Polish Journal of Environmental Studies Vol. 14, No. 2 (2005), 217-222

Original Research

Effects of Repeated Applications of Sewage Sludge and MSW Compost on the Bioavailability of Heavy Metals in Greenhouse Soil

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Received: 1 March, 2004
Accepted: 26 July, 2004

Abstract

In a two-year study, manure, sewage sludge and MSW compost were applied to greenhouse soil. A tomato plant was grown. Soil samples were collected after harvest and total and DTPA-extractable Zn, Cu, Ni, Pb and Cd contents of greenhouse soil were determined. Sludge and MSW compost used in a 2-year period increased both total and DTPA-extractable concentrations of Zn, Cu, Ni and Pb in the greenhouse soil. Cd increase was detected only in "total" form in the second year, by sewage sludge and MSW compost treatments. Bioavailable Cd content of soil was found below the detection limit in all treatments. The amount of bioavailable metals in the greenhouse soil were significantly high for the sewage sludge and MSW compost treatments, almost including a 9-, 6- and 3-fold increase in Zn, Cu and Pb, respectively. Total and bioavailable metal contents of soil in sewage sludge and MSW compost applications were higher in comparison with manure application. In sewage sludge and MSW compost treatments, "total" concentrations of all metals were found below pollutant limits, but the increase in available fractions was more marked than those of total concentrations.

Keywords: sewage sludge; MSW compost; heavy metal bioavailability

Introduction

Land disposal of sewage sludge is a major environmental problem. Increased urbanization and industrialization, especially in developing countries, requires municipal authorities to handle larger volumes of sewage sludge, often with limited resources. The use of sewage sludge in agriculture is now a widespread disposal practice.

Sewage sludge and MSW compost contain valuable plant nutrients and organic matter that can improve soil fertility. The phytonutritive capacity of compost has often been demonstrated to be analogous to that of manure; the same level of productivity, both quantitatively and qualitatively, can be maintained by replacing manure with compost [1, 2]. However, sewage sludge and MSW compost often contains potentially toxic elements that can cause soil contamination, phytotoxicity and undesirable residues in plant and animal products [3]. As a matter of fact, pollution problems may arise if toxic metals are mobilized into the soil solution and are either taken up by plants or transported in drainage waters. The risk to human health may then occur through consumption of such crops and intake of contaminated waters. In the long term, the use of sewage sludge and MSW compost can also cause a significant accumulation of Zn, Cu, Pb, Ni and Cd in the soil and plants [4].

Heavy metal pollution of agricultural soils and crops through the application of sewage sludge and MSW compost as organic fertilizers is of great concern. At the present time, legislation in different countries lim-

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Table 1. The analytical characteristics of the experimental greenhouse soil before treatment.

Parameters	Characteristics		Limit values in soil, (mg kg^{-1} dry wt) [6]
Texture	Loam		
pH- H_2O (1:5 w/v)	7.36		
$CaCO_3$, %	7.70		
Organic matter, %	2.20		
Total N, %	0.12		
P (ex), mg kg^{-1}	13.7		
K (ex), mg kg^{-1}	96		
Ca (ex), mg kg^{-1}	1716		
Mg (ex), mg kg^{-1}	211		
Zn, mg kg^{-1}	88[1]	6.6[2]	150-300[3]
Cu, mg kg^{-1}	25	2.7	50-140
Ni, mg kg^{-1}	16.6	0.48	30-75
Pb, mg kg^{-1}	45	4.0	50-300
Cd, mg kg^{-1}	*	*	1-3

[1]: Total concentrations, [2]: DTPA-extractable concentrations, [3]: Total concentrations at soil $6<pH<7$, *: Below detection limit (< 0.1 mg kg^{-1})

iting the use of sewage sludge in agriculture, refers to the total amounts of heavy metals in these wastes and in soils and recommends that soil pH be maintained at 6 or higher. Nevertheless, these criteria are insufficient since mobility, environmental diffusion and bioavailability largely depend on soil physico-chemical characteristics and, likewise, on trace metal chemical forms [5]. From an environmental point of view, the evaluation and forecast of food contamination is related to the bioavailable fraction of heavy metals in soil. Long-term studies are needed to improve our understanding of the effects of land application of sewage sludge on soil chemical properties.

The use of sewage sludge for agricultural purposes in Turkey is restricted. Information on the fertilizing value of municipal solid waste composts and their effects on the heavy metal loading potentials on greenhouse soil are scarce. The aim of this study was to assess the effects of repeated applications of sewage sludge and MSW compost on total and bioavailable (DTPA-extractable) contents of Zn, Cu, Ni, Pb and Cd in the greenhouse soil.

Materials and Methods

The experiment was conducted from 2001 to 2002 on the new constructed greenhouse representative of the major greenhouse tomato growing area of Turkey, Antalya Aksu. The analytical characteristics of the greenhouse soil are shown in Table 1, which also shows the pollutant limits of soil permitted by EU legislation [6].

