SOIL SOLID PHASE CONTROLLING ZN ACTIVITY IN PORE WATER FROM SOIL PREVIOUSLY TREATED WITH SEWAGE SLUDGE

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ABSTRACT

Ten soil samples were used to measure free Zn^{2+} in soil pore water obtained from soil treated previously with sewage sludge. The samples were chosen to cover soils having different enrichment rates of heavy metals to sewage sludge. The cation exchange resin method was used to measure free Zn^{2+} in soil pore water. Soil total Zn values ranged from 87 to 282 within an average 165 $mgkg^{-1}$. DTPA, NH_4NO_3 extractable-Zn, and pore water soluble Zn represented approximately as average 12, 0.91, and 0.73 % from the total, respectively. Pore water Free Zn^{2+} represented approximately 0.17, 1.46, 26, and 37% from total, DTPA, NH_4NO_3 extractable-Zn, and soluble Zn, respectively. The Zn activities were very low, ranged from $10^{-6.5}$ to $10^{-8.01}$ M, and were inversely related to pH, with a correlation coefficient ($R^2 = 0.95$; $P < 0.01$). The activity of Zn^{2+} in the soil could be predicted from the equation:

$$\text{Log} (Zn^{2+}) = 6.49 - 2pH$$

The measured Zn^{2+} activities were compared to the solubility of various Zn minerals using a -log Zn^{2+} vs. pH solubility diagram. The diagram suggests that zinc ferrite ($ZnFe_2O_4$) in equilibrium with soil-Fe is a likely solid phase controlling (Zn^{2+}) activities in these soils.

Keywords: Zinc activity, Zinc solubility, free Zinc, polluted soils, heavy metals, Soil pore water, Speciation.

INTRODUCTION

Increased levels of heavy metals in soils pose potentially serious hazards in the soil-plant-animal system. Knowledge of the total contents of metals in soils provides only limited information about their chemical behaviour. Heavy metals are present in soil in different forms with varying degree of mobility and availability to plants. One of the major sources of heavy metals to individual agricultural fields is sewage sludges when used as soil amendments. Sewage sludge additions, although carefully regulated by legislation formatted to avoid phytotoxic effects of metals on plants and possible entry into the human food chain, vary from country to country (McGrath et al., 1994). All the regulations that define a maximum concentration in the receiving soil are based on total soil concentrations, which take no account of bioavailability fraction in the soil pore water.

However, it is now generally accepted that plant uptake of metals depends on metal concentrations in the soil pore water and particularly the free ionic form which is, also, the fraction sometimes toxic to the soil microflora and fauna at larger concentrations (Chaudri *et al.*, 1999). Hence, it is the concentration of a metal in its soluble bioavailable form that is crucial to understanding metal toxicity, and therefore, metal loading limits for agricultural soils receiving sewage sludges need updating to allow this.

In most Zn studies, concentrations of free Zn have not been measured. Usually total Zn concentrations have been measured directly, or Zn has been speciated using only inorganic speciation models. Lindsay and Norvell (1969) used the following empirical relationship to express the Zn activity relationships:

$$\text{soil Zn} + 2H^+ \rightleftharpoons Zn^{2+}$$
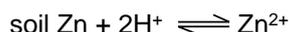
Ma and Lindsay (1990); El-Falaky et al., 1991; Badawy, 1992; Badawy and Helal, 1994, succeeded to measured Zn^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+}, respectively, in alkaline soils by using the developed competitive chelation method, which was described by Workman and Lindsay (1990). Recently, the cation exchange resin method (Holm et al., 1995) was successfully used to measure free Zn^{2+} in sewage sludge treated soils.

Identification of the sparingly soluble compounds controlling Zn solubility in the swage sludge treated soils is of great important at for maintaining and improving the fertility of the soils (Lindsay, 1979). In this respect, free Zn^{2+} is essential. In this study the cation exchange resin method was used to measure free Zn^{2+} in soil pore water obtained from sewage sludge treated soils by soil moisture samplers (SMS). The measured Zn^{2+} activities were compared with the solubility of various Zn minerals expected to regulate Zn^{2+} activity in the tested soils.

Theory

The method presented determines the activity of free divalent Zn^{2+} in the samples. This theoretically well-defined determination, is based on the equilibrium established between the activities of the metal ions in the sample solution and the amount of metal ions exchanged onto a cation exchange resin originally saturated with *Ca*.

