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# Composted municipal waste effect on chosen properties of calcareous soil

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A b s t r a c t. A 3-year field study was conducted to assess effects of composted municipal waste on some properties, distribution of Zn, Cu in a calcareous soil and uptake of these metals by wheat. The treatments were 0, 25, 50 and 100 Mg ha<sup>-1</sup> of municipal solid waste which was applied in three consecutive years. The application of composted municipal waste increased the saturated hydraulic conductivity, the aggregate stability, the organic carbon content and electrical conductivity, whereas it slightly decreased the soil pH and bulk density. A significant increase in the concentration of Zn and Cu were observed with increasing number and rate of compost application. The distribution of Zn and Cu between the different fractions in untreated and treated soils showed that the majority of Zn and Cu were higher in grains of wheat grown in composttreated plots compared to that grown in the control plots.

K e y w o r d s: composted municipal waste, fractionation, Zn, Cu, calcareous soil

## INTRODUCTION

Soil incorporation of composted materials (like municipal solid waste, sludge) usually results in a positive effects on the growth and yield of a wide variety of crops and the restoration of ecologic and economic functions of land. Agricultural uses of compost have shown promise for a variety of field crops *eg* maize, sorghum, forage grasses and vegetables for human consumption *eg* lettuce, cabbage, beans, potatoes, cucumbers. Responses by plant systems have ranged from none to over a twofold increase in yield. Specific responses are crop and site dependent. In most cases, yields were higher when composts were applied with fertilizer management programs (Zorpas, 2008). Compost obtained from the organic fraction of municipal solid waste and from other selected waste biomasses can be used effectively as an organic fertilizer on agricultural soil. The high content of stabilized organic matter and the presence of nutrients of good quality compost are a guarantee of agronomic advantages; at the same time, the use of compost makes the reuse of organic wastes possible and has numerous advantages. An increase in soil organic matter and nutrient availability after compost application has been observed by many researchers (Hargreaves *et al.*, 2008; Price *et al.*, 2009).

Micronutrients deficiency is a widespread problem in plants grown on calcareous soils. Application of composted municipal waste (CMW) can effectively alleviate micronutrients deficiencies in plants and especially cereals grown on calcareous soils. Majority of the agricultural arid and semi-arid soils are suffering from high lime, high pH; and the low levels of organic materials. On the other hand, micronutrient deficiency especially Zn-deficiency is common on soils low in organic matter and of high pH.

Micronutrient malnutrition is a growing concern in the developing world, resulting in diverse health and social problems, such as mental retardations, impairments of the immune system and overall poor health (Cakmak, 2008; Walker and Black, 2007). Because the concentration of Zn in cereal crops is inherently very low, growing cereals on potentially Zn-deficient soils further decreases grain Zn concentrations. Zinc deficiency incidence in humans occurs predominantly in areas where soils are deficient in plant-available Zn, as shown in many Southeast Asian countries (Cakmak, 2008).

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Calcareous soils in Iran are among the most Zn-deficient soils in the world (Alloway, 2007). The Zn-deficiency problem in Iranian soils is related to low levels of plantavailable Zn concentrations caused generally by high soil pH, high CaCO<sub>3</sub>, low organic matter and low soil moisture (Karami *et al.*, 2009). Total Zn concentrations in soils lie between 17 and 125 mg kg<sup>-1</sup> and for Cu between 13 and 24 mg kg<sup>-1</sup> (Kabata-Pendias and Pendias, 2000). The average values of Cu and specially Zn in most calcareous soils in central Iran are lower than these concentrations. Amini *et al.* (2005) reported 4.6 and 16.7 mg kg<sup>-1</sup> for the average concentrations of Zn and Cu respectively, in the agricultural soils of central part of Iran. Thus incorporation of organic amendments such as composted municipal waste may correct trace elements deficiencies in plants grown on calcareous soils.

It is also reported that Cd accumulates in wheat grain under Zn-deficient conditions. Adequate Zn supply may inhibit Cd uptake by roots and re-translocation from leaves into shoot tips and seeds (Köleli et al., 2004). This inhibitory effect of an adequate Zn nutrition on grain Cd concentration is of great importance for human health because Cd has a high toxic potential for human health and environment (Cakmak, 2009). On the other hand, increased amounts of municipal solid waste has raised environmental problem for many cities in developing countries. Composting the municipal wastes may alter their undesirable properties and the application in the agricultural soils as fertilizers enables the recycling of valuable components such as organic matter and many plant nutrients such as N, P, K and micronutrients (Singh and Agrawal, 2007). Moreover, the added organic matter can improve soil physical properties such as water holding capacity, aeration and porosity (Głąb, 2008). However, repeated compost application may result in excessive concentrations of heavy metals such as Pb, Cd, Zn, Cu and Ni in soils in which can contaminate human and animal food chain (Achiba et al., 2009; Keller et al., 2001).