The experiment entailed the use of the following organic materials for the fertilization of the greenhouse soil.

- Composted cattle manure (CM): Produced by dairy-cows in sheds with straw bedding.
- Sewage sludge (SS): Sewage sludge was collected from the GATAP Kemer Waste Water Treatment Plant in Antalya. Sludge samples were air-dried and sieved through a 2-mm mesh and mixed well.
- Municipal solid waste compost (MSWC)was obtained from MSW composting plant in Kemer, Antalya. Compost was produced by the composting of the organic fraction of unseparated municipal solid waste, selected mechanically at the plant.

The mean analytical characteristics of organic materials tested are given in Table 2, which also shows the EU limits [6] for sewage sludge.

Organic materials were applied from 2001 to 2002 to greenhouse soil as an oven-dry basis at the following rates:

- Control: 50 ton ha^{-1} of cattle manure
- SS_{50}: 50 ton ha^{-1} of sewage sludge
- SS_{100}: 100 ton ha^{-1} of sewage sludge
- $MSWC_{50}$: 50 ton ha^{-1} of municipal solid waste compost
- $MSWC_{100}$: 100 ton ha^{-1} of municipal solid waste compost

The control is representative of the normal fertilization practice adopted in the province of Antalya. The lowest rate of organic materials (SS and MSWC) (50 ton ha^{-1}) was studied in order to introduce quantities of dry organic matter analagous to those of the control. In order to maximize the effects of the heavy metal contamination a study

Table 2. Average analytical characteristics of organic materials used.

	Cattle Manure	Sewage sludge	MSW compost	Limit values in sewage sludge [6], (mg kg^{-1} dry wt)
Moisture, %	54	38.6	35.4	
pH- H_2O (1:5 w/v)	7.96	6.45	7.66	
Ash, %	26.2	44.2	48.5	
Total N, %	2.12	1.88	1.15	
P_2O_5, %	1.77	2.14	0.77	
K_2O, %	1.56	0.48	0.55	
Total Zn, mg kg^{-1}	180	1660	1220	2500-4000
Total Cu, mg kg^{-1}	46	236	105	1000-1750
Total Ni, mg kg^{-1}	15	54	43	300-400
Total Pb, mg kg^{-1}	21	443	196	750-1200
Total Cd, mg kg^{-1}	*	2.8	1.6	20-40

*: Below detection limit (< 0.1 mg kg^{-1})

was also carried out on the SS_{100} and MSW_{100} treatments for which the amount of compost used is double that of normal practices. Both in February 2001 and 2002, 50% of the amount of organic materials to be used for each treatment was distributed. Organic materials were manually incorporated into the greenhouse soil and mixed throughout the upper 20 cm.

The experimental plots were cultivated in two consecutive years, 2001-02, with tomato (Lycopersicom esculentum L. cv. Target F1) at a density of 35,710 plants ha^{-1} using 0.4 m by 0.70 spacing and each plot (5.6 m^2) consisted of 20 tomato plants in a randomized block design with four replications. Complete greenhouse operations were carried out in the trials. Basic fertilizer was applied with sprinkler irrigation in all plots at the rate of 300, 200 and 300 kg ha^{-1} of N, P and K, respectively.

Tomato seedlings were planted in March and harvested in June. After the harvest of tomato in 2001-02, soil samples were collected from each plot at a depth of 0-20 cm and these were air-dried and sieved (< 2 mm). The study of heavy metal accumulation was carried out by analyzing the Zn, Cu, Ni, Pb and Cd contents in the soil samples corresponding to the above-mentioned treatments.

For the determination of 'total' heavy metal concentrations, soil, SS and MSWC samples were digested in aqua regia (1:3 HNO_3/HCl) according to the international standard [7]. Bioavailable fractions of metals were extracted from soil with diethylenetriaminepentaacetic acid-$CaCl_2$-triethanolamine adjusted to pH 7.3 (DTPA) procedure [8]. Total and bioavailable metal concentrations, adjusted to values for oven dried (12 h at 105°C) soil, were determined by flame atomic absorption spectrometry (FAAS) under optimized measurement conditions.

A statistical ANOVA F test was applied to the results and treatment means were compared by the least significant difference test at P=0.05.

Result and Discussion

Total Metal Contents in Soil

The heavy metal contents of untreated greenhouse soil (Table 1) and organic materials studied (Table 2) are well within the accepted normal range of values. A comparison of metal contents of organic materials with that of untreated soil showed that the metals Zn, Cu, Ni, Pb and Cd were present in both SS and MSWC in greater concentrations than in the soil. The three organic materials tested differed notably in their heavy metal content (Table 2). Sludge metal concentrations are considerably higher than those of MSW compost and cattle manure for all metals examined. The metal concentrations in cattle manure were the lowest. The heavy metal concentrations of all organic materials are below the levels indicated by the EU (86/278/CEE) for the agricultural use of sewage sludge.

