Asian Journal of Chemistry

Heavy Metals Distributions and Uptake in Field-Grown Maize after Application of Sewage Sludge in Soil of South Eastern, Iran

MARYAM VARAVIPOUR*, SAEID GIVEHCHI[†] and MAHMOUD MASHAL Faculty of Soil and Water, University of Tehran, Tehran, Iran E-mail: daneshpajooh1@yahoo.com

The use of toxic metals in sewage sludge's applied to agriculture land in Iran to improve crop nutrition as well as to illustrate the metal behaviour in soils and plant up take is difficult to generalize, because it is strongly dependent on the nature of the metal sludge, soil properties and crop. Two year's field study was performed to evaluate heavy metal accumulation in the maize crop growing on clay-loam soil amended with waste water, to determine heavy metal up take and distribution in maize plants grown in this soil.

Key Words: Wastewater, Heavy metal, Accumulation, Forage corn.

INTRODUCTION

Cadmium and lead could possibly pose of risk to human health because of their toxicity and application of sewage sludge has been practised for decades. Sludge acts as soil conditioner to facilitate nutrient transport, increase water retention and serves as a partial replacement for expensive chemical fertilizers¹.

Recycling sewage sludge in agriculture has resulted in accumulation of heavy metals in soils, specially, cadmium, lead, chromium, copper, nickel and zinc and mainly when the residue is originated from industrial areas²⁻⁴. This practice pollutes the soil and water resources and causes toxicity to crops, animals and humans through the tropic chain⁵.

Soil pollution by heavy metals is also become a critical environmental concern due to it potential adverse ecological effects, Heavy metals occur naturally at low concentration in soils. However, they are considered as soil contaminants due to their widespread occurrence acute and toxicity. Among the heavy metals, cadmium is of special concern due to its relatively high mobility in soils and potential toxicity to biota at low concentrations⁶.

[†]Urban and Environmental Planning, University of Tehran, Tehran, Iran.

Asian J. Chem.

Madyiwa *et al.*⁷ established that the grass absorbed lead and cadmium way beyond the 40 mg/kg and 1 mg/kg limits (respectively) recommended for pasture grass. The addition of both lead and cadmium increased the levels of both metals in American Sycamore over uptake observed with single metals added⁸.

Sewage-sludge has been used as a source of nutrients for plant growth and as soil conditioner to improve physical properties in many countries⁹⁻¹¹. However land application of sewage-sludge has been limited by its enriched pathogens and heavy metal content¹². Excess levels of heavy metals introduced to soil by sewage sludge can lead to elevated uptake of heavy metals by plants, which will case damage to plants and affect human health. To reduce the availability of heavy metals in sewage-sludge is therefore one of the major concerns in land application of sewage-sludge.

McGrath and Cegarra¹³ observed that after 20 years of the application of sludge in a soil, 70 % of the organic matter was already decomposed and relatively constant percentage of metals (cadmium, chromium, lead, nickel and zinc) extracted from soil fractions was found. Other authors have reported a decrease on metal availability with time¹⁴.

These studies were followed by field experiment tests in an inert medium to assess the effects of sludge on maize seedling. The nutrient and heavy metal concentration were also monitored in the soil and maize. The present research aimed at studying the effects of sewage sludge application, in a long-term field experiment on the accumulation of heavy metals in the soil and their availability to maize crop.

EXPERIMENTAL

Experiments were done at Aboureyhan campus research farm located in pakdasht, 25 km southeast of Tehran at 35° 28' N, 51° 41' E, 1021 m above sea level at summer season of 2005 when corn cropped. The climate of the site may be defined as arid and semiarid with an annual rainfall about 180 mm. The soil texture is loamy in the upper 90 cm. The experiments were performed in complete completely blocks designs with 4 treatments.

Sewage sludge used in the study obtained from mechanical biological sewage treatment plants located in Pakdasht and was anaerobically digested.