The use of sequential extraction techniques provides some essential information to understand the behaviour of heavy metals in soils, which includes their potential mobility, availability and assimilation by plants (Kabala and Singh, 2001). For soils and sludge, several sequential extraction techniques have previously been used (Zorpas et al., 2008). These techniques vary in the number of extracted fractions and the type and order of reagents used. Generally, reagents with increasing strength are applied sequentially. The mobility of heavy metals in soils may be assessed on the basis of their absolute and relative content in fractions weakly bound to the soils (Kabala and Singh, 2001). The total Cu and Zn content of soil provides only limited information about its potential behaviour and bioavailability. In soils, Cu and Zn is associated with various soil components in different factions, such as water soluble, exchangeable, chelated and complexed forms associated with organic matter, occluded in the sesquioxides and as part of the lattice structure of primary- and secondary-minerals. The intensities of different chemical fractions of heavy metals determine its mobility and availability to the plants differentially (Han and Banin, 2000; Kabata-Pendias and Pendias, 2000). Water soluble and exchangeable fraction(s) of heavy metals are mobile and easily available for uptake by plants, while the fraction incorporated into crystalline lattices of clays appears to be relatively inactive in terms of bioavailability to plants. The other chemical forms could be either relatively available or poorly available to plants, depending on the actual physicochemical properties of soil. Under natural conditions, the residual- and oxides bound-fractions of Cu and Zn are more abundant pools, whereas, in polluted soils, the carbonate-, hydrous oxide-associated and the residual- fractions tend to increase with time at the expense of the exchangeable and organic matter bound-fractions (Tewari *et al.*, 2009).

The addition of organic amendments to soil can contribute to metal immobilization through formation of stable complexes with OH or COOH groups on the solid surfaces of the organic polymers (Madrid *et al.*, 2007). Udom *et al.* (2004) reported that the increase of organic matter content contributes to fix the heavy metals in soils by the formation of organo-metallic complexes and therefore, decreases their mobility and their phytotoxicity. However, fresh manure and immature compost, with relatively high soluble organic matter content, may increase the metal mobility (Madrid *et al.*, 2007). Several studies have been done on plots with low compost application (Zorpas, 2008). Limited information is available on long-term repetitive effects of composted municipal waste on bioavailability and fractionation of Zn and Cu calcareous soils.

The objectives of this study were to determine the repetitive effects of 3-successive year application of composted municipal waste on:

- the distributions of Cu and Zn among different fractions of a calcareous soil,
- some physicochemical properties of a calcareous soil,
- the plant availability and concentrations of Zn and Cu in wheat.

### MATERIALS AND METHODS

The experiment was conducted at Isfahan University of Technology Research Station Site. Mean annual rainfall and temperature at the site are 140 mm and 14.5°C, respectively. The soil texture of the experimental plots was silty clay loam. Corn (*Zea mays*) was planted as spring crop, followed by wheat (*Triticum aestivum*) as winter crop. The composted municipal waste used in this experiment was obtained from a local company (Municipal Waste Treatment Plants of Isfahan, Iran). Selected chemical properties of the compost are given in Table 1.

The experimental field design was a randomized complete block with treatments arranged in split plots with three replications. Starting in November 2000, air dried compost was uniformly applied at rates of 0 (control), 25, 50, and 100 Mg ha<sup>-1</sup> (dry mass) to plots of  $15 \times 3$  m<sup>2</sup> and mixed into the

рН	EC	Total organic carbon (%)	otal anic bon (%)	OM	Р	К	Fe	Zn	Cu	Cd	Pb	Ni	Co	Mn	Cr
	$(dsm^{-1})$			(%)					(	mg kg <sup>-1</sup>	)				
7.8	14.7	15.7	1.3	26.7	3 000	7 318	14 215	217	160	4.5	148.5	48	13	335	0.5

T a b l e 1. Chemical properties of the composted municipal waste

T a ble 2. Layout of treatments and CMW application doses in different years of research

