to edge due to 1s→4p transition was exhibited for tetrahedral structure of metal complex [16]. Principal Component Analysis (PCA) analysis to define the number of absorbing component in the copper- soil system XANES spectrum and linear combination fit (LCF) use to quantify the species composition by comparing with standard spectrum. From LCF analysis, the main copper compounds were $CuSO_4$ (41%), $CuCl_2$ *(39%), and Cu_2O (19%) in the illegally wire-burnt residue contaminated soil [17].

The association of copper on clay and organic matter rich soil have been continuously reported, the coordination mode of copper adsorption on inert clay and low organic matter soil, the majored colloid in tropical soil, was lacking. The objective of this study is to investigate the copper speciation in 5 copper-spiked tropical soils. Information is critical for understanding the long-term fate and best management practice for copper in the environment.

2. Experimental

2.1 Soil samples

Soil samples of the surface layer (0-15 cm depth) were collected from different types of soils in lower northern Thailand. These soils were chosen according to their geological forming factors, mineral classed and physical-chemical properties. The soils are classified as Endoaquepts (SAR and BAN), Kandiustults (DAS and KRT) and Endoaqualfs (PHN) and the mineral class is [18].

Soil samples were air-dried and ground to pass through a 2-mm sieve before use. Physical and chemical characteristics of soils such as soil organic matter, clay content, pH and total copper content are presented in Table 1. Soil organic matter (%OM) was determined by wet oxidation method using 1 N potassium dichromate [19], clay content (%Clay) was determined by particle size distribution using hydrometer method [20], soil pH was measured at 1:1 soil/water ratio and total copper content (%Cu) was determined by Aqua regia extraction and AAS detection [21]. Soil SAR and BAN is clay-rich soil with relatively high organic matter content and strong acid. DAS is medium textured soil, with relatively low organic matter and very strong acid. PHN and KRT soil are coarse textured soil. Soil texture is sandy loam and soil acidity is extremely acid. Soil organic matter content for KRT and PHN is relatively low and low.

The Copper-sorbed soils were prepared by equilibrating 2 g soil sample with 30 ml of 0.01 M $Ca(NO_3)_2$ solution containing 240 $mg \cdot L^{-1}$ copper in polypropylene tube for 24 h at 25°C. The residual soil mixture was dried in 50°C oven, homogenized and keep in -18°C. Final copper concentration in soil is range from 0.23% to 0.34% (Table 1).

Table 1. Classification physical and chemical characteristics.

Soil sample	Soil classification	Soil texture	Clay (%)	OM (%)	pH	Total Cu (%)
SAR	Endoaquepts	Clay	56.6	3.4	5.0	0.34
BAN	Endoaquepts	Clay	41.8	3.1	5.3	0.34
DAS	Kandiustults	Sandy Clay Loam	20.6	1.4	4.9	0.33
PHN	Endoaqualfs	Sandy Loam	18.6	0.6	4.1	0.33
KRT	Kandiustults	Sandy Loam	14.9	1.3	4.4	0.23

2.1 XAS Spectroscopy

The soil powders were pressed by hydraulic press machine into a mold to disc samples with a 20 mm diameter and mounted on XAS sample holder. The copper *K* edge x-ray absorption spectrum were collected at BL8, Synchrotron Light Research Institute (SLRI), Thailand [22,23]. XANES and EXAFS measurements were carried out in fluorescence mode using a 13-channel array germanium detector in which XANES and EXAFS spectrum were recorded in a photon energy region of 8,879-9,179 eV and 8,779-9,837 eV, respectively. A Ge (220) double crystal monochromator was employed for photon energy scanning, and photon energy calibration was done against the K-edge of Cu foil (8,979±0.3 eV). Spectrum of chemical models of $Cu(OH)_2$, $CuPO_4$, $Cu(NO_3)_2$, $Cu(CH_3COO)_2$, $CuSO_4$ were measured as references.

The collected spectrum were processed using ATHENA software in the following procedures, two scans were aligned and merged, the spectrum were normalized using pre-edge and post-edge background subtraction. The normalized spectrum were transformed to *k*-space and Fourier transform form k-space to *R*-space. ARTEMIS software was employed with EXAFS spectrum to fit theoretical model with experiment data in *R*-space. The validity of the theoretical functions was used as reference compounds of known crystallographic structure as copper acetate ($CuH_6(CO_2)_4$) for Cu-O and Cu-C wave [24] . The determined fitting parameters were amplitude reduction factor (S_0^2), Coordination number (CN), mean-square relative displacement of the atoms included in path (σ^2), energy shift for each path (E_0), and change in the path length distance (ΔR). The Amplitude reduction factor was calculated from chemical models and applied for all fitting at 0.895.

