Speciation and Bioavailability of Heavy Metals in Long-Term Sewage Sludge-Amended Soil

Bülent Topcuoğlu

***Abstract*—**A greenhouse experiment was carried out to assess heavy metal loading and its bioavailability and trace metal speciation on the greenhouse soil following sewage sludge (SS) application. SS was applied from 2005 to 2009 to greenhouse soil as an oven-dry basis, totaly at 100 ton ha^{-1}(SS_{100}) and 200 ton ha^{-1} (SS_{200}) levels. An uncontaminated greenhouse soil at the same location was used as a control treatment for comparison with the results. After the end of 4 years of successive SS applications to greenhouse soil, the residual effects of SS on bioavailable heavy metal status and metal speciation of greenhouse soil were tested.

The greenhouse soil treated with SS contained higher concentrations of DTPA-extractable Zn, Cu, Ni, Pb and Cd than that of untreated soil. The Cd, Cr, Ni and Zn in SS were predominantly bound within the residual components. The amount of bioavailable (DTPA-extractable) metals in the greenhouse soil was significantly high for SS treatments. In SS treatments, total soil metal concentrations were found below the permissible pollutant limits, but the increase in available metal fractions (water soluble and exchangeable fraction) was more marked than those of total concentrations. The mobility factor of metals was increased by SS treatments, and mobility factor of Cd was the highest among the metals.

The results indicated that in SS amended soil, trace metals were mainly in bioavailable forms, and metals entering to soil by SS treatments have potential mobility in soil-water system.

***Keywords*—**Metal Bioavailability, Metal Speciation, Sewage Sludge

I. Introduction

TREATED/composted sewage sludge (SS) and its subsequent application to agricultural land is gaining popularity because of environmental concerns associated with the disposal of this material in landfills. Several studies have shown that use of SS in agriculture has many benefits to soil, crops and environment [1]. However, SS often contains potentially toxic elements, that can cause soil contamination, phytotoxicity and undesirable residues in plant and animal products [2]. In the long term, the use of SS can also cause a significant accumulation of Zn, Cu, Pb, Ni and Cd in the soil and plants [3].

The maximum permissible concentrations of heavy metals in surface soils amended with SS are normally based on total concentration, although it is the bioavailable metal fraction that posses environmental concern [4]. 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].

Bülent Topcuoğlu, Akdeniz University Vocational School of Technical Sciences,07058, Antalya, TURKEY. (+902423106751, email: btoglu@akdeniz.edu.tr)

From an environmental point of view, the evaluation and forecast of food contamination is related to the bioavailable fraction of heavy metals in soil.

Although total heavy metal content in soils provide a convenient means of expressing a measure of pollution, such measure are generally deficient in predicting toxicity of metal pollutants. Therefore, the chemical form is of great significance in determining the potential bioavailability and remobilization of the soil metals [6].

Information on the fertilizing value of SS and their effects on the heavy metal loading potentials on greenhouse soil are scarce. The aim of this study was to provide information on the metal fractionation in soil, the residual effects of successive SS applications on the total and bioavailable (DTPA-extractable) contents of Zn, Cu, Ni, Pb and Cd in the greenhouse soil.

II. Materials And Methods

The experiment was conducted from 2005 to 2009 on the greenhouse representative of the major greenhouse vegetable growing area of Turkey Antalya Aksu. The analytical characteristics of the greenhouse soil and SS are shown in Table 1 which also shows the pollutant limits of soil and also organic materials used as soil amendments, permitted by EU legislation [7].

SS was obtained from water treatment plant in Kemer, Antalya. SS was applied from 2005 to 2009 to greenhouse soil as an oven-dry basis, totaly at 100 ton ha^{-1}(SSC_{100}) and 200 ton ha^{-1} (SSC_{200}) levelsSS was manually incorporated into the greenhouse soil and mixed throughout the upper 20 cm. An uncontaminated soil for the control treatment was used to compare the effectiveness of SS application in the same greenhouse.Soil samples were taken at a depth of 10-20 cm in September 2009; and these were air-dried and sieved (< 2 mm).