Treatment $(Mg ha^{-1})$	2000	2001	2002	Total amount of CMW applied	Sampling: years after last application
25	25	0	0	25	3
25×2	25	25	0	50	2
25×3	25	25	25	75	1
50	50	0	0	50	3
50×2	50	50	0	100	2
50×3	50	50	50	150	1
100	100	0	0	100	3
100×2	100	100	0	200	2
100×3	100	100	100	300	1
Control	0	0	0	0	-

topsoil (20 cm depth). To study not only cumulative, but also residual effects, applications were discontinued in subsequent years on part of the area to which compost had been applied in the preceding year. Thus, in second year (November 2001), each plot was divided into two subplots ( $9 \times 3$  and  $3 \times 3$  m), and CMW was applied only to the larger subplot, using the same dosage as in the first year. In the third year (November 2002), the same compost dosages were applied on twothirds (6×3 m) only. As a result, total CMW dosages were, 25, 50 and 100 Mg ha<sup>-1</sup> for single applications, 50, 100 and 200 Mg ha<sup>-1</sup> for two applications, 75, 150 and 300 Mg ha<sup>-1</sup> for three years of compost applications. In addition, a control plot was prepared and treated in the same way as the others, except that no composted municipal waste was applied. Thus, there were 10 treatments in total, with different numbers and rates of CMW applications (Table 2).

During the experimental period, wheat (*Triticum aesti-vum*) was planted as a winter crop and was irrigated using border irrigation system as needed. Wheat grains and stems were harvested at the end of June 2003. In 2003, after the wheat had been harvested, five soil cores (0-20 cm depth) were taken from each subplot and were mixed to make a composite sample and then stocked in plastic bags. Soil samples were air-dried, sieved (2 mm), and analyzed for pH, cation exchange capacity (CEC), electrical conductivity (EC) in soil saturation extracts and organic carbon by standard methods (Baruah and Barthakur 1997).

Dry bulk density (the core method), saturated hydraulic conductivity (the constant head method) and aggregate stability (the wet-sieving method) were determined (Baruah and Barthakur, 1997).

Stalks and grains were separated and washed by distilled water, dried at 65°C for 48 h to a constant mass for determination of the Zn and Cu concentrations. Total Zn and Cu in plant stalks and grains were determined by AAS after digestion with a solution of 70% *aqua regia* (HNO<sub>3</sub> + concentrated HCl) and 30% H<sub>2</sub>O<sub>2</sub> (Benton Jones, 2001).

Chemical fractionations of Zn and Cu in soils collected after the field trial were investigated using the procedure of Salbu *et al.* (1998). It subdivides the metals into six operationally defined fractions (Table 3):

- 1. the water-extractable fraction, which is assumed to contain soluble heavy metals,
- 2. the NH<sub>4</sub>OAc-extractable fraction at pH 7, which is assumed to recover exchangeable heavy metals,
- 3. the NH<sub>4</sub>OAc-extractable fraction at pH 5, which is assumed to recover specifically sorbed and carbonate bound heavy metals,
- 4. the hydroxylamine (NH<sub>2</sub>OH HCl)-extractable fraction, which includes metals sorbed or occluded mainly on iron and manganese oxides,
- the H<sub>2</sub>O<sub>2</sub>-extractable fraction assumed to retain metals complexed by OM and released after OM oxidation,

6. the HNO<sub>3</sub> (7 *M*)-extractable fraction, which is called residual form, in which crystalline minerals are dissolved and metals constituting the lattices are solubilise.

A brief description of the sequential extraction procedure is presented in Table 3. Two grams of soil were weighed and placed in a 50-ml polycarbonate centrifuge tube. All the solid phases, except the residual form were washed with 10 ml of water before the next extraction step. The washes were collected and analyzed with supernatant from the previous fraction. After each extraction, supernatant was separated by centrifugation for 30 min at 10 000×g. To verify the sum of sequential extractions, the total concentration of Cu, and Zn was determined after digestion with 0.1 mol *aqua regia*. Concentrations of Cu, and Zn in each extract were measured by flame atomic absorption spectrometry (Perkin Elmer Spectra AA 220 FS). An analysis of variance was used to test significance ( $P \le 0.05$ ) of treatment effects and Duncan multiple range test ( $P \le 0.05$ ) was used to compare the means (SAS, 2002).