The sludge was chemically characterized yearly and the main physical and chemical characteristics of the soil and sewage sludge added to the soil are presented in the Tables 1 and 2. The analysis has been performed by the following procedure: 1.000 g samples were digested with 50 mL of 4 mol L^{-1} HNO₃ solution, at 180 °C, for 1 h. The digested samples kept at room temperature and the volume was adjusted to 50 mL with deionized water and filtered through filter paper. The filtered digested solutions were analyzed for potassium by flame photometry; phosphorus by the vanadomolybdate spectrophotometer method. Ca, Mg, Fe, Cu, Ni, Mn and Zn have been analyzed by atomic absorption spectrophotometry.

The total nitrogen concentration in sludges was determined by the micro-Kjeldhal method and the total carbon by oxidation of organic matter using 0.17 mol L⁻¹ potassium dichromate solution and titration of the excess bichromate with a 0.5 mol L⁻¹ ferrous ammonium sulfate solution, using diphenylamine as indicator¹⁵. Cadmium and lead were also determined by atomic absorption spectrofotometry, but their total contents were below the detection limit (< 0.01 mg Kg⁻¹).

Trials were set up in a totally randomized, complete blocks design. The sludge was applied in each band at rates:

Treatment including: (a) application of effluent (W_1); (b) application of 2/3 of effluent and 1/3 of sludge (W_2); (c) application of 1/3 of effluent al 2/3 of sludge (W_3); (d) application of only sludge;

In a single application and 40, 60 and 80 Mg ha⁻¹ split in two, three and four equal yearly applications, respectively. Each experimental unit consisted of 42 m² plots, with six rows (7 m length, 1 m spacing) cultivated with maize, the central rows used at harvest (10 m²) for plant yield evaluations.

The sewage sludge was applied by hand and in corporated into the soil in the 15 cm depth layer, during October 1983. The plots corresponding to the split doses of sludge, received new applications in 1984 and 1985. The band of each plot treated with lime, received two applications of 6.0 and 3.5 Mg ha⁻¹ calcinated lime (43.8 % CaO and 27.2 % MgO) to rise base saturation to 70 %, during October 2003 and September 2004. All plots received a P-K fertilization consisting of 100 kg P₂O₅ ha⁻¹ as simple superphosphate and 60 kg K₂O ha⁻¹ as potassium chloride, applied to rows before sowing.

Soil samples (ten subsamples) were taken during the two planting years from each treated plot after harvest. Soil samples were analyzed for pH (CaCl₂ 0.01 mol L⁻¹); Cu, Ni, Zn concentrations in extracts obtained with DTPA¹⁶. The total heavy metals were determined by AOAC methods¹⁷ and DTPA-extractable metals by the Lindsay and Norvell method¹⁶. An atomic absorption spectrophotometer with single-element cathode lamps was used for analysis of heavy metals. Duplicate samples were run and mean values are reported¹⁸. Copper, nickel and zinc concentrations present in leaf were determined by atomic absorption spectrometry.

Total contents of heavy metals in maize plants were estimated from concentration and dry matter yield data of shoots and grain. The total dry matter and grain yield data was obtained at harvest, using all plants from the central rows of each plot.

The effects of sewage sludge on the extractable metal concentrations and the total-metal concentrations in the soil samples were interpreted on

the basis of the polynomial regression analysis for the data obtained in the treatments correspondent to the doses of sludge in a single application at the beginning of the field experiments.

RESULTS AND DISCUSSION

From Table-1, it is inferred that the texture of soil is loamy sand. The percentage of $CaCO_3$ is 24.8 and low amount of total organic carbon and total nitrogen. High available of phosphorus is showed and value of the others element is in the normal rate (Table-1).