The region of 20 eV below to 80 eV above the absorption edges was isolated for XANES analysis. Linear Combination Fit (LCF) was performed using weighted combination of spectrum from 5 known standards and was done over and energy range of -10 to 50 eV relatively to E_0. All available standard spectrum were included in combination fit in the LCF analyses of each sample. A maximum of three standards was allowed in the fits. The results of the LCF analyses generated models with the best fit indicated by the lowest R-factor and reduced chi square values.

3. Results and discussion

The normalized XANES spectrum of copper in soils presented in Figure 1 and the final LCF combination fit in Figure 2 and Table 2 show copper species found in soil were $Cu(CH_3COO)_2$, $CuSO_4$, and $Cu(OH)_2$. In all soil, $Cu(CH_3COO)_2$ and $CuSO_4$ were the main component contributed 55-80% and 9-46%, respectively. The phase fraction of copper acetate was varied by soil organic matter which was higher in soil containing organic matter content more than 1% as SAR, BAN, DAS and KRT, but the phase fraction was lesser than 55% in extremely low organic matter PHN soil. The phase fraction of copper sulfate in soils was unproportioned corresponded with clay and organic matter content. Copper hydroxide was a significant chemical component (24%) in siliceous sandy KRT soil.

$Cu(CH_3COO)_2$ was the main component of copper sorbed in soil samples and corresponded to soil organic matter content (%OM) indicated that cooper binding site for copper in soil preferentially to carboxylic moiety of organic matter rather than phenols, thiols and amines functional groups. A significant fraction of $CuSO_4$ was existed in all soil samples indicated sulfate ligand involved in the sorption of copper on soil organic matter. Xia *et al.* (1998) insisted that sulfate is the greatest fraction of organic sulfur over thiol, thiophenic, sulfoxide, sulfonic and sulfonate in arable mineral soil mineralization [25]. Additionally, the proportion of Cu-S in cysteine increased as sulfur fertilizer increased in the rhizosphere [26]. Even sulfur existed in relatively low concentration compared to oxygen and carbon, functional group containing sulfur in organic matter may play disproportionate role in copper complexation. Minor fraction of copper hydroxide (24%) existed only in KRT, a siliceous sand-rich soil of relatively poor adsorptive surface component soil. XANES spectroscopy suggested that Cu-OM complexes are the predominant species (over 90%) of copper in soils [13]. This study result was in agreement with sorption of Cu(II) in wire-burnt residue contaminated area, the least-square fitting of the XANES spectrum revealed that $CuSO_4$ and $Cu(OH)_2$ were the main copper compounds at 41% and 46% in contaminated soil and downstream soil, respectively [17].

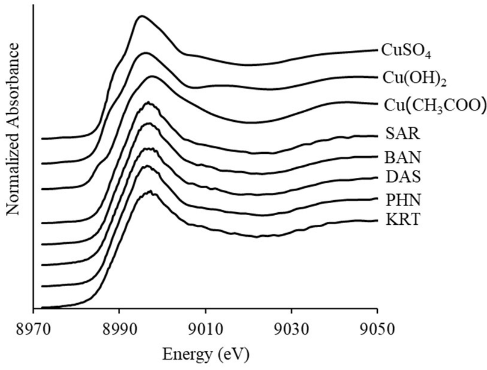

Figure 1. Normalized XANES spectrum (stacked plot) of copper standard Materials and copper sorbed on soils.