## RESULTS AND DISCUSSION

Selected soil physicochemical properties after compost applications are shown in Table 4. Soil pH gradually decreased with the application of compost. This may be due to degradation of organic matter and releasing of organic and inorganic acids such as carbonic, citric and malic acids as well as  $H^+$  produced from mineralization of nitrogen in the organic matter (Habteselassie *et al.*, 2006). Mohammad and Athamneh (2004) and Achiba *et al.* (2009) reported the decrease of soil pH from 8.2 in a control treatment to 7.2 after application of compost.

T a b l e 3. Sequential extraction procedure used in the experiment

Step	Fractions	Procedure
1	Water-soluble metals	2 g soil sample extracted with 20 ml of deionized water for1 h (20°C, on rolling table)
2	Exchangeable	Residue from step 1 extracted with 20 ml of 1 M $\rm NH_4OAc,pH$ 7 for 2 h
3	Carbonate bound	Residue from step 2 extracted with 20 ml of 1 M $\rm NH_4OAc,pH$ 5 for 2 h
4	Fe and Mn oxide bound (occluded)	Residue from step 3 extracted with 20 ml of 0.04 M $\rm NH_2OH.HCl$ in 25% HOAc for 6 h (water bath 60°C)
5	Organic	Residue from step 4 extracted with 15 ml of $30\%$ H <sub>2</sub> O <sub>2</sub> at pH 2 (adjusted with HNO <sub>3</sub> ) for 5.5 h (water bath $80^{\circ}$ C). After cooling, 5 ml of 3.2 M NH <sub>4</sub> OAc in 20% HNO <sub>3</sub> was added, sample was shaken for 30 min, and finally diluted to 20 ml with water
6	Residual	1 g of the residue from step 5, after drying, was digested in a conical flask with 10 ml of 7 M $HNO_3$ on a hot plate for 6 h. After evaporation, 1 ml of 2 M $HNO_3$ was added, and the residue after dissolution was diluted to 10 ml

T a ble 4. Selected physicochemical properties of soils (0-25) in control and after 1, 2 and 3 years application of composted municipal waste

Treatment	Bulk density (g cm <sup>-3</sup> )	Aggregate stability (%)	Ksat. $(\text{cm h}^{-1})$	OC (%)	EC (dS m <sup>-1</sup> )	pН
Control	1.41a	5.5f	0.7d	0.5h*	1.6k	8.3a
25(1)**	1.35b	7.8d	0.8d	0.7g	1.7i	8.1a
25(2)	1.37b	6.9e	2.1c	0.8e	1.9e	8.1a
25 (3)	1.35b	7.0e	2.1c	0.8e	2.1d	8.1a
50(1)	1.32c	10.7b	0.85d	0.8f	1.8g	8.3a
50(2)	1.35b	7.1e	2.5b	0.8e	3.38b	7.9a
50 (3)	1.34b	7.8d	2.2c	1.4c	1.9f	7.7a
100(1)	1.31c	15.1a	2.1c	0.98d	1.7hi	8.4a
100(2)	1.32c	7.8d	3.1a	1.45b	3.86a	7.5a
100(3)	1.32c	8.1c	3.2a	2. 5a	2.5c	7.8a

<sup>1</sup>Saturated water conductivity, \*values with the same letters are not significantly different from each other according to Duncan LSD at  $P \le 0.05$ , \*\*numbers in the parenthesis indicate the consecutive years of compost application.

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Fig. 1. Distribution of Zn among six fractions in different treatments, a - 2000, b - 2001, c - 2002.

Electrical conductivity (EC) of amended soils increased with increasing amounts and numbers of compost applications (Table 4). The highest EC was observed in plots which received 100 Mg ha<sup>-1</sup> of compost two consecutive years. However, the increase soil EC in all the treatments was lower than the critical value for wheat production. Electrical conductivity was lower in treatments that received 3 successive years of CMW as compared to those successively received CMW for 2 years. It is likely due to crop uptake and leaching of solutes overtime (Zhang *et al.*, 2006).

Addition of compost significantly increased soil organic carbon (Table 4). Organic carbon (OC) content increased from 0.5 % in control to 2.5% after three successive years

application 100 Mg ha<sup>-1</sup> of compost. Increasing the soil organic carbon content improves soil physical characteristics, such as soil water retention and movement, soil structure and porosity, and favours the establishment of carbon cycling and also enhances fixation of toxic heavy metals in soils by the formation of insoluble organo-metallic complexes and therefore, it decreases their mobility and phyto-toxicity (Achiba *et al.*, 2010; Zare *et al.*, 2010).