TABLE-1 PHYSICAL AND CHEMICAL PROPERTIES OF SOIL

Dropartias	Value	Dropartias	Valua
Flopenties	value	Flopenies	value
Coarse sand $(2 - 0.2 \text{ mm})$ (%)	62.33	P (mg/kg)	32.90
Fine sand $(0.2 - 0.05 \text{ mm})$ (%)	17.00	K (mg/kg)	4.10
Silt (0.2 – 0.05 mm) (%)	4.83	Fe (mg/kg)	4.20
Clay (< 0.002 mm) (%)	8.83	Zn (mg/kg)	2.80
Texture	Loamy Sand	Mn (mg/kg)	4.30
pH (H ₂ O 1: 2.5)	7.80	Cu (mg/kg)	2.10
$CaCO_{3}(\%)$	24.80	Pb (mg/kg)	1.95
Total organic C (%)	28.40	Cd (mg/kg)	0.08
Total nitrogen (%)	1.90	Ni (mg/kg)	0.42
		Cr (mg/kg)	0.12

Table-2 presents physical and chemical properties of sewage slude added to the soil. From Table-2, it is inferred that zone of study has alkaline pH. Appreciable of organic matter and total nitrogen and low level of phosphorus and potassium.

TABLE-2 PHYSICAL AND PERTIES CHEMICAL PROPERTIES OF S AND EWAGE SLUDE ADDED TO THE SOIL

Property	Value	Property	Value
pН	7.50	Mn (mg/kg)	95.22
EC (ds/m)	4.32	Cu (mg/kg)	325.20
OM (g/Kg)	338.00	Pb (mg/kg)	162.20
N (g/Kg)	18.20	Cd (mg/kg)	9.20
Fe (g/Kg)	812.40	Ni (mg/kg)	82.60
Zn (mg/Kg)	8.25	Cr (mg/kg)	62.80

Total organic carbon and nitrogen contents in the control at 1st year were higher that those in control in 2nd year (Table-3). This result showing the accumulation of partially decomposed plant debris in the surface layer, while at 2nd year plant debris was removed leaving the surface bare. The Vol. 21, No. 1 (2009) Heavy Metals Uptake in Maize after Application of Sewage Sludge 27

high C/N ratio is found in 2nd year of experiment. The application of (W_3) significantly increase in carbon relative to (W_1) . In term of total nitrogen, the effect of sludge application was only significant at 1st year. Where all three rate sludge treatments had higher soil nitrogen levels compared to W_1 .

$W_4 = ONLY SLUDGE$				
Years	Sludge	Total organic C (%)	Total N (%)	C/N
	\mathbf{W}_1	0.80	0.09	14.2
First year	W_2	1.90	0.18	13.8
	W_3	1.80	0.18	9.8
	\mathbf{W}_4	1.50	0.13	10.4
Second year	\mathbf{W}_1	1.70	0.90	17.6
	W_2	2.10	0.13	13.2
	W_3	3.20	0.27	15.8
	W_4	2.50	0.18	13.2

TABLE-3 ORGANIC CARBON, NITROGEN AND C/N RATIO FOR THE DIFFERENT TREATMENTS (W_1 = CONTROL (EFFLUENT), W_2 = 2/3 OF EFFLUENT OF + 1/3 OF SLUDGE, W_3 = 1/3 OF EFFLUENT + 2/3 OF SLUDGE, W_4 = ONLY SLUDGE

With a few exceptions, the mean distribution of heavy metals in the various plant parts (roots, stalks, leaves and grains) was constant and it was the same in plants grown both in treated and untreated plots. Copper and zinc, which are common micronutrients for the plants, were found in all plant parts and although the quantity absorbed by the plants from treated plots mwas higher, their distribution was uniform in all plants.

Of the phototoxic heavy metals (nickel, chromium and lead) studied, nickel is the most mobile although in present studies it was not detected in the grains. Chromium and lead are less mobile and accumulated exclusively in the root tissues. Only in the last 3 years of the experiment, traces of lead was also found in the stalks.

Tables 4-7 shows the heavy metal concentrations in the whole corn plant grown in amended and unamended plots. The mean whole corn plant weight shows a significant increase in the treated plots as early as the first year of application. Heavy metal concentrations in plants grown in amended soil were significantly higher than in the controls for varying periods.