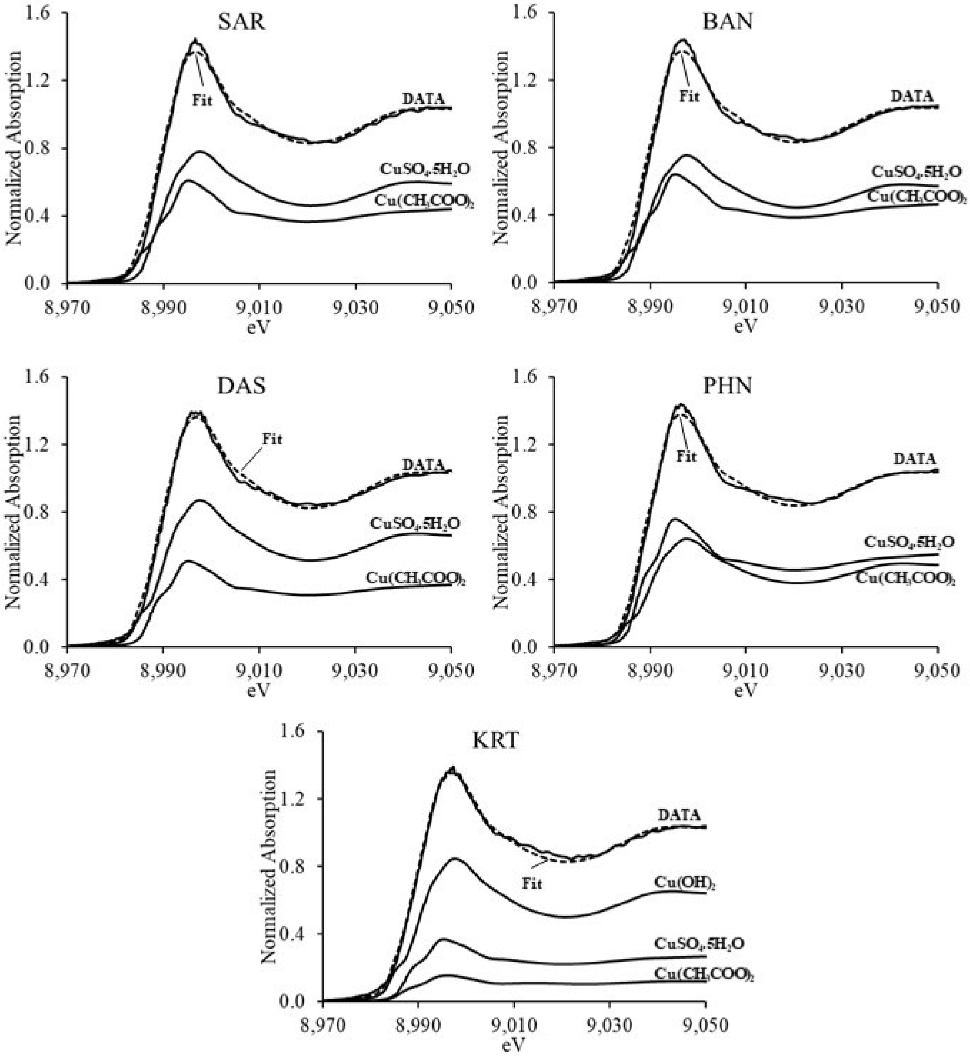

Figure 2. Linear combination fit of XANES spectrum of chemical copper standard chemicals and copper sorbed on soils.

Table 2. Phase fraction of copper compounds presented of the linear combination in selected copper standard materials and copper sorbed soils.

Soil Sample	Phase fraction of copper compounds, %			R-factor
	$Cu(CH_3COO)$	$CuSO_4.5H_2O$	$Cu(OH)_2$	
SAR	64.8±2.9	35.2±5.0	±	0.003772
BAN	79.3±3.6	20.7±9.6	±	0.006204
DAS	69.9±2.5	30.1±4.3	±	0.002811
PHN	55.0±2.6	45.5±4.5	±	0.002915
KRT	67.1±2.6	8.8±2.8	0.24±0.06	0.001788

The experimental EXAFS Spectrum of copper adsorption on 5 soil samples are presented in Figure 3 (a). The spectrum produced from weighting factor oscillate at equal amplitude across the entire k-space range. The radial structure function (RSF) derived from Fourier transform of EXAFS for Copper adsorption on 5 soils samples are presented in Figure 3 (b). The distances on the radial structure axis are not corrected for phase shift. The peaks positions corresponded to relative distance between Cu(II) and neighbored atoms in local coordination shell. The strongest peak without phase correction for all soil samples appeared between 1.38-1.52 Å and a small peak at 2.5 Å. The final fitting results in *k*-space (Table 3) show that the first coordination shell atoms fit with 3.62-4.02 oxygen atoms at a distance about 1.91-1.974 Å for all soil samples. The second coordination shells fit to 0.73-1.99 Carbon atoms at 2.73-2.91 Å in SRB, BAN and DAS soils, additionally, with four carbon atoms at 2.86 and 2.85 Å in SAR and BAN soil.