The application of compost significantly reduced soil bulk density and increased saturated hydraulic conductivity and aggregate stability percentage for all the treatments (Table 4). The decrease in bulk density may be to the dilution effect of adding less dense organic matter to more dense mineral fraction of the soil and also to increased soil aggregation (García-Orenes *et al.*, 2005). The concurrent increase in hydraulic conductivity and aggregate stability percentage due to organic materials added into the soil is also supported by other studies (Franzluebbers, 2002; Zare *et al.*, 2010). According to Franzluebbers (2002), soil organic matter as a key index of soil quality impacts soil aggregation and accordingly increases hydraulic conductivity.

A significant increase in total Zn and Cu concentrations were observed with increasing number and rate of compost application. The highest increase in total Zn and Cu occurred in the treatments 100 Mg ha<sup>-1</sup> compost application. Three consecutive years application of 100 Mg ha<sup>-1</sup> compost increased total-Zn and -Cu more than twice relative to the respective fractions in the unamended soil.

This could be attributed to relatively high contents of Zn  $(217 \text{ mg kg}^{-1})$  and Cu  $(160 \text{ mg kg}^{-1})$  in the applied compost. However, the total Zn and Cu concentrations in soils of all treatments remained in the ranges of the respective limits of maximum acceptable concentrations (MAC<sub>Zn</sub>=150-300 mg kg<sup>-1</sup> and MAC<sub>Cu</sub>=50-140 mg kg<sup>-1</sup>) in agricultural soils for these metal in European Communities (Kabata-Pendias and Pendias, 2000). Zinc was mainly in the residual form (72%) in the unamended treatment (Fig. 1). Zinc distribution in the

unamended treatment was in the order of: RES (72%)> Fe and Mn oxides bound (8.6%)>ORG (7.2%)>CAR (1.2%)> EXCH (0.79%)>DIS (0.02%). Compost application significantly changed Zn distributions in all the forms as compared with the control treatment. The water-soluble fraction is readily mobile and easily available to plants but less than 0.15% of Zn was in this form. This is attributed to high soil pH and calcareous properties of the soil. Moreover, no significant differences noticed in water soluble-Zn with increasing the rate of compost application. The exchangeable form of Zn was in the range of 0.60-1.4% of the total Zn after the additions of different rates of the compost. Only 3 consecutive years application of 100 Mg ha<sup>1</sup> of compost significantly increased the exchangeable forms as compared to the control treatment. Similar finding was observed by Shuman et al. 2001 who related this behaviour to increasing of soil CEC after application of compost.

A slight increase in the carbonated -Zn was observed with increasing rate and number of compost application (Table 5). The highest percentage of carbonated -Zn was found in the plots with 3 times application of 100 Mg ha<sup>-1</sup> of compost. This was because of the reaction of Zn with  $CO_2$  as results of increasing of microbial activity in the higher applied compost.

**T a ble 5.** Fractionations of Zn and Cu in soil in control and after 1, 2 and 3 successive years application of compost at different rates (25, 50 and 100 Mg  $h^{-1}$ ). Results are expressed on soil dry mass basis

