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Speciation of Zinc Metal in Paddy Soils by Chemical Sequential Extraction and Synchrotron X-ray Spectroscopy

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A severely zinc-contaminated paddy soils were collected and analyzed by the chemical sequential extraction and synchrotron X-ray spectroscopy. Results show that Zn, Pb and Cu were the major heavy metals in paddy soils. The carbonates and Fe-Mn oxide fractions were the main form for Zn whereas a considerable residual fraction was detected for Pb. In addition to Zn-O, many bonding structures between zinc and other metals were also examined. The possible species of zinc would be Zn-Al(Si) with a bonding distance of 2.18 Å and a Zn-Fe structure with a bonding distance of 3.07 Å.

Key Words: Paddy soils, Chemical sequential extraction, Synchrotron X-ray spectroscopy.

INTRODUCTION

Paddy soils are one of the important economic media for cereal growth in Taiwan. Unlike other soils, the paddy soils can not be considered natural because they have been highly modified by management practices such as leveling, cultivation, puddling, submerging and fertilizers and pesticides use might introduce toxic heavy metal into soils[1]. Zinc is an essential nutrient and often deficient for plants and soils[2]. The Zn contents in agricultural soils is usually higher than other heavy metals because of the addition of fertilizers, liming materials or manures[3]. Zinc can accumulate in agricultural soils, achieving values considerably higher than its optimum concentration as a nutrient and it may be toxic to soil organisms[2]. In addition to total content analysis, chemical sequential extraction procedures are commonly applied to determine the chemical form of metal. Most of the chemical sequential extraction procedures include a number of stages between three and eight[4-8]. In our previous study, a series of spectroscopic experiments such as Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were carried out to investigate the speciation of zinc in the contaminated soils[9]. For detailed structure, the bond distance and coordination number can be determined through an extended X-ray absorption fine structural spectroscopy (EXAFS). Combined EXAFS, chemical sequential extraction procedures and our previous study, basic information regarding chemical state, interaction, valence status, bonding distance and coordination number would be thoroughly obtained. In the current study, the chemical sequential extraction technique was used to determine the distribution of zinc in the contaminated paddy soils and understood the fine structure of zinc using synchrotron X-ray spectroscopy. The study will provide to chemical and environmental scientists which remediation technology will be the optimal choice to treat heavy metal contaminated paddy soils according to the bonding structure of heavy metal in the contaminated soils.

EXPERIMENTAL

Paddy soils sampling: The paddy soils were collected from the one of severe contaminated sites recognized by the environmental protection administration, Taiwan. The paddy soils were sampled at a depth of 0 to 15 cm from a site that is near metallurgical factories around the side of Erh-Jen River in southern Taiwan. The samples were dried at ambient temperature for a week and ground with an agate mortar and sieved to pass through a 2-mm sieve.

Soil physical and chemical properties: Several soil physical and chemical properties including particle size distribution, pH value, organic matter, electrical conductivity cation exchange capacity and total nitrogen, phosphorous and potassium were determined. The detailed methods for which were described in our previous study[9]. The basic chemical and physical property of the paddy soils is given in Table-1.

TABLE-1
BASIC CHEMICAL AND PHYSICAL PROPERTIES OF PADDY SOILS

Soil properties	Studied area
Sand (%)	53
Silt (%)	19
Clay (%)	28
Texture	Sandy clay laom
pH (1:1 with H_2O)	7.6
Organic matter (%)	1.9
EC (μS cm^{-1})	237
CEC (cmol kg^{-1})	4.4
Total N (%)	0.13
Total P (mg kg^{-1})	2815
Total K (%)	1.7

Chemical sequential extraction procedure: A five-step chemical sequential extraction was carried out. The chemical sequential extraction procedures was closely adopted followed the scheme proposed by Tessier[10]. The five fractions could be consisted of: (i) exchangeable form (ii) carbonates form (weakly adsorbed) under slightly acidic conditions (iii) Fe-Mn oxides form (iv) organic matter and metals associated with easily oxidizable solids or compounds (v) residual and strongly held complexes. The detailed extraction procedure for the five fractions is described by Chen *et al.*[11].

