

BIOSOLIDS CONDITIONING AND THE AVAILABILITY OF Cu AND Zn FOR RICE

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ABSTRACT: Sewage treatment process is a factor to be considered for biosolid use in agriculture. The greatest sewage treatment facility of São Paulo State (Barueri/SP) altered in the year 2000 of its sludge treatment. The addition of ferric chloride and calcium oxide was substituted by the addition of polymers. This change can modify heavy metal phytoavailability. A green house experiment, using 2 soils treated with biosolids (three with and one without polymers with and without polymers) was performed to evaluate Cu and Zn phytoavailability using rice (*Oryza sativa* L.) as test plant. Three kilograms of two soils (Haphorthox and Hapludox) were placed in pots and the equivalent to 50 Mg ha⁻¹ (dry basis) of biosolid was added and incorporated. The statistical design adopted was completely randomized experiment, with five treatments (control plus four different biosolids) each soil and four replications. Soil pH before and after harvesting, Cu and Zn concentrations in shoot were evaluated. Tukey (5%) was used to compare the results. DTPA, HCl 0.1 mol L⁻¹ and Mehlich 3 were used to estimate soil available Cu and Zn. Amounts extracted were correlated to those presented in rice shoot, to evaluate the efficiency of predicting Cu and Zn phytoavailabilities. Biosolids with polymers presented higher Cu and Zn phytoavailabilities, possibly due to the lower pH of these residues. In this case soil presented lowest values of pH and plant shoot had highest. All extractants were representative of Cu and Zn availability to rice plants.

Key words: sewage sludge, heavy metal, phytoavailability, extractant

CONDICIONAMENTO DE BIOSÓLIDOS E A DISPONIBILIDADE DE Cu E Zn PARA ARROZ

RESUMO: O processo gerador do biossólido é um fator a ser considerado na avaliação do uso agrícola deste resíduo. Em 2000, a adição de cloreto férrico+cal virgem durante o tratamento do esgoto foi substituída pela adição de polieletrólitos na maior Estação de Tratamento de Esgotos de São Paulo (Barueri), o que pode gerar mudanças na fitodisponibilidade dos metais pesados. Um experimento em casa de vegetação, com dois solos (Latossolo Vermelho Amarelo e Latossolo Vermelho Escuro) tratados com quatro diferentes biossólidos foi montado para avaliar a disponibilidade de Cu e Zn utilizando arroz (*Oryza sativa* L.) como planta teste. Os vasos receberam 3 kg de solo e o correspondente a 50 Mg ha⁻¹ (base seca) de biossólido. O delineamento utilizado foi inteiramente casualizado, com cinco tratamentos (testemunha + 4 diferentes biossólidos) e quatro repetições. Avaliaram-se pH do solo antes e após a colheita do arroz e teor de Cu e Zn na parte aérea das plantas. Os extratores químicos DTPA, HCl 0,1 mol L⁻¹ e Mehlich 3 foram utilizados para avaliar a fitodisponibilidade de Cu e Zn para plantas de arroz. O biossólido tratado com polieletrólitos apresentou maior fitodisponibilidade de Cu e Zn, possivelmente devido ao menor pH que este confere ao solo. Os três extratores avaliados foram representativos da fitodisponibilidade de cobre e zinco.

Palavras-chave: lodo de esgoto, metal pesado, fitodisponibilidade, extrator

INTRODUCTION

The feasibility of the biosolid or sewage sludge use within the agriculture is related to the origin of the residue, and to the treatment that it is submitted on the Municipal Sewage Treatment Plant (MSTP). The presence of pathogens and persistent organic compounds, the heavy metal drift, as well as characteristics checked during the treatment, can restrict its use on agriculture.

The Metropolitan Region of São Paulo city may produce around 785 tons (dry basis) of sewage sludge per day on the year 2015 (Tsutiya, 2000), and the majority of the MSTPs uses the process of treatment known as anaerobic digestion. For the Barueri/SP MSTP, one of the

most important on this region, the estimated biosolid production for the years 2005, 2010, and 2015 will be of 227, 294 and 310 tons (dry basis) per day, respectively (Santos & Tsutiya, 1997). Therefore, if the agricultural use of the biosolid becomes broadcasted, this MSTP would have an important role as a residue supplier. Recently, Barueri's Plant changed the sewage treatment phase called Chemical Conditioning. On this phase, ferric chloride and calcium oxide were added to raise the efficiency of the dewatering process. The biosolid produced presented a pH varying between 10 and 13, what increased the pathogen control and decreased the heavy metal availability by precipitation and/or occlusion at the crystalline layer of iron amorphous hydroxide that was created. The greatest disadvantage of the residue