	Control	25(1)**	25(2)	25(3)	50(1)	50(2)	50(3)	100(1)	100(2)	100(3)
$Zn (mg kg^{-1})$										
Water soluble	Nd	$0.2^{ab^{*}}$	$0.2^{ab}$	$0.2^{ab}$	$0.2^{ab}$	$0.2^{ab}$	$0.2^{ab}$	0.25 <sup>a</sup>	$0.2^{ab}$	0.25 <sup>a</sup>
Exchangeable	$0.7^{cd}$	0.6 <sup>d</sup>	0.75 <sup>cd</sup>	$0.7^{cd}$	0.7 <sup>cd</sup>	$0.8^{bcd}$	1.1 <sup>bc</sup>	$0.7^{cd}$	$0.8^{bcd}$	2.7 <sup>a</sup>
Carbonated	1.1 <sup>d</sup>	1.1 <sup>d</sup>	1.2 <sup>cd</sup>	1.4 <sup>cd</sup>	1.2cd	1.3 <sup>cd</sup>	2.6 <sup>b</sup>	1.5 <sup>cd</sup>	1.7 <sup>c</sup>	3.5 <sup>a</sup>
Fe and Mn oxides bound	7.6 <sup>f</sup>	12.5 <sup>def</sup>	16.6 <sup>cde</sup>	15.4 <sup>def</sup>	15.3 <sup>cd</sup>	20.4 <sup>cd</sup>	32.6 <sup>b</sup>	19.8 <sup>cd</sup>	24.2 <sup>c</sup>	81.0 <sup>a</sup>
Organic	14.1 <sup>g</sup>	$19.5^{\text{def}}$	22.4 <sup>cde</sup>	24.7 <sup>cd</sup>	$20.6^{\text{def}}$	24.1 <sup>cd</sup>	31.0 <sup>b</sup>	19.2 <sup>def</sup>	28.3 <sup>bc</sup>	43.4 <sup>a</sup>
Residual	64.4 <sup>a</sup>	65.3 <sup>a</sup>	69.6 <sup>a</sup>	68.6 <sup>a</sup>	68.3 <sup>a</sup>	64.0 <sup>a</sup>	72.0 <sup>a</sup>	66.6 <sup>a</sup>	$70.0^{a}$	65.2 <sup>a</sup>
Total	$87.9^{\mathrm{f}}$	99.2 <sup>def</sup>	110.7 <sup>cd</sup>	110.8 <sup>cd</sup>	106.3 <sup>de</sup>	110.8 <sup>cd</sup>	139.5 <sup>b</sup>	108.1 <sup>cd</sup>	125.2 <sup>bc</sup>	200.7 <sup>a</sup>
					Cu (mg kg	-1)				
Water soluble	0.2 <sup>d</sup>	$0.2^{d}$	0.25 <sup>cd</sup>	0.25 <sup>cd</sup>	$0.2^d$	0.25 <sup>cd</sup>	0.25 <sup>cd</sup>	0.25 <sup>cd</sup>	0.5 <sup>b</sup>	$0.8^{a}$
Exchangeable	0.66 <sup>g</sup>	1.8 <sup>b</sup>	1.55 <sup>bc</sup>	1.35 <sup>cd</sup>	$1.1^{\text{def}}$	$1.3^{cde}$	1.65 <sup>bc</sup>	1.3 <sup>cde</sup>	1.9 <sup>b</sup>	2.7 <sup>a</sup>
Carbonated	1.57 <sup>c</sup>	1.85 <sup>bc</sup>	1.8 <sup>bc</sup>	2.45 <sup>ab</sup>	1.45 <sup>c</sup>	1.45 <sup>c</sup>	$2.1^{abc}$	1.5 <sup>c</sup>	2.05 <sup>abc</sup>	2.8 <sup>a</sup>
Fe and Mn oxides bound	5.4 <sup>ab</sup>	5.7 <sup>ab</sup>	6. 2 <sup>ab</sup>	7.8 <sup>ab</sup>	6.3 <sup>ab</sup>	6.7 <sup>ab</sup>	7.3 <sup>ab</sup>	6.4 <sup>ab</sup>	7.3 <sup>ab</sup>	7.9 <sup>a</sup>
Organic	$9.9^{\mathrm{f}}$	$15.4^{\text{def}}$	16. 8 <sup>def</sup>	22.7 <sup>cd</sup>	$13.4^{def}$	19. 7 <sup>de</sup>	29.3 <sup>bc</sup>	$15.4^{def}$	33.7 <sup>b</sup>	54.3 <sup>a</sup>
Residual	36.2 <sup>cd</sup>	$40.8^{bcd}$	43.6 <sup>abcd</sup>	47.8 <sup>abc</sup>	$43.4^{abcd}$	41.9 <sup>bcd</sup>	49.8 <sup>ab</sup>	43.9 <sup>abcd</sup>	50.8 <sup>ab</sup>	54.1 <sup>a</sup>
Total	54.0 <sup>de</sup>	65.6 <sup>cde</sup>	69.7 <sup>cd</sup>	82 <sup>bc</sup>	65.6 <sup>cde</sup>	70.6 <sup>cd</sup>	90.4 <sup>b</sup>	68.7 <sup>cde</sup>	95.9 <sup>b</sup>	122.6 <sup>a</sup>

\*All the values are means of three replicates, values at the same line for the same sample followed by the same letter are not significantly different at  $P \le 0.05$ , Nd-below detection limit; \*\*numbers in the parenthesis indicate the consecutive years of compost application.