Synchrotron X-ray spectroscopy: Zn K-edge (9659 eV) EXAFS spectra were undertaken on the Wiggler beam-line at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan. The electron storage ring operated at the energy of 1.3 GeV and the beam current varied (current of 80-200 mA). A Si(111) double-crystal monochromator (DCM) was used for providing highly monochromatized photo beams with energies 1-9 KeV.

RESULTS AND DISCUSSION

Total content of heavy metals and background value for the paddy soils in different depths were collected and analyzed (Table-2). It is noted that Zn, Cu and Pb are the major heavy metals in paddy soils. The contents of other heavy metals such as Cr, Cd, Ni and Co are much lower than Zn, Cu and Pb. The mean contents of Cr, Co and Ni were 10, 2 and 22 mg/kg, respectively and no Cd was detected in paddy soils. The Zn content is much higher than any other heavy metals. The highest content 10, 234 mg/kg was detected in the 0-15 cm of paddy soils, implying this site was contaminated by Zn metal. The contents of heavy metals are decreased with soil depth. Although Zn content is about 1600 mg/kg, this value is acceptable according to the regulation limit proposed by EPA. To understand the distribution of Zn, a five-step chemical sequential extraction procedures was carried out and results are shown in Fig. 1. Most of Zn was found in the carbonate and Fe-Mn fractions and residual fraction was the main form

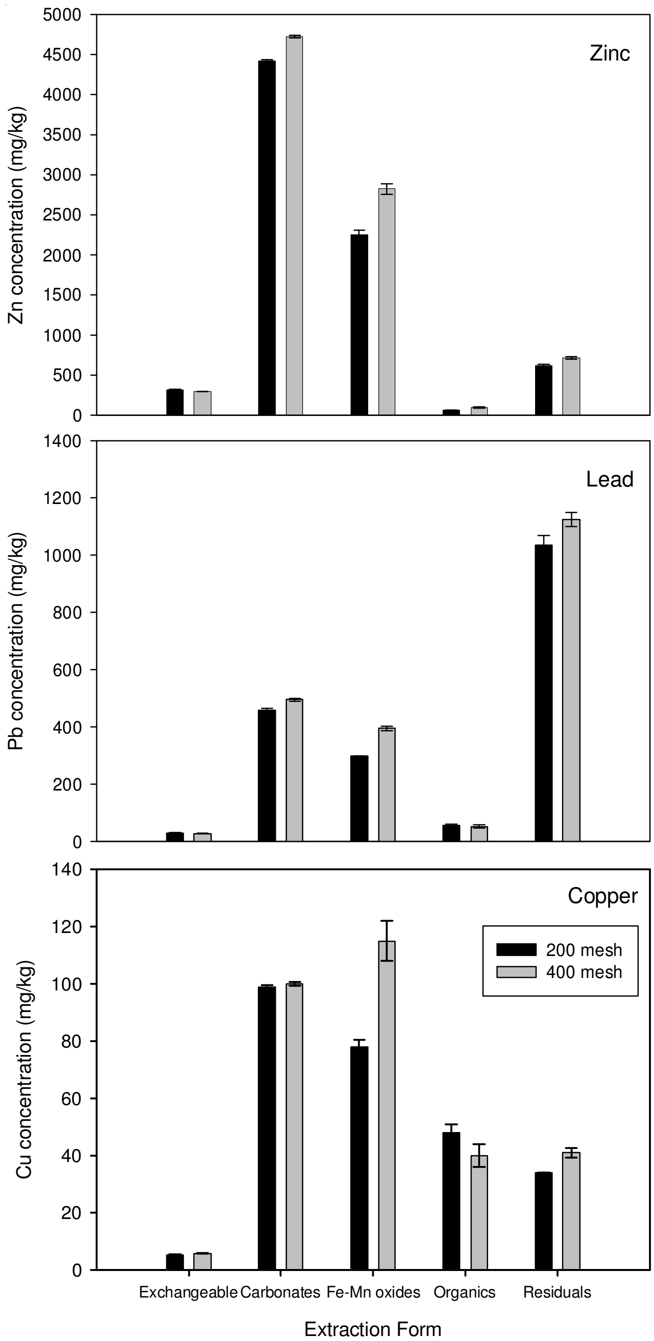

Fig. 1. Distributions of zinc, lead and copper by chemical sequential extraction procedure for paddy soils