The bond length of Cu-O corresponded with copper bound on soil composition as expandable aluminosilicate clay, hydrous oxide and humus surface [11,14,27,28]. The four coordination number of oxygen in the first shell indicates that copper is most likely positioned in the equatorial plane of a Jahn-Teller distorted octahedral [11,14,27,28]. The more 2 axial oxygen of the octahedron were not significantly contributed to the EXAFS spectrum, although a small peak at 2.5 Å was existed, since an axial oxygen form weak bonds with copper atom that giving rise to higher thermal disorder [29]. The first shell oxygen atom possibly from an acidic functional group of organic colloid, a surface ligand of layered and amorphous clay and precipitated salts. Existing of Cu-C scattering in SAR, BAN and DAS soil was correlated to colloidal particle, clay and organic matter, in soil. Despite the remarkable $CuSO_4$ found in LCF of XANES, S backscatter was not explicated in EXAFS signals accounted by the closed bond distance of Cu-S and Cu-O [13]. The result insisted that organic matter is a significant site for copper binding in soil. Similar structure fit parameter was found with copper binding in soil humic substance [16]. At an equal distance, Cu-N may contribute to EXAFS signals that difficult to differentiate from Cu-O. However, Xia *et al.* [16] anticipated that the first shell atom of soil copper was the primary oxygen atom from acidic functional ligand of humic substance rather than nitrogen.

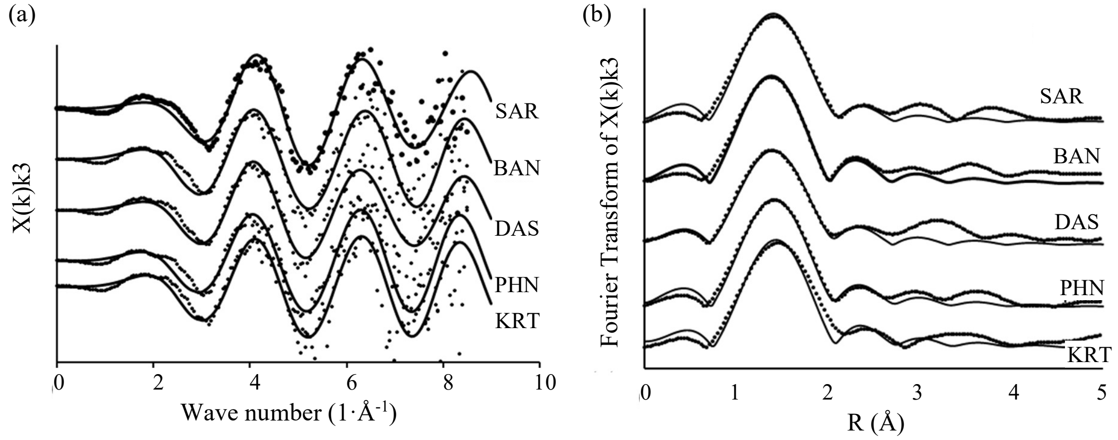

Figure 3. EXAFS and fourier transform of EXAFS for copper sorbed on 5 soils samples. Solid and dotted lines represented data and fitted models.

Table 3. Final fits to EXAFS data in *k*-space for copper sorbed in 5 soil samples.

Sample name	Shell	Shell	ΔE (eV)	N	R (Å)	σ^2	R-factor
SB	1	Cu-O	-6.06±2.44	4.02±0.17	1.91±0.02	0.005±0.001	0.0081
	2	Cu-C		1.99±0.50	2.91±0.05	0.004±0.003	
BAN	1	Cu-O	-4.71±2.39	3.98±0.15	1.91±0.02	0.005±0.001	0.0007
	2	Cu-C		0.73±0.71	2.73±0.09	0.010±0.012	
DS	1	Cu-O	-3.94±3.76	3.98±0.22	1.93±0.03	0.006±0.001	0.0143
	2	Cu-C		1.00±0.56	2.91±0.13	0.003±0.008	
PH	1	CuO	-3.44±1.77	3.65±0.61	1.97±0.01	0.003±0.002	0.005
KT	1	CuO	-1.11±3.46	3.62±1.14	1.94±0.03	0.003±0.005	0.030

4. Conclusions

X-ray Absorption Spectroscopy provided microscopic scale information on copper binding onto 5 different soils. Linear combination fit analysis of XANES spectrum revealed that the main species of copper were copper acetate (55-79%) and copper sulfate (9-46%) in all soils, while, copper hydroxide was additional existed (24%) in siliceous coarse-texture soil. Predominant fraction of $Cu(CH_3COO)_2$ and $CuSO_4$ compound in LCF insisted that carboxyl functional group and sulfated ligand were the significant biding mechanism for copper on soil organic matter. EXAFS analysis using copper acetated model structure found four oxygen surrounded copper atom in the first shell which positioned in the equatorial plane of a Jahn-Teller distorted octahedral without the existing of weak binding of two axial oxygen atom. Carbon atoms presented in the second shell and its coordination number related to soil organic matter content. In conclusion, XAS technique is applicable technique in the determination of the mechanisms and speciation of copper binding in soil. However, to characterized completed fractionation for copper bioavailability estimation in different heterogeneous soil composition, the local structure of element bond to copper in longer distance should be investigated in minimum noise spectrum.

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