The application of compost increased Zn bound to Fe and Mn oxides significantly from 8.6% in the control to 12.6-15, 14.3-23.3, and 18.3-41% after application of 25, 50 and 100 Mg ha<sup>-1</sup> of compost, respectively. Application of 25, 50 and 100 Mg ha<sup>-1</sup> compost significantly increased the organic form of Zn by 10-12.6, 10-15.9 and 9.8-22.4% of total Zn, respectively. This probably is due to the higher amounts of organic carbon (OC) in soils treated with compost than with control (Table 4). The OC content encouraged the formation of stable organo-metallic complexes that could decrease the solubility of the metal ions in the soil (Udom *et al.*, 2004). Similar results were reported by Mohamed *et al.* (2010). These authors found that organic matter

fixed most of the Zn and that the Zn concentration associated with organic matter increased significantly with the application rate of organic amendments.

The majority of Zn was found in the residual form. On the average about 64, 59 and 49% of total Zn was in the residual form in 25, 50 and 100 Mg ha<sup>-1</sup> compost treatments, respectively. The percentage of Zn present in residual form decreased with increasing of the rate and number of compost application indicating tendency of Zn to become available with time. The highest percentage of residual Zn was recorded in control treatments, whereas the lowest values were found in treatments which received 3 consecutive years of 100 Mg ha<sup>-1</sup> of compost.



Fig. 2. Distribution of Cu among six fractions in different treatments, a - 2000, b - 2001, c - 2002.

Overall distribution of Zn in different fractions was in the sequence residual > Fe and Mn oxides bound > organic >carbonated> exchangeable > water soluble. This series was similar to a study on calcareous soil in Tunisia (Achiba *et al.*, 2009).

Copper distribution in the unamended soil was in the following order: residual (67%) > Fe and Mn oxides bound (10.9%) > organic (18.3%) >carbonated (2.9%) > exchangeable (1.2%) > water soluble (0.37%). Compost application significantly increased Cu in all the forms as compared with soil in the control treatment (Table 5).

The lowest percent of Cu was in the water soluble form. Low and moderate levels of compost did not increase the water soluble forms of Cu in comparison with control. While, the total Cu concentration in treatments that received two and three successive years of 100 Mg ha<sup>-1</sup> of compost were 2 and 4 times higher than in unamended soils (control).

The application of compost significantly increased exchangeable Cu both in absolute (Table 5) and relative amounts (Fig. 2) as compared to the control soil. The addition of composted municipal waste had not significant effects on the carbonated fraction of Cu (Table 5). Our results differed from those reported by Achiba et al. (2009), who found that the application of composted municipal wastes significantly increased carbonated fraction of Cu. Although, the addition of compost had no significant effects on Cu bound to Fe and Mn oxides, the relative amounts of this fraction decreased from 11% in control soil to 6% in treatments which received three successive years of 100 Mg ha<sup>-1</sup> of compost (Fig. 2c). This may be due to redistribution of Zn from this form to organic and exchangeable forms. Among the fractions, the organic fraction showed the highest changes. Application of compost increased the organic fraction from 18% in the control to 44% in the plots that received 3 times compost in the rate of 100 Mg ha<sup>-1</sup>. This is related to the higher amounts of OC in soil treated with compost (Table 4). Because of the high affinity of organic compounds for Cu, the increase soil OM content encouraged the formation of stable organic complexes with Cu in compost treated soils. These results are similar observation of other researchers who have reported

the application of composted sewage sludge increased Cu in organic fraction (Achiba *et al.*, 2010; Mohamed *et al.*, 2010).

Similar to Zn, Cu was mainly found in the residual form. On the average about 64, 58 and 52% of total Cu was in the form of residual for the soils amended with 25, 50 and 100 Mg ha<sup>-1</sup> of compost, respectively. The percentage of Cu present in residual form decreased with increasing of the applied compost levels indicating redistribution of Cu to organic and exchangeable forms. In contrast to organic form, the highest percentage of residual Cu was in control treatment (67%), whereas the lowest values were found in the treatments which received 3 consecutive years of 100 Mg ha<sup>-1</sup> of compost (44.2%). In general, distribution of Cu in different fractions of amended soils was in the sequence residual > organic > Fe and Mn oxides bound >carbonated > exchangeable > water soluble.

The levels of Zn and Cu were greater in grain of wheat grown in compost-treated plots compared to that grown in the control plots (Table 6). However, no trends with compost application rate and time were observed for metal concentrations of grains. This may be due to high grain yield produced by compost application and consequently dilution of metals in grain tissue. Copper concentrations in stalk were lower in wheat grown in compost-treated plots compared to that grown in the control plots. Except for treatments of  $25 \times 1$  and  $100 \times 3$  Mg ha<sup>-1</sup> of compost application, similar findings were observed for Zn concentrations in wheat stalk.