for Pb. On the other hand, small particle size of paddy soils (400 mesh) have higher content of heavy metals in this study. In addition to Zn metal, Cu distribution is similar to Zn distribution, in which carbonate and Fe-Mn fractions are the major form. Comparison of these results, it is summarized that Zn and Cu are more easy to be removed than Pb in this study. The higher residual fraction of Pb may be resulted in the strong

TABLE-2
TOTAL CONTENTS OF HEAVY METALS AND BACKGROUND VALUE FOR THE STUDIED AREA IN DIFFERENT DEPTHS (mg kg^{-1}, n = 10)

Soil depth	Zn	Pb	Cu	Zn-Background	Pb-Background	Cu-Background
0-15 cm	5396 ± 49	642 ± 5	226 ± 2	184 ± 10	64 ± 9	170 ± 22
15-30 cm	2840 ± 32	264 ± 11	157 ± 18	138 ± 17	60 ± 16	128 ± 25
30-45 cm	1609 ± 41	99 ± 3	110 ± 2	129 ± 19	54 ± 11	80 ± 12

interaction with other species and makes Pb contaminated soils more difficult to be treated. Fig. 2 shows Fourier transform of the EXAFS spectrum for 400 mesh paddy soils. Fitting results shows two obvious peaks located at 1.63 Å and 2.18 Å together with two spitting peaks at about 2.18 and 3.07. Peaks at 1.63 Å and 2.18 Å are assigned Zn-O with a tetrahedral and octahedral coordination, respectively. For pure ZnO powder only two peaks were fitted at about 1-2 Å and 2.5-3 Å, which revealed the bonding of Zn-O and Zn-Zn, respectively. A spitting peak located at 2.18 Å maybe attributed to Zn-O octahedral or Zn-S structure. Correspondingly, another spitting peak 3.07 Å would be contributed to Zn-Fe bonding, indicating that Zn is sorbed to either Fe or Mn oxides. This is consistent with the CSEQ result, in which the result showed that Fe-Mn oxides fraction is one of important forms for paddy soils. Based on the EXAFS results, the presence of Zn in paddy soils was not in a simple form and decreased the remediation of paddy soils because of many strong bonding between Zn and other metals.

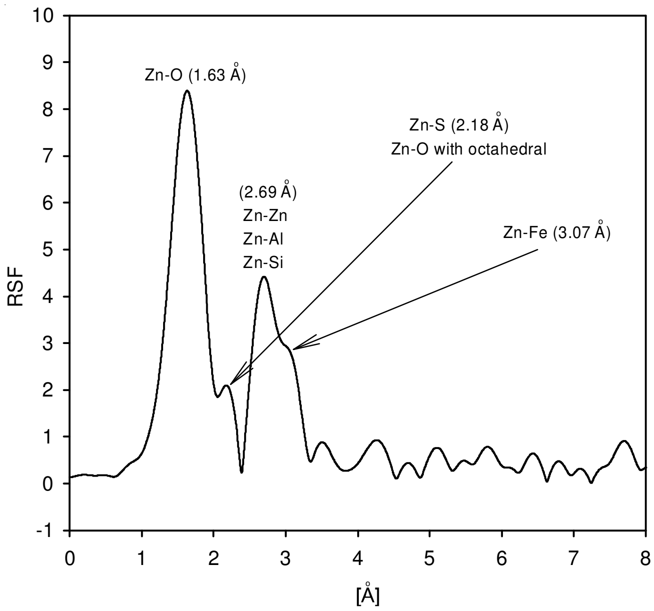

Fig. 2. Fourier transforms of the EXAFS spectra for the 400 mesh paddy soils

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