Because lead is the limiting factor for safe urban waste compost application to agriculture, it seemed useful to determine whether or not lead mobility within the corn plant could be enhanced in the presence of massive quantities of lead from repeated soil treatments with urban waste compost.

Corn yield and cumulative yield efficiency of maize significantly increased with sludge addition in this study. This result may be attributed

Asian J. Chem.

TABLE-4 DISTRIBUTION OF HEAVY METALS IN ROOT OF MAIZE PLANT (%)

Year	Levels	Cu	Pb	Cr	Ni	Cd
	W ₁	24.2	91.0	98.0	29.1	21.0
F ' (W ₂	24.6	91.2	98.1	29.4	21.2
First year	Ŵ,	24.9	41.2	98.1	31.2	21.2
	W_4	25.2	91.2	98.2	33.1	21.4
	\mathbf{W}_{1}	29.1	92.5	100.0	35.2	24.3
Second	W ₂	29.4	92.6	100.0	37.1	24.7
year	Ŵ,	29.8	93.0	100.0	37.4	24.8
	W_4	3.2	93.4	100.0	37.9	24.9

TABLE-5

DISTRIBUTION OF COPPER(II) IN GRAIN OF MAIZE PLANT (%)

TABLE-6

DISTRIBUTION OF COPPER(II), LEAD(II), NICKEL(II) AND CADMIUM(II) IS STALKS MAIZE PLANT (%)

Year	Levels	Cu	Pb	Ni	Cd
First year	W ₁	15.2	5.1	28.2	1.20
	W ₂	15.0	5.1	28.0	1.10
	W ₃	15.0	5.0	27.4	1.00
	W_4	14.1	4.8	27.0	0.90
	W	13.1	4.2	25.3	0.80
Second year	W ₂	13.0	4.0	25.1	0.72
	W ₃	12.8	3.8	25.1	0.71
	$\mathbf{W}_{4}^{\mathbf{J}}$	12.1	3.6	24.2	0.68

TABLE-7

Year	Levels	Cu	Ni
	\mathbf{W}_{1}	39.0	31.00
First year	\mathbf{W}_2	32.1	30.20
First year	W ₃	38.0	25.40
	\mathbf{W}_{4}^{2}	37.2	25.01
	\mathbf{W}_{1}	30.1	23.20
Casandraan	W ₂	25.4	23.00
Second year	W ₃	25.1	22.10
	$\mathbf{W}_{4}^{\mathbf{J}}$	24.3	21.40

to the high organic matter and macro and micronutrient concentrations of applied sewage sludge. Sewage sludge applications increased yield in various plant species¹⁹. Solov and Khomyakov²⁰ stated that the application of sewage sludge resulted in fairly high biomass production in corn. Awad *et al.*²¹ found that the growth of seedlings was significantly increased by the application of dried sewage sludge.

Sewage sludge application to corn decreased leaf lead and cadmium contents, but did not decresec lead, cadmium and copper contents at the grain.

At the end of the experiment, leaf iron, manganese and zinc concentrations increased with sludge addition. Copper, nickel, chromium and cadmium concentrations did not change significantly with treatment. but decreased by changing these elements. While the nitrogen, phosphorus, magnesium, iron, manganese and copper contents of corn leaves were sufficient calcium contents were rich, but the zinc content was insufficient when these values were compared with predetermined limit values²².

Tables 4-7 report the total absorbed copper, zinc, lead, chromium and nickel and their distribution expressed as a percentage in plant parts during the 6 years of soil amendment. The heavy metals absorbed by the corn crop in the treated plots remained higher than those in the untreated plots. The apparent corn plants grown in treated soil can be explained by the high adsorption capacity of the soil for DOM and by the presence in the compost of lead as tetraalkyl-lead.