alkalinization is the possibility of its addiction to cause soil salinity (Cripps & Matocha, 1991; Fine et al. 1989), and contamination of the underground water by nitrate produced by organic matter degradation associated to high soil pH (Anjos, 1999; Oliveira, 2000). Some MSTPs substituted the chemical conditioning by the industrial polymer addiction, known as polyelectrolytes too. The pH of the new generated residue varies between 5 and 7, what can cause a higher phytoavailability of heavy metals.

To estimate the Cu and Zn phytoavailability in biosolid treated soils is important within the risk evaluation on its agricultural use in agriculture is assessed in relation to contamination problems and to nutritional plants unbalance, since they are micronutrients. Many methods are used today in order to determine the estimates of plant-available rates. Some authors suggest the use of neutral solutions, as water, or solutions with an ionic strength similar to that of the soil, such as CaCl_2 0.01 mol L^{-1} (Whitten & Ritchie, 1991). Acid solutions are also used, e.g. HCl 0.1 mol L^{-1} (Page et al., 1982) and Mehlich 3 (Mehlich, 1984). Another option is the use of chelating extractors, such as DTPA (Lindsay & Norwell, 1978). A third extractant used is Mehlich 3 (Mehlich, 1984) that has acid and chelating agents. Despite of the diversity of methods already proposed, the efficiency of these extractors is quite variable depending on the specification of the metal being evaluated and on soil type, as no standardization process exists regarding to the extractor that should be used. The ideal test plant for availability evaluation is one that responds to any variation in the available rates of the elements under study. Several studies of plant availability of Cu and Zn used rice as a test plant (Jorge, 2001; Singh et al. 1999; Seeda et al., 1997; Barbosa Filho et al., 1990).

The objectives of this project were to study the influence of the process of biosolid generation on soil pH and, consequently, on the availability of Cu and Zn on rice plants, as well as evaluating the efficiency of DTPA, HCl 0.1 mol L^{-1} and Mehlich 3 in estimating the availability of these metals on plants in soils treated with a single rate of biosolid.

MATERIAL AND METHODS

Two different soils were used in this study, one sandy and the other clayey soil, classified as a Haplorthox (HO) and an Hapludox (RH), respectively. One month prior to the experiment, samples from both soils were taken from the surface layer (0 - 30 cm), air-dried, homogenized and passed through a sieve (2 mm mesh). Some of the sample characteristics are: clay=249 g kg^{-1} ; silt=63 g kg^{-1} ; coarse sand= 211 g kg^{-1} and fine sand=477 g kg^{-1} ; SiO_2 =78 g kg^{-1} ; Fe_2O_3 =3 g kg^{-1} ; Al_2O_3 =7 g kg^{-1} ; organic matter=29 g dm^{-3} ; pH in CaCl_2 equal to 4.7; P=6 mg dm^{-3} and cation saturation=42%, expressed

as mmol dm^{-3} , K=1.0, Ca=14, Mg=7 and H+Al=31 for the Haplorthox; and, clay=500 g kg^{-1} ; silt=192 g kg^{-1} ; coarse sand=93 g kg^{-1} and fine sand=215 g kg^{-1} ; SiO_2 =17 g kg^{-1} ; Fe_2O_3 =12.6 g kg^{-1} ; Al_2O_3 =13.2 g kg^{-1} ; organic matter=26 g dm^{-3} ; pH in CaCl_2 equal to 4.3; P=12 mg dm^{-3} ; cation saturation=32% and expressed as mmol dm^{-3} , K=2.7, Ca=13, Mg=9 and H+Al=52 for the Rodic Hapludox. The granulometric soil analysis was made using methods described by Camargo et al. (1986), and the chemical soil analysis was performed according to Raij & Quaggio (1983) methods.