The heavy metal contents of the greenhouse soil treated with SS and MSWC during a 2-yr period, 2001-02, are given in Table 3. SS and MSWC led to a far greater introduction of the heavy metals examined and brought about a significant increase in their "total" form in the soil when compared with the control. After 2 yr of repeated SS and MSWC applications, significant changes in the total contents of Zn, Cu, Ni, Pb and Cd among the treatments were determined. These results agree with the increase of total metal content observed in soils submitted to repeated application of metal-contaminated sewage sludge [9, 10].

Metals extracted from the surface 20 cm of soil plots were generally increased yearly with each addition. The increases were highly significant at the 1% level for Zn, Cu and Pb, and 5% level for Ni and Cd (Table 3). Total Zn, Cu and Pb contents of soil at the beginning of the experiment were 88, 25 and 45 mg kg^{-1}, respectively. During the trial period, at high application levels of SS, these levels were

Table 3. Total and DTPA extractable concentrations of heavy metals in the greenhouse soil sampled in 2001and 2002.

Treatments	Zn			Cu			Ni			Pb			Cd		
	Total	DTPA	D/T	Total	DTPA	D/T	Total	DTPA	D/T	Total	DTPA	D/T	Total	DTPA	D/T
2001															
Control	89 e	7.1 e	8 e	25 d	2.8 d	11 e	17	0.52	3.1	44 d	4 d	9 c	< 0.10	< 0.10	-
SS_{50}	105 c	30 c	29 c	27 bc	12 b	46 b	17	0.61	3.6	47 bc	12 bc	25 b	< 0.10	< 0.10	-
SS_{100}	111 a	39 a	35 a	30 a	16 a	52 a	18	0.61	3.4	52 a	15 a	29 a	0.12	< 0.10	-
MSW_{50}	96 d	24 d	25 d	26 cd	10 c	37 d	17	0.54	3.2	45 cd	11 c	24 b	< 0.10	< 0.10	-
MSW_{100}	107 b	33 b	31 b	28 b	11 bc	41 c	17	0.60	3.5	48 b	13 b	28 a	< 0.10	< 0.10	-
Significance	**	**	**	*	*	*	NS	NS	NS	*	*	*	NS	NS	NS
2002															
Control	90 e	7.2 e	8 e	25 c	2.8 e	11 c	17 b	0.66	3.9	44 e	4 e	9 c	< 0.10	< 0.10	-
SS_{50}	131 c	43 c	33 c	30 b	16 b	52 a	17 b	0.73	4.3	54 b	18 c	33 b	0.11 b	< 0.10	-
SS_{100}	167 a	67 a	40 a	35 a	19 a	55 a	19 a	0.78	4.1	60 a	23 a	39 a	0.22 a	< 0.10	-
MSW_{50}	102 d	29 d	28 d	26 c	12d	47 b	17 b	0.64	3.8	47 d	15 d	32 b	< 0.10	< 0.10	-
MSW_{100}	146 b	51 b	35 b	29 b	13 c	46 b	19 a	0.70	3.7	52 c	20 b	39 a	0.11 b	< 0.10	-
Significance	**	**	**	*	**	**	*	NS	NS	**	**	**	*	NS	NS
Significance (Repetition)	**	**	**	**	**	**	*	NS	NS	**	**	**	*	NS	NS

All data are in mg kg^{-1} dry matter weight. Means followed by the same letter are not statistically different (Duncan tetst, P≤0.05), *: Significant with P≤ 0.05; **: Significant with P≤ 0.01; NS: not significant, D/T: DTPA/Total concentration rate (%)

increased to 167, 35 and 60 mg kg^{-1}, respectively. The increase in soil zinc content was less significant with manure than with SS and MSWC. The Zn and Cu variations were more marked with sewage sludge and consistent with the amounts of both SS and MSW compost tested. Increasing soil-metal concentrations with increasing SS and MSWC applications have been reported [11, 12, 13]. In spite of the important increases in Zn, Cu and Pb contents registered, the concentrations in the soil remained below the EU legislation (86/278/CEE) for soils.

Metals were also increased with rate of addition for any given year. Repeated applications in the second year, SS and MSWC treatments induced higher Zn, Cu, Ni and Pb contents than the first year of application. The first year, in the all treatments except SS_{100}, total Cd in the soil was always below the sensitivity of analytical method (0.1 mg kg^{-1}). In the second year, the increase in Cd content of soil was significant with SS and MSWC.