Zinc and Cu concentrations of grains in plants grown on control soil were 25.6 mg kg<sup>-1</sup> and 4.3 mg kg<sup>-1</sup>, respectively. These values were in border range of Zn- and Cu-deficiency (10-20 and 2-5 mg kg<sup>-1</sup> for Zn and Cu, respectively). While on the soils with compost application, grain concentrations of these metal were in the range of sufficiency (27-150 and 5-30 mg kg<sup>-1</sup> for Zn and Cu, respectively).

There were no significant differences in Zn and Cu concentrations of grains among plants grown on 25, 50 and 100 Mg ha<sup>-1</sup> of compost (Table 6). These results indicate the importance of applying low levels of compost in order to improve grain Zn and Cu concentrations.

T a b l e 6. Means of metals concentrations (mg kg<sup>-1</sup>) in wheat grains and stalks

Treatment	Control	25(1)**	25(2)	25(3)	50(1)	50(2)	50(3)	100(1)	100(2)	100(3)
					Zn (mg kg	g <sup>-1</sup> )				
Grain	25.88 <sup>bc*</sup>	32.0 <sup>ab</sup>	30.0 <sup>ab</sup> c	28.0 <sup>abc</sup>	28.7 <sup>abc</sup>	28.0 <sup>abc</sup>	30.0 <sup>abc</sup>	30.0 <sup>abc</sup>	27.3 <sup>bc</sup>	34.3 <sup>a</sup>
Stem	16.0 <sup>cd</sup>	20.3 <sup>ab</sup>	13.3 <sup>de</sup>	13.0 <sup>de</sup>	14.7 <sup>cd</sup>	15.0 <sup>cd</sup>	14.5 <sup>cd</sup>	14.0 <sup>cd</sup>	15.0 <sup>cd</sup>	22.7 <sup>a</sup>
					Cu (mg kg	g <sup>-1</sup> )				
Grain	4.3 <sup>cd</sup>	9.3 <sup>ab</sup>	11.3 <sup>a</sup>	7.0 <sup>bcd</sup>	7.0 <sup>bcd</sup>	$5.5^{bcd}$	5.5 <sup>bcd</sup>	6.6 <sup>bcd</sup>	6.3 <sup>bcd</sup>	$8.0^{abc}$
Stem	4.0 <sup>a</sup>	1.7 <sup>b</sup>	1.7 <sup>b</sup>	0.7 <sup>b</sup>	0.3 <sup>b</sup>	$0.7^{b}$	$1.0^{ab}$	1.7 <sup>b</sup>	1.3 <sup>b</sup>	$4.0^{a}$

\*Values at the same row with the same letters are not significantly different from each other according to Duncan test at  $P \le 0.05$ , \*\*numbers in the parenthesis indicate the consecutive years of compost application.

In general, from the plant nutrition point of view, this study showed that application of very high rates of compost over consecutive years may not be needed to correct Zn- and Cu-deficiency problem under field conditions. In addition, it is well documented that soil applied compost has an important residual effect on growth and yield of the next crops in cropping sequence. Our study showed that that application of compost can be effective in the soil up to 2-3 years for correcting Zn deficiency and improving yield. This residual effect of compost could be a very important in the cropping systems.

From the environmental implication point of view, although the Zn and Cu contents in the soil after 3 successive years application of compost were not high enough to classify the soil as polluted, effects of compost application on accumulation of toxic metals such as Cd and Pb in soils should be considered.

#### CONCLUSIONS

1. Application of the composted municipal waste increased the saturated hydraulic conductivity, the aggregate stability, organic carbon content and the electrical conductivity, whereas it slightly decreased the soil pH and bulk density.

2. A significant increase in the concentration of Zn and Cu were observed with increasing number and rate of compost application.

3. The distribution of Zn and Cu between the different fractions in untreated and treated soils showed that the majority of Zn and Cu were in the residual form.

4. Overall distribution of Zn in different fractions was in the sequence residual > Fe and Mn oxides bound > organic > carbonated > exchangeable > water soluble. Copper fractionations were similar to the one found for Zn, with the exception of organic form which was second after residual form.

5. The levels of Zn and Cu were higher in grains of wheat grown in compost-treated plots compared to that grown in the control plots.

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