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Chemical speciation and extractability of Zn, Cu and Cd in two contrasting biosolids-amended clay soils

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Abstract

An incubation experiment was conducted to study the chemical speciation and extractability of three heavy metals in two contrasting biosolids-amended clay soils. One was a paddy soil of pH 7.8 and the other was a red soil of pH 4.7 collected from a fallow field. Anaerobically digested biosolids were mixed with each of the two soils at three rates: 20, 40 and 60 g kg⁻¹ soil (DM basis), and unamended controls were also prepared. The biosolids-amended and control soils were incubated at 70% of water holding capacity at 25 °C for 50 days. Separate subsamples were extracted with three single extractants and a three-step sequential extraction procedure representing acetic acid (HOAc)-soluble, reducible and oxidisable fractions to investigate the extractability and speciation of the heavy metals. As would be expected, there were good relationships between biosolids application rate and metal concentrations in the biosolids-amended soils. The three heavy metals had different extractabilities and chemical speciation in the two biosolids-amended soils. Ethylene diamine tetraacetic acid extracted more Cu, Zn and Cd than did the other two single extractants. The oxidisable fraction was the major fraction for Cu in both biosolids-amended soils and the HOAc-soluble and reducible fractions accounted for most of the Zn. In contrast, Cd was present mainly in the reducible fraction. The results are discussed in relation to the mobility and bioavailability of the metals in polluted soils.

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1. Introduction

With continuing industrial development, urbanization and a growing human population, large quantities (>300 000 t dry weight per year) of biosolids are produced in China but the proportion of wastewater currently subjected to treatment processes is only slightly above 4.5% (Zhou et al., 1999). A rapid increase in the number of wastewater treatment plants with consequent improvements in water quality can be expected over the next several decades as government and the general public become more aware of environmental issues. Bio-

solids contain plant nutrients in addition to potentially toxic contaminants, and can therefore be used to recycle nutrients during disposal. The major disposal options currently available include application to agricultural land, incineration, land reclamation, landfill, forestry and application to 'dedicated' land (Matthews, 1992). Dumping at sea has been prohibited in many countries including China. Land filling and incineration are unpopular because of the high cost and environmental hazards involved. Land application has become more popular because of the relatively low cost and the benefits of recycling of nutrients and organic matter.

Despite the potential benefits, there is still much concern about land application of biosolids, mainly due to the potentially toxic elements present. Municipal wastewater in China is usually mixed with industrial wastewater before treatment and this results in much

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higher metal concentrations than in rural sludges. Zinc and Cu often have the highest concentrations in the biosolids. Cadmium is also of concern because of its potentially harmful effects on humans and animals. Despite the considerable international research effort on the environmental effects of heavy metals in biosolids-amended soils there remain some important questions. For example, the forms of heavy metals that are most available to plants and the mobility of metals in soils will determine the effects on vegetation and the environment. Total concentrations of heavy metals in soils provide little or no indication of their specific bioavailability, mobility and reactivity in biosolids-amended soils (Sterritt and Lester, 1980; McBride, 1995). Moreover, the metals tend to be associated mainly with solid soil components and exist in various physicochemical forms (Lake et al., 1984). Improved knowledge of metal speciation in biosolids-amended soils may be useful in answering these questions. In the past two decades, much effort has been expended in an attempting to quantify metals held in different soil fractions in polluted sites or soils treated with biosolids. Particular attention has been paid to those fractions thought to be mobile and bioavailable since these fractions can possibly leach to pollute groundwater or enter food chains via plant uptake. This paper presents an incubation study on the extractability and chemical speciation of Zn, Cu and Cd in two soils experimentally amended with anaerobically digested biosolids. The data are discussed in relation to potential plant uptake of metals and environmental risk associated with increased levels of mobile heavy metals in soils.

2. Materials and methods

2.1. Soil incubation

Samples of the two soils used were collected from the plough layer (0–20 cm). One was a paddy soil of pH 7.8 (Gleyi-Stagnic Anthrosol) from Changshu Ecological

Experiment Station, Jiangsu Province and the other was a 'red soil' of pH 4.7 (Agri-Udic Ferrosol) collected from a fallow field at Yingtian Ecological Experiment Station, Jiangxi Province. The anaerobically digested sewage sludge (biosolids) were collected from a wastewater treatment plant in Wuxi, Jiangsu Province. Selected physical properties of the soils and biosolids are shown in Table 1 and concentrations of major nutrients and heavy metals are listed in Table 2. The fresh sludge had a dry matter content of 24.5% and was air-dried to 57% DM before mixing with the soils.