The biosolid samples used resulted from the anaerobic treatment of the sewage generated by the city of São Paulo (Municipal Sewage Treatment Plant of Barueri/SP), Brazil. Three of the samples resulted from a chemical conditioning process that used ferric chloride and lime (Bio1, Bio2, and Bio3) and one had this step replaced by the addition of polymers (Po). Sludge sample were made in different seasons, as follow: Bio1: July / 1997; Bio2: November /1997, Bio3: January /1998; and Po: October /1997. Some chemical characteristics of the biosolid samples that were used are presented in Table 1. The total content of heavy metals in the residue was determined using nitro-perchloric digestion, and conventional atomic absorption spectrometry determination with an air-acetylene flame according to Eaton et al., (1995). This procedure was adopted since there is no standardization method suggested for this procedure. None of the biosolids presented a total Cu and Zn content that would limit their agricultural use, according to the standards listed in P 4,230 of Companhia de Tecnologia e Saneamento Ambiental (CETESB/1999).

The experiment was installed in pots, following a completely randomized design, with five treatments: control (Cont), Bio1, Bio2, Bio3 and Po and four replicates. Each pot received 3 kg of soil. In the biosolid treatments, the residue was incorporated in an amount corresponding to 50 Mg ha^{-1} (dry basis), followed by an incubation period of 45 days. The radius of the pots (9.0 cm) and the soil depth (20 cm) were taken into account to calculate the amounts of biosolids that would be used. After the incubation period, soil sample was taken for a pH analysis. The conventional fertilization for planting was performed according to what is recommended by Cantarella & Furlani (1997), before seeding the rice variety IAC-165.

Rice did not produce grain due to the occurrence of low temperatures during the growing period. Harvesting was made 160 days after planting. The aerial part of the plants was washed with distilled water, a 0.1 mol L^{-1} HCl solution and deionized water. After being dried in a laboratory oven at 65°C, the dry matter was quantified, and then submitted to grinding. Cu and Zn were quantified in an extract obtained by nitro-perchloric digestion and their content was determined by conventional atomic absorption spectrometry run with an

air-acetylene flame. After harvesting, the soil was sampled for a pH analysis, and Cu and Zn extraction by DTPA (Lindsay & Norwell, 1978), HCl 0.1 mol L⁻¹ (Page et al., 1982), and Mehlich 3 (Mehlich, 1984).

The Cu and Zn content in the plants, total amount of these metals absorbed in each pot, and soil pH in each treatment were compared by Tukey test (5 %). The contents extracted from the soil by DTPA, HCl 0.1 mol L⁻¹ and Mehlich 3 were correlated with the content in the plants to evaluate the efficiency of each extractor in estimating the availability of Cu and Zn to plants.

RESULTS AND DISCUSSION

Soil pH, treated by alkaline biosolids (Bio1, Bio2 and Bio3), increased relatively comparing to the control after incubation for 45 days (Figure 1), demonstrating that the alkalinity caused by lime addition to the process that generates these residues, acts upon the soil. A more pronounced pH increase in treatments involving Haplorthox can be noticed, probably because it presents a weaker buffer capacity. When the rice was harvested, after 205 days of the sludge incubation, the pH values in the soil were still close to those observed at planting.

The elevation of pH in soils and its maintenance for periods of up to two years after alkaline biosolid application has been reported by several authors, both in pots and in experimental field experiments (Sloan & Basta, 1995; Reis, 1998; Andrade & Mattiazzo, 2000;

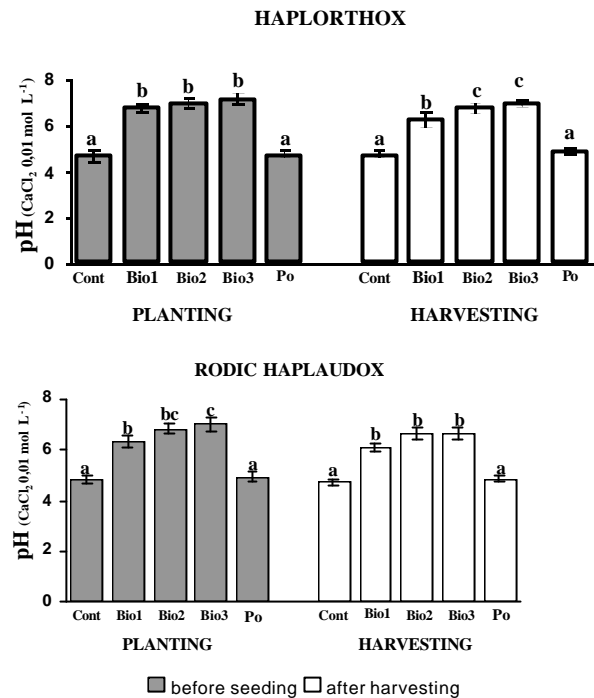


Figure 1 - Values of pH in soils collected at the time of planting and harvesting . Treatments with a common letter in the columns are equal (Tukey, 5%). Bio: Biosolids treated with lime and ferric chloride (chemical conditioning). Po: Biosolids treated with polymers. RSV: Relative Standard Deviation.