The equilibrium chemistry of the Zn in soil is generally described by the equation:

$$Zn^{2+} + L_n^{j-} \Leftrightarrow ZnL_n^{2-j} \qquad [1]$$

Where Zn^{2+} is abbreviation for the free *Zn* ion, L_n^{j-} is a general term for ligands
potentially complexing Zn^{2+}, n denotes the number of different ligands that are present in the sample, and ZnL_n^{2-j} is the complex formed from Zn^{2+} and L_n^{j-}. In the following equation, *j* is taken to be equal 2. The stability of ML_n

7396

complex is characterized by the corresponding stability constant, $K_{c.n}$.   For example,
Where ( ) denotes aqueous phase activities.

$$K_{c.n} = \frac{(ZnL_n)}{(Zn^{2+})(L^{2-})} \qquad [2]$$

The total metal zinc [Zn_T] in solution before adding resin, determined by atomic absorption spectrophotometer, is

$$\left[Zn_T\right] = \left[Zn^{2+}\right] + \left[ZnL_n\right] \qquad [3]$$

Where [ ] denotes concentration. The total zinc concentration [Zn_T] is the only directly measurable parameter in eq.[1] and [2].

The equilibrium of the interaction between the samples in contact with a solid phase such as a resin is described by:

$$RZn \Leftrightarrow Zn_s{}^{2+} + L_{n.s}{}^{2-} \Leftrightarrow ZnL_{n.s} \qquad [4]$$
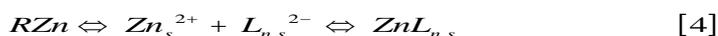
Where *RZn* refers to the Zn^{2+} exchanged onto the resin and the subscript *S* denotes the solution phase at equilibrium with the resin. Assuming that only the free divalent metal ion exchanges onto the resin the equilibrium distribution between the resin and the solution can be described by the distribution coefficient, K_d.

$$Kd = \frac{\left[Zn^{2+}\right]_R}{\left[Zn^{2+}\right]_S} \qquad [5]$$

Where [Zn^{2+}]$_R$ is defined as the concentration of Zn^{2+} in the resin phase, and [Zn^{2+}]$_S$ is defined as the activity in the solution phase at equilibrium with the resin.

The total zinc in solution at equilibrium with the resin is:

$$\left[Zn_T\right]_S = \left[Zn^{2+}\right]_S + \left[ZnL_n\right]_S \qquad [6]$$

Assuming that the concentration of metals on the resin is [Zn_T]$_R$, the mass balance yields at equilibrium:

Where
W = the weight of resin
V = volume of the sample solution
The distribution coefficient for the sample experiment is expressed by:

$$Kd = \frac{[Zn^{2+}]_R}{[Zn^{2+}]_S} = \frac{[Zn_T]_R}{[Zn^{2+}]_S f_2} = \frac{[Zn_T] - [Zn_T]_S}{[Zn^{2+}]_S f_2} \times \frac{V}{W} \qquad [8]$$

Where f_2 is the activity coefficient for divalent ions.
The distribution coefficient of the Zn^{2+} ion onto the resin will depend strongly on the ionic strength, cation composition and pH of the samples. A reference experiment mincing the sample with respect to these characteristics, but without ligands, must be conducted to determine the distribution coefficient.

$$Kd^* = \frac{[Zn^{2+}]^*}{[Zn^{2+}]^*_S} = \frac{[Zn_T]^*_R}{[Zn^{2+}]^*_S f_2^*} \frac{[Zn_T]^* - [Zn_T]^*_S}{[Zn^{2+}]^*_S f^*_2} \times \frac{V^*}{W^*} \qquad [9]$$

Where superscript* refers to the reference experiment.
Assuming that the free divalent Zn^{2+} has the same affinity for the resin in both the samples and reference experiment, the distribution coefficients for the samples and reference experiment are the same, and that $W = W^*$, $V = V^*$, $f_2 = f_2^*$ the following can be derived from Eq.[8] and [9]:

$$\frac{[Zn_T] - [Zn_T]_S}{[Zn^{2+}]_S} = \frac{[Zn_T]^* - [Zn_T]^*_S}{[Zn^{2+}]^*_S} \qquad [10]$$

Rearranging and dividing by $[M_T]_S$ for the sample in equilibrium with the resin yields:

$$\frac{[Zn^{2+}]_S}{[Zn_T]_S} = \frac{[Zn_T] - [Zn_T]_S}{[Zn_T]_S} \times \frac{[Zn_T]^*_S}{[Zn_T]^* - [Zn_T]^*_S} \qquad [11]$$