Conclusion

Recycling sewage sludge in agriculture has resulted in accumulation of heavy metals in soils, specially, cadmium, lead, chromium, copper, nickel and zinc and mainly when the residue is originated from industrial areas. Result of this research performed in Iran indicates that concentration of heavy metals in maize plant is function of plant element and some body of plants can absorb and store heavy metals more than the others. Total absorbed copper, zinc, lead, chromium and nickel and their distribution expressed as a percentage in plant parts during the 6 years of soil amendment.

REFERENCES

- 1. L. Korentejar, Water SA, 17, 189 (1991).
- 2. A.C. Chang, J.E. Warnede, A.L. Page and J. Lund, J. Environ. Qual., 13, 87 (1984).
- 3. R. Krebs, S.K. Gupta, G. Furrer and R. Schulin, J. Environ. Qual., 27, 18 (1998).
- 4. D.E. Williams, J. Vlamis, A.H. Pukite and J.E. Corey, Soil Sci., 129, 119.
- 5. M.B. McBride, J. Environ. Qual., 24, 5 (1995).
- 6. P. Das, S. Samantaray and G.R. Rout, Environ. Pollut., 98, 29 (1997).
- 7. S. Madyiwa, M. Chimbari, J. Nyamangara and C. Bangira, *Phys. Chem. Earth*, **27**, 747 (2002).
- 8. R.W. Carlson and F.A. Bazzaz, *Environ. Pollut.*, **12**, 243 (1977).

Asian J. Chem.

- 9. P.T. Bowen, M.K. Jacken and C. Corbittra, Water Environ. Res., 64, 378 (1992).
- 10. T.J. Logan and B.J. Harrison, J. Environ. Qual., 24, 153 (1995).
- 11. J.W.C. Wong, R.F. Jiang and D.C. Su, Soil Sci., 161, 182 (1996).
- 12. J.T. Sims and J.S. Kline, J. Environ. Qual., 20, 387 (1991).
- 13. S.P. McGrath and J. Cegarra, J. Soil Sci., 43, 313 (1992).
- 14. A.M. Bidwell and R.H. Dowdy, J. Environ. Qual., 16. 438 (1987).
- 15. B. Van Raij and J.A. Quaggio, Metodos de analise desolo para fins de fertilizer. Campinas: instituto Agronomico, p. 31 (1983).
- 16. W.L. Linday and W.A. Norvell, Soil Sci. Soc. Am. J., 42, 421 (1978).
- 17. Association of Official Agricultural Chemists, Official and Tentative methods of Analysis, AOAS, Washington, D.C. (1980)
- 18. D.E. Williams, J. Vlamis, A.H. Pukite and J.E. Corey, Soil Sci., 129, 119 (1980).
- 19. C. Keller, S.P. McGrath and S.J. Dunham, J. Environ. Qual., 31, 1550 (2002).
- 20. I.S. Solov and D.M. Khamyakov, Soviet Agric. Sci., 6, 30 (1989).
- F. Awad, L. Kahl, R. Kluge and J. Abadia, Environmental Aspects of Sewage Sludge and Evaluation of Super Absorbent Hydrogel under Egyptian Conditions, In: Iron Nutrition in Soil and Plants, Proceedings of the Seventh International Symposium, Zaragoza, pp. 53-62 (1995).
- 22. J.B. Jones Jr, B. Wolf and H.A. Mills, Plant Analysis Handbook, Micro Macro Publishing, Inc Athens, Georgia, USA (1991).

(<i>Received</i> : 30 May 2007;	Accepted: 8 August 2008)	AJC-6736
(

THE FOURTH INTERNATIONAL SYMPOSIUM ON THE NEW FRONTIERS OF THERMAL STUDIES OF MATERIALS

30 NOVEMBER — 2 DECEMBER 2008

YOKOHAMA, JAPAN

Contact:

Assoc. Prof. Hitoshi Kawaji, Executive Secretary, Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226–8503, Japan E-mail: sympo@thermo.msl.titech.ac.jp; Website: http://thermo.msl.titech.ac.jp/sympo/