The <2 mm air-dried soils were mixed with sludge (also <2 mm) at four application rates: 0, 20, 40, 60 g kg⁻¹ soil (DM basis). Aliquots (equivalent to 500 g DM) of amended and unamended soil were placed in 1890-cm³ plastic boxes adjusted to 70% of water holding capacity (WHC), covered with plastic film and incubated at 25 °C for 50 days. The subsamples were adjusted to 70% WHC by adding water and weighing on a weekly basis. There were four replicates of each treatment. Subsamples were analyzed for extractable metals by using three single extractants: ammonium acetate (NH₄OAc), acetic acid (HOAc) and ethylene diamine tetraacetic acid (EDTA) and a three-step sequential extraction procedure.

2.2. Single extraction

Aliquots of incubated moist soil equivalent to 5 g (DM basis) were added to 25 ml of 1 mol l⁻¹ NH₄OAc (adjusted to pH 7.0 using ammonia or HOAc) in 50-ml polyethylene centrifuge tubes and shaken on a New Brunswick Scientific orbital shaker at room temperature at 120 rpm for 16 h (overnight). The supernatants were filtered through Whatman no. 40 paper. Further 5-g aliquots were subjected to the same procedure but using 0.43 mol l⁻¹ HOAc and 0.05 mol l⁻¹ EDTA (adjusted to pH 7.0 with ammonia) as the extractants, and the suspensions in EDTA were shaken for only one hour before filtration.

Table 1
Selected chemical and physical properties of the soils and biosolids

	pH (in water)	OM (g kg ⁻¹)	CEC (cmol kg ⁻¹)	Clay < 0.002 mm (%)		
Taihu soil	7.8	15.8	21.6	34		
Red soil	4.9	6.7	11.2	31		
Biosolids	6.7	232.0	ND	ND		
	N (g kg ⁻¹)	P (g kg ⁻¹)	K (g kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Cd (mg kg ⁻¹)
Taihu soil	2.25	0.75	17.4	25	70	0.24
Red soil	0.59	0.57	10.2	30	151	0.05
Biosolids	21.6	20.4	7.6	404	2130	8.42

ND, not determined.

Table 2

Extractable Cu, Zn and Cd in two biosolids-amended soils (Taihu paddy soil and red fallow soil) and unamended controls

Biosolids rate (g kg ⁻¹ soil)	NH ₄ OAc		HOAc		EDTA	
	Taihu	Red	Taihu	Red	Taihu	Red
<i>Copper (mg kg⁻¹)</i>						
0	1.55	1.15	0.69	0.47	15.6	0.97
20	1.70	1.38	0.83	1.15	17.7	3.72
40	1.81	1.50	0.96	1.43	20.6	6.16
60	1.94	1.73	0.99	2.61	23.9	8.26
Significance ^a due to:						
Soil type	***		***		***	
Biosolids rate	***		***		***	
Soil × rate	*		***		***	
Extractant	***					
Soil × extractant	***					
Rate × extractant	***					
<i>Zinc (mg kg⁻¹)</i>						
0	0.59	0.57	0.2	0.0 ^b	1.9	0.0 ^b
20	1.05	1.72	9.8	14.0	22.3	19.8
40	1.65	3.31	16.0	22.6	50.4	42.3
60	2.24	6.94	23.7	48.2	67.3	61.5
Significance ^a due to:						
Soil type	***		*		***	
Biosolids rate	***		***		***	
Soil × rate	***		NS		***	
Extractant	***					
Soil × extractant	***					
Rate × extractant	***					
<i>Cadmium (μg kg⁻¹)</i>						
0	7.4	5.7	12.3	4.4	139.0	14.4
20	15.5	21.9	16.3	14.7	171.3	45.0
40	22.2	33.1	13.9	21.9	198.0	81.0
60	27.6	53.9	20.9	38.9	222.5	89.9
Significance ^a due to:						
Soil type	***		NS		***	
Biosolids rate	***		***		***	
Soil × rate	*		***		***	
Extractant	***					
Soil × extractant	***					
Rate × extractant	***					

^a By analysis of variance of log₁₀-transformed data; ****P* < 0.001; ***P* < 0.01; **P* < 0.05; NS, not significant.^b Not detected (below detection limit).