All variables on the right side of the equation can be measured (Fig.1) and in the following it is shown that the fraction of the total metal in solution present as free divalent ions in the sample in equilibrium with the resin is the same as the fraction of free divalent metal in the original sample.
If the ligand concentration substantially exceeds the total metal concentration, the ratio of M^{2+} to the total metal concentration does not change when the sample is exposed to the resin. This statement can be expressed as follows:
If $L^{2-} >> Zn_T^{2+}$, then $L^{2-} = L_T$, where $L_T = L^{2-} + Zn_L$
and

$$[Zn_T]_R \times W = ([Zn_T] - [Zn_T]_S) \times V \qquad [7]$$

Fig   1

Table 1

7400

$$K_C(L_T) = \frac{(ZnL)}{(Zn^{2+})} \qquad [13]$$

Because the ligand complexed with Zn^{2+} as ZnL constitutes only a minor part of the total ligand (L_T). This means that $[ZnL] = K_c \times [L_T] \times [Zn^{2+}]$ and that

$$\frac{[Zn^{2+}]}{[Zn_T]} = \frac{[Zn^{2+}]}{[ZnL]+[Zn^{2+}]} = \frac{[Zn^{2+}]}{[Zn^{2+}](K_c[L_T]+1)} \qquad [14]$$

As longs as the assumption $L^{2-} \gg M_T^{2+}$ is satisfied, the fraction of the total metal in solution present as free divalent ions does not depend on the total metal concentration expressed as:

$$\frac{[Zn^{2+}]_S}{[Zn_T]_S} = \frac{[Zn^{2+}]}{[ZnT]} \qquad [15]$$

Relating this to Eq.[11] yields the final equation for determining the free divalent Zn^{2+}

$$\frac{[Zn^{2+}]}{[Zn_T]} = \frac{[Zn_T]-[Zn_T]_S}{[Zn_T]_S} \times \frac{[Zn_T]^*_S}{[Zn_T]^* - [Zn_T]^*_S} \qquad [16]$$

MATERIALS AND METHODS

Soil samples:

  The soils were sampled in spring 1999 from a long-term sewage field experiment held at ADAS Rosemaund, Herefordshire, United Kingdom. Initially, the experiment was established in 1968 at the Luddington Experimental Husbandry Station, Warwickshire, on a sandy loam textured soil (14% clay). Sewage sludges obtained from sewerage works which had sludges 'naturally' rich in either Zn, Cu, Ni or Cr were applied to attain a range of soil metal concentrations (Table 1). The Cr-sludge was also contaminated with Cd. Control non-metal enriched sludge was used where necessary to make up quantities, so that all sludged plots received 125 tds ha^{-1} in 1968, or as four annual applications of 31 tds ha^{-1} between 1968 and 1971. Ten metal treatments were established along including untreated soil and

uncontaminated sludge control treatments (Table 1). The design was a randomised block with four replicate plots per treatment. The initial soil pH was 6.2 and plot sizes were 1.8m x 4.5 m. In July 1991, the soils were excavated and transferred to ADAS Rosemaund, Herefordshire, where isolated plots (1.2m x 1.2m) were established using oil tempered hardboard.

Table 1 shows the treatments sampled in April 1999, thirty years after sludge addition ceased. Twenty soil cores were collected from each plot to a depth of 25 cm using a Dutch auger made of tempered steel, and bulked in the field to give representative samples of each plot. The samples were sieved moist to <3 mm, thoroughly mixed and separated into 1 kg (oven dry basis) portions to give triplicate samples for each plot.

Soil Analysis:
Representative sub-samples of the soils were air dried, ground to <150 ìm in an agate ball mill and digested using concentrated HNO_3/HCl acids (4:1 v/v), (McGrath and Cunliffe, 1985). Total Zn concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; Accuris). Soil pH and EC ware determined in deionised distilled water (1: 2.5 w/v), and soil %C and %N using a Leco combustion analyser (Leco® CNS-20000). DTPA-extractable Zn: Zinc was determined for all tested soils samples using 0.005 M DTPA (diethylene triamine penta acetic acid) extract as described by Lindsay and Norvell (1978). NH_4NO_3 -extractable Zn: Zinc was extracted using 1M NH_4NO_3 and measured for all tested soil samples using inactively coupled-plasma atomic emission spectrophotometer (ICP-AES; Accuris).