Table 1 - Some chemical characteristics of the biosolids^{1,2} of Barueri, SP, Brazil.

Constituent	Bio1	Bio2	Bio3	Po	Maximum concentration permitted in sewage sludge
Moisture (g kg ⁻¹)	595	587	592	408	-
pH (H ₂ O)	9.8	8.6	8.1	6.3	-
C- oxidable (g kg ⁻¹)	195	191	183	154	-
Organic matter (g kg ⁻¹)	315	302	294	213	-
C/N ratio	10	10	10	5	-
N-total (g kg ⁻¹)	19	19	18	32	-
Total - P (g kg ⁻¹)	11	10	9	21	-
Total - K (g kg ⁻¹)	1.1	1.1	1.2	1.4	-
Total - Ca (g kg ⁻¹)	132	139	144	24	-
Total - Mg (g kg ⁻¹)	4.0	4.0	3.8	3.3	-
Total - Na (g kg ⁻¹)	0.6	0.6	0.6	0.7	-
Total - Fe (g kg ⁻¹)	48	47	45	54	-
Total - Cd (mg kg ⁻¹)	15	13	14	17	85
Total - Cr (mg kg ⁻¹)	361	347	324	609	-
Total - Cu (mg kg ⁻¹)	414	770	2460	878	4300
Total - Mn (mg kg ⁻¹)	239	234	233	329	-
Total - Ni (mg kg ⁻¹)	199	201	199	408	420
Total - Zn (mg kg ⁻¹)	2048	5472	2087	3488	7500

¹EATON et al. (1995).

²Results expressed in the dried material at 65°C.

³CETESB (1999).

Bio: Biosolids treated with lime and ferric chloride (chemical conditioning).

Po: Biosolids treated with polymers.

Anjos & Mattiazzo, 2000). The alkaline residues (Bio) used contains an alkalinizing power due to the addition of quicklime (CaO). When the lime reacts with water, calcium hydroxide [Ca(OH)₂], which is a strong base, is produced. The calcium hydroxide reacts with the acidity components in the soil, neutralizing them and causing the pH in the soil solution to increase. No increase in pH was observed in the treatment involving the Po biosolid, as expected, since this residue did not receive lime during the treatment process.

The dry matter production (shoot + root) in the treatments with the Po biosolid was higher than in other treatments (Table 2). Since all pots received the same mineral fertilization, the difference is related to the higher amounts of N and P that were provided to the soil by the Po residue (Table 1) as compared to Bio1, Bio2 and Bio3. Plants in treatments Bio3 in the Hapludox, presented a reduced root growth, with lower

branching, in addition to chlorosis in young leaves, which resulted in a decrease of dry matter production. In this treatment and also the Cu/Zn ratio observed was around 1, the amount of Cu present in the residue was higher as compared to the other treatments, in such a way that the lower dry matter production could be associated to the desbalancing of the Cu/Zn ratio.

The Cu content in the plants cultivated on the Haplorthox was higher in treatments with Po and with Bio3 (Figure 2). Since the total Cu concentration in the Po biosolid is about three times lower than in Bio3 (Table 1), this results indicates a higher availability of this element for the plants in the Po treatments, that can be credited to the lower soil pH in this treatment. With pH values above seven, the predominant form of Cu in soil is copper hydroxide, which is a form not available within plants. Therefore, when the pH increases, the availability of copper in plants is reduced