2.3. Sequential extraction

The sequential extraction procedure was described in detail by Luo and Christie (1998a). Briefly, aliquots of 1 g (DM equivalent) of moist incubated soil were extracted using the following sequential extraction procedure. Firstly, samples were shaken at room temperature with 20 ml of 0.11 M CH₃COOH for 16 h (overnight) in 50-ml polyethylene centrifuge tubes and centrifuged at 3000 rpm for 10 min. The supernatants were filtered through Whatman no. 40 paper and then the weights of the tubes (with their contents) were recorded. This extracted primarily the water-soluble and exchangeable

fraction of the metals that was weakly bound with organic matter and carbonates ('HOAc-soluble' fraction). Secondly, the resulting residue was shaken at room temperature with 20 ml of 0.10 M NH₂OH · HCl adjusted to pH 2.0 with high purity HNO₃ for 16 h (overnight), centrifuged, filtered and tube weights recorded as above. This step extracted mainly iron and manganese oxides bound forms ('reducible' fraction). Thirdly, to the residue were added 10 ml of 30% H₂O₂ to avoid losses due to violent reaction. The mixture was allowed to digest in the cold for 1 h. It was then taken to dryness on a water bath heated to 85 °C. A second 10-ml aliquot of H₂O₂ was then added and taken to dryness on

a water bath at 85 °C with intermittent manual shaking. After cooling, 25 ml of 1 M NH_4OAc adjusted to pH 5.0 with HOAc were added to the dry residue to prevent the readsorption of extracted metals on to the oxidized solid residue. The mixture was extracted by shaking for 16 h (overnight), followed by centrifugation and filtration as before. This step extracted primarily organically bound and sulfide metals ('oxidisable' fraction). The formula $F_i = \{C_i(V_i + R_j) - C_{i-1}R_j\}/W$ was used to calculate the amount of metal (in mg) in each of the extracts as described by Luo and Christie (1998a).

The soil water content was also measured to calculate the metal concentrations in the dry matter. All soil extracts were analyzed for Cu and Zn by flame atomic absorption spectrophotometry and for Cd by graphite furnace atomic absorption spectrophotometry using a Hitachi Z-8200 atomic absorption spectrophotometer.

2.4. Statistical analysis

Data were subjected to analysis of variance in a factorial design of two soils and four application rates of biosolids (including unamended controls). Linear and quadratic contrasts were calculated for the four application rates of biosolids and for the interaction between soil type and biosolids application rate to compare the trends in extractable metals in the two soils with changing biosolids application rate. All of the data for the single extractions were also combined to compare the three extractants and the three metals. Most variables were not normally distributed and were $\log_{10}$ -transformed prior to statistical analysis but the mean values presented are non-transformed.

3. Results

3.1. Single extraction

NH_4OAc and EDTA extracted more Cu, Zn and Cd from Taihu paddy soil than from red fallow soil, but differences between HOAc-extractable metals were smaller (Table 2). Although HOAc-extractable Cu was significantly lower in Taihu paddy soil on average ($P < 0.001$), the differences were numerically small. HOAc-extractable Zn was also higher ($P < 0.05$) in Taihu paddy soil, but Cd showed no difference between the two soils. The magnitude of the difference between the two soils in NH_4OAc - and EDTA-Cu and Zn became more pronounced with increasing application rate of biosolids. The interaction between soil type and biosolids application rate was always significant (except for HOAc-Zn) because the rate of increase in extractable metal with increasing biosolids rate was always more pronounced in red fallow soil than Taihu paddy soil. Linear contrasts for the soil $\times$ biosolids rate (not

presented) were always significant ($P < 0.001$ or $P < 0.01$) except for HOAc-Zn, indicating that soil extractable metals increased linearly with increasing biosolids rate and increased more sharply in the red fallow soil than in Taihu paddy soil. Quadratic contrasts for Cu and Zn were not significant (except for HOAc-Cd at $P < 0.05$), but were significant for EDTA-Cu ($P < 0.05$) and EDTA-Zn and Cd (both $P < 0.001$). Overall, the amounts of metals extracted by the three extractants followed the sequence EDTA > NH_4OAc > HOAc for Cu and Cd, and EDTA > HOAc > NH_4OAc for Zn (Table 2). When the mean extractable metal fractions in the two soils were compared with biosolids application rate by linear regression and correlation, the correlation coefficients were always significant (at least $P < 0.01$) except for HOAc-Zn in Taihu paddy soil which still had a large correlation coefficient (r) of 0.861 (data not shown).

3.2. Sequential extraction

The metal fractions in the sequential extraction scheme are shown in Fig. 1. Oxidisable Cu was the largest extractable fraction in unamended Taihu paddy soil, while HOAc-extractable Cu and oxidisable Cu together comprised most of the extractable Cu in the red fallow soil. Biosolids application increased all three extractable Cu fractions in the red soil, while the distribution of the fractions in Taihu soil was similar in unamended soil and at all three biosolids application rates. Biosolids produced a large increase in the reducible Cu fraction in the red soil which became more pronounced with increasing biosolids application rate. Mean metal concentrations in the three sequential fractions were compared with biosolids application rate by linear regression and correlation and all of the correlation coefficients (except HOAc-Cu in Taihu paddy soil) were significant (data not shown).