Determination of free Zn^{2+} concentration in soil pore water:
Rhizon soil moisture samplers from Rhizosphere Research Products, Wageningen, Holland were used to extract soil pore water following the procedure of Knight et al., (1998). Briefly, as shown in Fig.1, these samplers consist of a length of inert porous (0.2 μm) plastic tubing, capped with nylon at one end, through which the soil pore water is extracted. The other end is attached to a 5 cm length of polyethylene tubing joined to a female luer lock. Two samplers were placed diagonally opposite each other from the lip of the pot to the base into each of three replicate 1.0 kg (dry weight) pots of soil. Initially, the soil was made up to 50% water holding capacity (WHC) with deionised water, and two weeks prior to extraction, to 75% WHC. Acid washed disposable syringes, attached to the 'luer lock', and was used to extract pore water from the soil. Free Zn^{2+} concentrations in soil pore water were determined using a calcium saturated cation exchange resin method (Holm *et al.*, 1995).

Statistical Analysis:
Genstat 5 (1987, 3rd ed.) was used for all statistical procedures.

RESULTS AND DISCUSSION

Soil total Zn values (Table, 2) in all plots ranged from 87 to 282 within an average 165 mgkg^{-1} ; the highest value was found in high Zn application rate and represented approximately 3 times comparing with the control treatment. Determination of DTPA-extractable Zn in the soils was carried out to evaluate the availability status of Zn in the soils. Refereeing to the analytical figures reported by Viets and Lindsay, 1973 based on the DTPA soil test, the critical concentration of Zn in soils varied from 0.5 to 1.0 ppm. Accordingly, it seems that most of the soils in this study are sufficient in available Zn. DTPA and NH_4NO_3 extractable values (Table, 2) ranged from 5 to 69 within an average 23, and from 0.34 to 8 within an average 2 mgkg^{-1}, respectively. The highest value was found in high Zn application rate and represented approximately 14, and 16 times for DTPA and NH_4NO_3, respectively, comparing with the control treatment. The percentage of Zn content extracted by DTPA and NH_4NO_3 ranged from 6 to 28 within an average 12 %, and from 0.01 to 3.5 within an average 0.91% from total content, respectively. Highly significant relationships were found between both DTPA and NH_4NO_3 – extractable with total Zn (R^2 = 0.89, and R^2 = 0.91, respectively; $P < 0.01$). Also, the data show (Fig.2c) the linear increased in NH_4NO_3 as increasing in DTPA extractable-Zn (R^2 = 0.82; $P < 0.01$). There were increases in soil pore water soluble Zn as of total soil content increases (Fig.3a; R^2 = 0.91; $P < 0.01$). The percentage value of soluble Zn ranged from 0.38 to 2.8 within average 0.73 % from the total.

Table (2): Zinc content of studied soils.

No.	Treatment	Soil Zn contents (mgkg^{-1})		
		Total	DTPA-extractable	NH_4NO_3-extractable
1	No sludge control	92±5	6.90±0.42	0.43±0.09
2	Uncont. Sludge	89±2	5.42±0.34	0.51±0.05
3	Low Zn	212±15	34.35±4.4	1.80±0.23
4	High Zn	279±3	63.85±5.3	7.75±0.92
5	Low Cu	164±7	20.19±1.4	1.05±0.15
6	High Cu	217±4	35.65±4.7	2.96±0.34
7	Low Ni	162±3	19.25±2.2	1.35±0.16
8	High Ni	187±13	28.15±2.9	1.92±0.23
9	Low Cr (low Cd)	116±13	6.45±0.11	0.40±0.07
10	High Cr (high Cd)	153±6	16.52±3.2	0.71±0.03

All treatment values are means of 4 replicate plots ± Standard Errors of Means (SEM)

Data in Table (3) show that the free Zn^{2+} in soil pore water in all plots ranged from 0.06 to 1.94 within an average 0.33 ppm, which represented approximately as average 0.17% of soil total Zn; 1.46% of DTPA-extractable; and 25.5% of NH_4NO_3 extractable Zn. However, it represented 37% from soluble Zn. Figures 2a, 2b, 3b, and 3c, shows relationships (R^2 = 0.89, R^2 = 0.84, R^2 = 0.92, and R^2 = 0.94, respectively; $p < 0.01$) between each of NH_4NO_3, DTPA, soluble, and total contents of Zn with the pore water free Zn^{2+} , respectively.

Badawy, S.H.

Fig 2

7404

Fig 3

Table (3): Zinc content of studied soils.