The tendency of metal accumulation in the soil in relation to amendments of SS and MSWC was in the following order: Zn>Pb>Cu>Ni>Cd. It has been reported that increased Zn, Cu and Pb levels have often been observed, both in the soil and plants, while other heavy metals-such Ni and Cd- increase less consistently [14]. Based on the cumulative research in Europe into the agronomic use of compost, heavy metals tend to accumulate in soil and plants in the following order: Zn>Cu>Pb>=Cd>Ni>Cr [15].

DTPA Extractable Metals in the Soil

In this study, bioavailability of metals was expressed in terms of concentrations extractable with DTPA. All amounts of SS and MSWC brought about significant increases in DTPA-extractable Zn, Cu and Pb concentrations in comparison with the control. These results are in concordance with the data [16]. DTPA-extractable Zn, Cu and Pb also registered significantly higher values in 100 ton/ha than 50 ton/ha application level of SS and MSW compost (Table 3). In the second year, although the content of Ni in “total” form was increased by the application of SS and MSWC, DTPA-extractable form of Ni was unaffected. In the all treatments, DTPA-extractable Cd in the soil was always below the sensitivity of analytical method (0.1 mg kg^{-1}).

The maximum permissible concentrations of heavy metals in surface soils amended with sewage sludge are normally based on total concentration, although it is the bioavailable metal fraction that posses environmental concern [17]. Total concentrations of all metals were found below the pollutant limits, but the increase in DTPA-extractable fractions was more marked than those of total concentrations.

The application of SS and MSWC caused a significant increase in the extractability of metals in the soil. The relative increase of heavy metals Zn, Cu and Pb for SS and

Table 4. Simple linear coefficients between DTPA-extractable metals and "total" metals in the soil.

	DTPA-extractable metals				
	Zn	Cu	Ni	Pb	Cd
Total metals, in 2001	0.968 **	0.891 **	0.454 *	0.831 **	-
Total metals, in 2002	0.978 **	0.854 **	0.618 **	0.886 **	-

*: Significant with P≤ 0.05; **: Significant with P≤ 0.01

MSWC, in comparison with the control, were higher for the DTPA-extractable than for the "total" form. To compare the relative availability of different soil metals, DTPA/Total ratio is used to give available metals as a percentage of total soil metal. Relative availabilities calculated in this way are given in Table 3. Relative metal availability, expressed as DTPA/Total ratios, was greater for Zn, Cu and Pb than the other metals in the greenhouse soil. Metals in control (manure) treatment were the least relative availability. Relative availability of Zn was the highest in SS_{100} treatment. Copper was more available in MSW_{50}-treated plots. Relative availability of Pb was almost similar in SS and MSW compost treatments. It should be noted that available metal may be quite large when the total metal present in the soil is great. Repeated applications of SS and MSWC in the second year increased DTPA-extractable and relative availabilities of Zn, Cu and Pb.

In the untreated soil (Table 1), DTPA solution extracted about 7.5% of total Zn, 10.8% of total Cu, 2.9% of total Ni, 8.9% of total Pb and 0.7% of total Cr. DTPA-extractable Ni and Cd did not change significantly among the treatments, while DTPA-extractable Zn, Cu and Pb gradually increased in direct proportion to the amounts of SS and MSWC added to soil. These results are in concordance with the data [18, 19], and support the hypothesis that metals added with sewage sludge may be more mobile in soil than native metals [20].

Relationship between DTPA-Extractable Metals and "Total" Metals in the Soil

Simple correlation coefficients (r) between "total" metals and DTPA-extractable metal content are reported in Table 4. With the exception of Cd (due to the unavailability of the relevant data) statistically significant and positive correlations were observed between "total" and DTPA-extractable concentrations in the soil for all metals. Correlation coefficients between DTPA-extractable metals and "total" metals were increased by the repeated applications of SS and MSWC for all metals except Cu.

Conclusion

The results of the present study indicate that soil application of SS and MSWC increased total and DTPA-extractable levels of Zn, Cu and Pb in the soil compared to the manure. Relative metal availability, expressed as DTPA/total ratios, was greater for Zn, Cu and Pb in SS than in MSWC treatments. Compared to manure application, SS and MSWC treated soil often show significantly increased heavy metal contents, especially Zn, Cu, Pb, Ni and Cd. Repeated applications of SS and MSWC in two years significantly increased bioavailable metals in the greenhouse soil compared to the control. In this short-term study no detrimental effects on soil properties were detected and metals in treatments were not higher than the allowed guideline level. However, taking into consideration the high potential bioavailability of heavy metals, repeated applications of SS and MSWC would carry a risk of progressive build-up of available trace elements in the soil in the course of time. For environmentally safe disposal of sewage sludge, immobilisation strategies for heavy metals in organic materials will be investigated in the long term studies. Results demonstrate the importance of measuring extractable as well as total concentrations in topsoil when assessing likely effects on plant yields and metal uptakes, and settings soil quality criteria

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