4. Discussion

4.1. Single extraction

In Taihu paddy soil the extractability sequence for Cu was EDTA > NH_4OAc > HOAc, while in red fallow soil, it was EDTA > HOAc > NH_4OAc . The difference is likely to be related to soil properties, especially organic matter content and pH. The greater amounts of Zn extracted by HOAc in the biosolids-amended soils were compared with those extracted by NH_4OAc may be attributable to the sensitivity of Zn to soil acidity, the factor also implicated by the difference in the extraction efficiency of HOAc in the two soils. Extractable Cd showed similar trends to Cu in both soils irrespective of biosolids amendment.

Fig. 1. Speciation of Cu, Zn and Cd in biosolids-amended: (a) Taihu paddy soil and (b) red fallow soil.

Although there has been much debate about which part of metals in soils is the 'bioavailable' fraction, plant uptake in biosolids-amended soils has often been correlated with some extractable fraction of the soil metal. The aim has been to use a relatively quick and simple chemical extraction to describe the mobility and bio-availability of heavy metals. A wide range of extractants have been employed including EDTA, DTPA, NH_4NO_3 and HOAc with varying success, but there is no fully satisfactory extractant for all soil-plant systems because of varying properties of different soil types and plant

species. Considerable efforts have been made to measure accurately extractable trace metal concentrations in soil samples (Quevauviller, 1996, 1998). The single extractants used in our experiment were employed by Ure et al. (1993) to determine the extractable concentrations of Cd, Cr, Cu, Ni, Pb and Zn in sewage sludge-amended soils. As in our study, metal extractability was found to differ among the three extractants. NH_4OAc is a mild extractant that can extract only the easily exchangeable metals, HOAc can dissolve part of the metals from soil solids because of its weak acidity and EDTA is the

strongest of the three extractants. The complex constants of EDTA with most metals are fairly large, and a rather large percentage of total metals can be extracted.

4.2. Sequential extraction

Biosolids amendment led to a dramatic increase in reducible Cu in red soil which became more pronounced with increasing biosolids application rate. Differences in the distribution of metal fractions between the two soils was likely to be affected by soil properties, especially soil organic matter content and pH. Taihu paddy soil has a much higher pH and organic matter content than red fallow soil. There has been a rather long fertilization period before the maturation of red soil, which has resulted in a much higher iron:alumina ratio in red soil than in Taihu paddy soil. The extraneous metals may be readily absorbed or occluded by iron-alumina oxides and iron-manganese concretion in the acid conditions of the red soil.

Compared with Cu, the oxidisable fraction of Zn was much smaller and there was much more HOAc-soluble Zn in both soils (Fig. 1). This may be explained by differences in chemical characteristics between Cu and Zn. Copper can be preferentially combined with organic matter (Luo and Christie, 1998b), while Zn appears to be more sensitive to soil acidity. The reducible fraction of Zn accounted for the largest proportion of extractable Zn in Taihu paddy soil after biosolids application, while HOAc-Zn was the dominant fraction in biosolids-amended red fallow soil, and this may have been due in part to differences in soil pH.

The reducible fraction of Cd was predominant in Taihu paddy soil irrespective of biosolids amendment, but HOAc-Cd and the reducible fraction together accounted for a large proportion of Cd in the red fallow soil because of the lower pH. There were some similarities between the distributions of Zn and Cd, with small oxidisable fractions and large reducible fractions. However, Cd may be more readily fixed by iron-aluminium oxides and iron-manganese concretions than Zn or Cu.

Single chemical extraction of sewage sludge-amended soils is usually used for assessment of bioavailability of sludge-borne heavy metals. It is more appropriate for the estimation of short and medium term metal risks (Tack and Verloo, 1996). However, the use of single extraction in the study of the distribution of heavy metals in biosolids-amended presents some problems. It is almost impossible to study metal speciation using only one extractant. It is also very difficult to estimate the environmental effects in the long term using single extraction techniques. Soil components and properties vary greatly in different soils, and these can have a very important influence on the mobility and bioavailability

of heavy metals. Sequential extraction can provide more information about the chemical speciation of metals.

5. Conclusions

Most of the differences in the sizes of the single extraction and sequential extraction fractions of the three metals in the two soils can be explained by differences in soil organic matter content and pH and the influence of these soil properties on the behaviour of the metals in the soil. The fraction of metal available to plants may not be the same as the fraction at risk of loss by leaching to the environment. Further studies are therefore required to determine plant uptake of the metals in the two biosolids-amended soils and to study leaching of the metals from the soils in the presence and absence of plant uptake.

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