No.	Treatment	Soil pore water				
		pH	EC (mScm^{-1})	DOC (mgl^{-1})	Soluble Zn (µgl^{-1})	Free Zn^{++} (µgl^{-1})
1	No sludge control	7.7±0.2	1.66±0.12	7.9±0.9	448±40	92±36
2	Uncont. Sludge	7.5±0.3	1.55±0.10	7.3±0.3	490±20	115±34
3	Low Zn	7.4±0.3	1.79±0.05	8.7±0.6	804±170	364±140
4	High Zn	7.3±0.3	1.75±0.13	7.2±0.6	2116±300	1615±230
5	Low Cu	7.1±0.1	1.37±0.11	9.2±0.7	523±40	208±48
6	High Cu	7.7±0.2	1.54±0.21	11.9±0.7	760±80	283±49
7	Low Ni	7.5±0.1	1.45±0.14	8.8±1.2	572±50	155±48
8	High Ni	7.4±0.1	1.49±0.12	8.3±0.4	541±30	111±50
9	Low Cr (low Cd)	7.3±0.2	1.37±0.11	8.6±0.8	509±40	186±36
10	High Cr (high Cd)	7.1±0.1	1.44±0.16	8.6±0.2	530±10	216±27

All treatment values are means of 4 replicate plots ± Standard Errors of Means (SEM)

The measured Zn^{2+} activities (Table 4) of the tested soils decreased with increasing soil pH. Lindsay and Norvell1, 1969; and Ma and Lindsay, 1990 reported the same trend; they found the Zn^{2+} activity in soil solution increased with decreased soil pH. A highly significant negative correlation was found between pore water free $Zn^{2+}$and soil pH ($R^2 = 0.95$; $P < 0.01$; Fig. 4). The figure shows that the Zn^{2+} activities in these soils can be predicted from the following equation:

$$Log\ (Zn^{2+}) = 6.49 - 2\ pH$$

The calculated Zn^{2+} activities varied widely among the soils, and ranged between $10^{-6.5}$ to $10^{-8.01}$ .The obtained Zn^{2+} activities were plotted on a pH-solubility diagram comprised of various Zn minerals using a -log Zn^{2+} vs. pH solubility diagram. Fig. (5) shows that the measured Zn^{2+} activities are undersaturated with respect to those maintained by $Zn(OH)_2$ (amorphous), ZnO (zincite), Zn_2SiO_4 (willemite), and $ZnCO_3$ (smithsonte). The data are very close to $ZnFe_2O_4$ (franklinite) soil-Fe solubility line, and less than that of $ZnFe_2O_4$-maghemite line. This leaves $CdFe_2O_4$ as the only known mineral that could possibly control (Zn^{2+}) activity in these soils. The Zn^{2+} activity values reported by Norvell et al (1987); Singh (1982); and Ma and Lindsay (1990), strongly suggest the $ZnFe_2O_4$ (franklinite) may control Zn activities in soils.

Our results are consistent with the hypothesis that franklinite is the solid phase controlling Zn solubility in soils.

Table (4): Equilibrium soil pH and free zinc in the tested soils.

No.	Soil pH	Log Zn^{++} (M)
1	7.21	-8.01
2	7.08	-7.92
3	6.89	-7.58
4	6.53	-6.70
5	6.27	-6.05
6	7.07	-7.58
7	6.95	-7.35
8	6.84	-7.25
9	6.64	-7.01
10	6.50	-6.50

Fig 4

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الطور الصلب المتحكم فى نشاط الزنك فى المحلول الأرضى للأراضى المعاملة مسبقاً بالحمأة

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أجريت هذه الدراسة بهدف استخدام طريقة التبادل الكاتيونى للراتنجات فى تقدير الزنك الحر $Free\ Zn^{2+}$ فى محلول التربة السابق معاملتها بالحمأة ، كذلك معرفة ما هو المعدن الأرضى المتحكم فى نشاط الزنك فى المحلول الأرضى. وقد تم الاستعانة بقيم ثوابت الدنياميكا الحرارية (Lindsay, 1979) فى رسم منحنيات ذوبان معادن الزنك المختلفة.