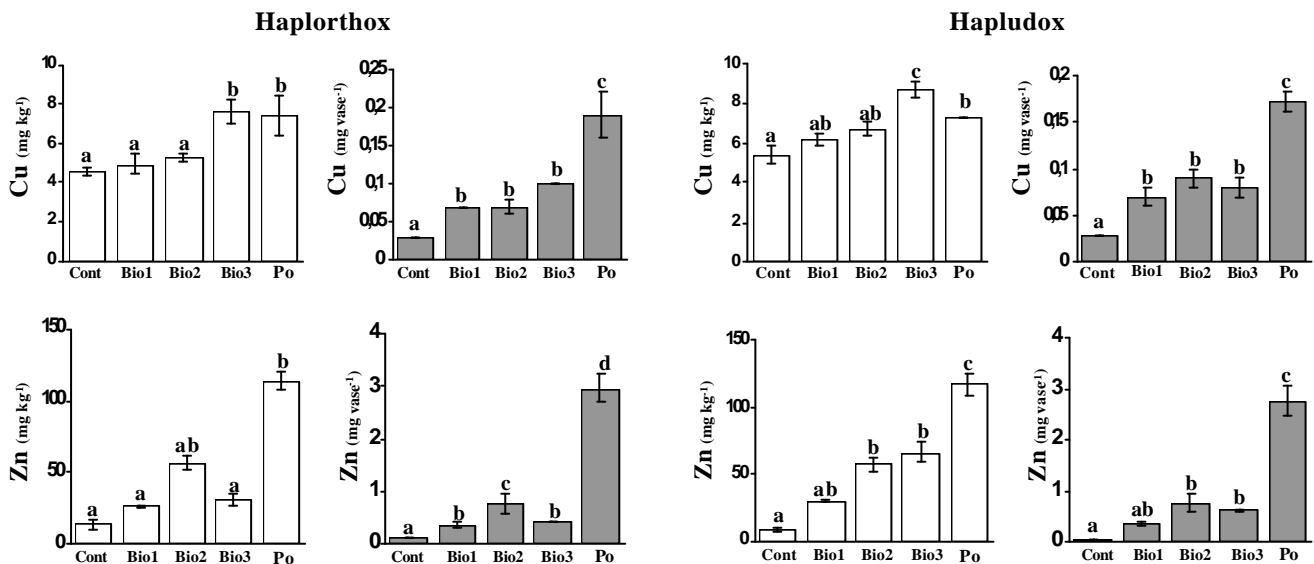


Figure 2 - Content and absorbed amount of Cu and Zn in rice plant leaves cultivated in soils treated with different biosolids.

Treatments with a common letter in the columns are equal (Tukey, 5%).
 Bio: Biosolids treated with lime and ferric chloride (chemical conditioning).
 Po: Biosolids treated with polymers.
 RSV: Relative Standard Deviation.

Table 2 - Dry matter production by rice plants cultivated in soils treated with different biosolids.

Treatment	Haplorthox			Hapludox		
	Root	Shoot	Total	Root	Shoot	Total
----- g pot ⁻¹ -----						
Control	3.0 a	6.6 a	9.6 a	1.5 a	4.8 a	6.2 a
Bio1	3.3 a	13.7 b	17.1 b	2.7 b	11.9 b	14.6 bc
Bio2	4.1 a	13.7 b	17.8 b	2.8 b	13.0 c	15.8 c
Bio3	3.6 a	12.7 b	16.3 b	1.7 a	9.2 b	10.9 b
Po	6.9 b	26.2 c	33.1 c	6.0 c	24.6 d	30.6 d
RSV %	13.1	5.4	6.4	12.3	11.8	10.6

Treatments with a common letter in the columns are equal (Tukey, 5%).
 Bio: Biosolids treated with lime and ferric chloride (chemical conditioning).
 Po: Biosolids treated with polymers.
 RSV: Relative Standard Deviation.

(Alloway, 1990; Smith, 1994; Reddy et al., 1995). For the Hapludox, the Cu content found in the plants corresponds to the amounts that were added, that is Bio3's plants presented higher concentrations than Po's plants.

The higher Cu content in the plants from treatment Bio3 can be credited to a lower dry matter production in this treatment (Table 2). Cu forms complexes with organic ligands, and shows great affinity with organic matter (Alloway, 1990). In the present study, the alkaline residues show organic matter contents that are similar and higher than those of the biosolid treated with polymers. However, the influence of organic matter complexes with Cu on the availability of this element to plants does not become evident due to the availability caused by the low pH.

The Bio2 biosolid contains one and a half times more Zn than the Po (Table 1). However, for the Haplorthox there was no difference between the Zn content in plants from these two treatments, while for the Hapludox, plants in the Po treatment showed higher rates than those of Bio2. The decrease on Zn availability with the increase on soil pH has been observed by several authors (King & Hajjar, 1990; Smith, 1994; Reddy et al., 1995). In addition, at higher pH values, the co-precipitation of Zn with Fe and Al oxides is favored, decreasing its availability (Mattiazzo, 1994). Another important aspect is that zinc availability is negatively correlated with saturation by calcium (Cavallaro & McBride, 1978; Kabata-Pendias & Pendias, 1985). These authors suggest that the absorption mechanism for calcium and zinc is the same, so that an increase of Ca concentration in the soil decreases zinc absorption by the plants. Since the Bio biosolids have a Ca content that is

higher than Po (Table 1), it could have been a negative interaction between these two elements. In the Hapludox, plants from the Po treatment showed the highest Zn contents, probably due to the lower content of Ca within this residue.