لذا تم إختيار ١٠ عينات (٤٠ مكرر) لتمثل أرض سبق معاملتها منذ ما يقرب من ٣٠ عاماً بالحمأة المختلفة فى محتواها من الفلزات الثقيلة (١٠ معاملات) . وأوضحت النتائج المتحصل عليها من تلك الدراسة الآتى:-

١- تراوحت القيم الكلية للزنك فى الأرض من ٨٧ إلى ٢٨٢ (بمتوسط ١٦٥) جزء/مليون والكميات المستخلصة بمحلول الـ DTPA تراوحت من ٥ إلى ٦٩ (بمتوسط ٢٣) جزء/مليون والكميات المستخلصة بمحلول NH_4NO_3 تراوحت من ٠,٣٤ إلى ٨ (بمتوسط ٢) جزء/مليون. وكان تركيز الزنك الذائب يتراوح من ٠,٤٥ إلى ٢,١١ جزء/مليون. كانت هناك علاقة إرتباط موجبة عالية المعنوية بين كل من المحتوى الكلى للزنك وكل من الكميات المستخلصة بمحلول DTPA و NH_4NO_3 والكميات الذائبة ($R^2 = 0.89$, 0.91 , 0.91 ; $P < 0.01$).

٢- تراوحت قيم الزنك الحر Zn^{2+} فى المحلول الأرضى من ٠,٠٦ – ١,٩٤ (بمتوسط ٠,٣٣) جزء/مليون والتى كانت تمثل تقريباً ٠,١٧ % من المحتوى الكلى و ١,٤٦ % من القيم المستخلصة بمحلول DTPA و ٢٥,٥ % من القيم المستخلصة بواسطة NH_4NO_3، بينما كانت تمثل تقريباً ٣٧% من الزنك الذائب فى المحلول الأرضى.

٣- كانت قيم نشاط الزنك فى هذه الدراسة منخفضة جداً حيث تراوحت من $10^{-6.05}$ إلى $10^{-8.01}$ مولر ؛ وكانت هناك علاقة إرتباط عكسية عالية المعنوية لتلك القيم مع رقم الـ pH لتلك الأراضى ($R^2 = 0.95$; $P < 0.01$) ويمكن توقع قيم نشاط الزنك فى المحلول الأرض من المعادلة الآتية:-

$$Log\ (Zn^{2+}) = 6.49 - 2pH$$

٤- أظهرت قيم نشاط الزنك الموقعة على منحنى الذوبان لمعادن الزنك المختلفة أنها كانت تحت درجة التشبع لكل من المعادن الآتية:- $Zn\ (OH)_2$, ZnO, $Zn\ CO_3$, $Zn_2\ SiO_4$. وكانت فوق درجة التشبع لمعدن الفرانكلينيت $Zn\ Fe_2\ O_4$ مما يدل على أن هذا المعدن هو المتحكم الرئيسى فى نشاط الزنك فى المحلول الأرضى.

Table (1): chemical characteristics of studied soils.

No.	Treatment	Metal concentrations	Soil				Soil Oxides (mgkg^{-1})		
			pH	C (%)	N (%)	C/N	Al	Fe	Mn
1	No sludge control		7.2±0.3	1.42±0.04	0.152±0.005	9±0.40	515±3	2730±45	209±6
2	Uncont. Sludge		7.1±0.2	1.79±0.10	0.156±0.004	11±0.45	528±11	2722±55	201±8
3	Low Zn	8000 mg Zn/ kg	6.9±0.5	1.69±0.12	0.156±0.009	11±0.33	531±9	2824±65	227±17
4	High Zn	16000 mg Zn / kg	6.5±0.3	1.74±0.06	0.160±0.003	11±0.21	545±11	2884±64	231±24
5	Low Cu	4000 mg Cu/ kg	6.3±0.4	1.76±0.07	0.167±0.005	11±0.40	643±20	3152±74	228±22
6	High Cu	8000 mg Cu/ kg	7.1±0.4	2.03±0.08	0.201±0.006	10±0.17	642±12	3138±64	225±21
7	Low Ni	2000 mg Ni / kg	7.0±0.3	1.81±0.03	0.161±0.003	11±0.08	565±10	3071±18	253±28
8	High Ni	4000 mg Ni/ kg	6.8±0.1	1.68±0.04	0.169±0.004	10±0.06	545±16	3099±109	213±7
9	Low Cr*	4400 mg Cr/ kg	6.7±0.2	1.62±0.08	0.152±0.004	11±0.26	533±11	2868±82	209±3
10	High Cr*	8800 mg Cr/ kg	6.5±0.2	1.66±0.05	0.177±0.006	9±0.07	579±17	3008±56	213±2

All treatment values are means of 4 replicate plots ± Standard Errors of Means (SEM)
*Cr sludges contaminated with Cd