Also in the Hapludox, the Zn content in the Bio3 treatment was related to the amount that was added, probably due to a smaller dry matter production and the consequent concentration effect. Another factor that indicates the concentration effect in plants from the Bio3 treatment in this soil is that the amount of Zn removed from soil by plants in Bio3 treatment in Bio3 is smaller than in Bio2.

All studied extractors (DTPA, HCl 0.1 mol L⁻¹ and Mehlich 3) (Table 3) were efficient in previewing the availability of Cu and Zn to rice plants (Table 4). The extraction of micronutrients in the State of São Paulo is performed with the use of DTPA by official recommendation since 1993 (Abreu et al., 1994). The procedure for analysis of heavy metals available for plants in biosolids has not yet been standardized by CETESB. The extraction methods that utilize DTPA and Mehlich's-3 are less operational when compared to the HCl 0.1 mol L⁻¹ method, because more time and work have to be dedicated to prepare those extractors, they require a longer agitation time, and extract filtering is slower. In addition, the DTPA removal capacity depends on various factors such as pH (Camargo et al., 1982) and soil mineralogy (Fagbami et al., 1985). In this present study, the correlation coefficient values were in closely proximity (Table 4) indicating their efficiency was identical; however we chose to indicate the use of HCl 0.1 mol L⁻¹ because this method is more operational.

Table 3 - Contents of Cu and Zn removed by DTPA, HCl 0.1 mol L⁻¹ and Mehlich's-3 from an Haplorthox (HO) and an Hapludox (RH) treated with different biosolids.

Soil	Treatment	Cu			Zn		
		DTPA	HCl 0.1 mol L ⁻¹	Mehlich 3	DTPA	HCl 0.1 mol L ⁻¹	Mehlich 3
----- mg kg ¹ -----							
HO	Control	0.3	0.3	0.6	0.5	1.0	1.0
	Bio1	1.2	1.7	1.9	4.5	10.0	6.5
	Bio2	1.4	1.8	2.3	14.0	33.5	26.5
	Bio3	15.4	11.9	22.6	4.5	12.5	9.0
	Po	2.2	2.6	2.6	27.0	16.0	16.5
	RSV %	3.8	3.8	8.5	3	6	4
RH	Control	0.8	1.2	1.8	0.5	1.0	1.0
	Bio1	1.4	1.9	2.7	4.5	7.5	6.5
	Bio2	2.0	2.2	4.0	17.5	34.0	32.0
	Bio3	12.0	12.5	25.5	4.5	12.0	9.5
	Po	2.2	2.2	3.3	10.5	15.5	15.0
	RSV %	1.7	5.2	4.5	2	5	3

Bio: Biosolids treated with lime and ferric chloride (chemical conditioning).

Po: Biosolids treated with polymers.

RSV: Relative Standard Deviation.

Table 4 - Correlation coefficients (r) between amounts of Cu and Zn absorbed by rice plants cultivated in soils treated with biosolids and extracted by DTPA, HCl and Mehlich 3.

Haplorthox			
Cu			
	Plant	Mehlich 3	HCl 0.1 mol L ⁻¹
DTPA	0.85	1.00	0.99
HCl 0.1 mol L ⁻¹	0.85	0.99	-
Mehlich 3	0.84	-	-
Zn			
	Plant	Mehlich 3	HCl 0.1 mol L ⁻¹
DTPA	0.93	0.89	0.73
HCl 0.1 mol L ⁻¹	0.89	0.95	-
Mehlich 3	0.90	-	-
Hapludox			
Cu			
	Plant	Mehlich 3	HCl 0.1 mol L ⁻¹
DTPA	0.92	1.00	1.00
HCl 0.1 mol L ⁻¹	0.95	0.99	-
Mehlich 3	0.87	-	-
Zn			
	Plant	Mehlich 3	HCl 0.1 mol L ⁻¹
DTPA	0.93	0.97	0.95
HCl 0.1 mol L ⁻¹	0.93	0.99	-
Mehlich 3	0.92	-	-

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