The heavy metal sequential extraction procedure [8] had the following steps:

F1. 1 M $MgCl_2$ (1:8 w/v, pH 7) for 1 h at room temperature; metals in soil solution and in exchangeable forms.

F2. 1 M NaOAc (1:8 w/v, pH 5) for 5 h at room temperature; metals mainly in the carbonate fraction.

F3. 0,04M NH2OH/HCl in 25 % (v/v)HOAc (1: 20 w/v) for 6 h at 96 °C ; metals associated with Fe and Mn oxides.

F4. 3 ml 0,02 M HNO3+5 ml 30 % H2O2 (pH 2) for 3 h at 85 °C; metals associated with organic matter.

F5. HNO3-HCl digestion; residual fraction.

TABLE I
THE ANALYTICAL CHARACTERISTICS OF THE EXPERIMENTAL SOIL AND SS BEFORE TREATMENT, AND THEIR POLLUTANT LIMITS.

Parameters	Soil	Limit values in soil [7]	Sewage sludge	Limit values in organic materials[7]
Texture	Loam		-	
pH- H_2O (1:5 w/v)	7.37		7.55	
$CaCO_3$, %	7.68		-	
Total N, %	0.17		0.68	
Organic Matter, %	2.33		58	
EC (dS m^{-1})	0.04		8.77	
Zn, mg kg^{-1}	77[1]	150-300[1]	1110[1]	2500-4000[1]
Cu, mg kg^{-1}	17	50-140	96	1000-1750
Ni, mg kg^{-1}	14	30-75	47	300-400
Pb, mg kg^{-1}	33	50-300	164	750-1200
Cd, mg kg^{-1}	0,010	1-3	1.3	20-40

[1]: Total concentrations (mg kg^{-1} dry wt).

For the determination of 'total' heavy metal concentrations, soil and SS samples were digested in aqua regia (1:3 HNO_3/HCl) according to the international standard [9]. Bioavailable fractions of metals were extracted from soil with diethylenetriaminepentaacetic acid-$CaCl_2$-triethanolamine adjusted to pH 7.3 (DTPA) according to Lindsay and Norwell (1978) [10] procedure. Total and bioavailable Zn, Cu, Ni, Pb and Cd concentrations of greenhouse soil were determined by flame atomic absorption spectrometry (FAAS) under optimised measurement conditions, and values were adjusted for oven dried (12 h at 105 °C) material.

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

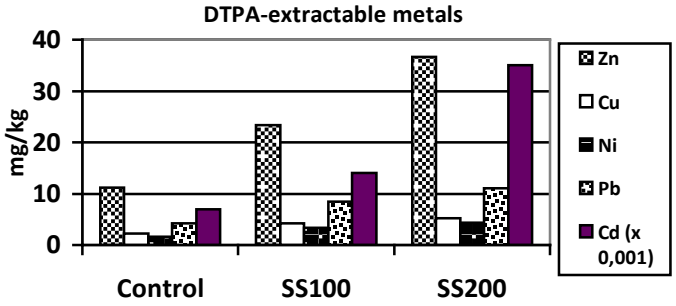
III. RESULTS AND DISCUSSION

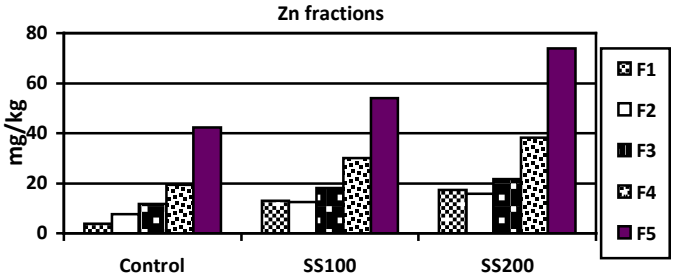
The heavy metal contents of untreated greenhouse soil and SS studied (Table I) are well within the accepted normal range of values. A comparison of metal contents of organic materials with that of untreated soil showed that the metals Zn, Cu, Ni, Pb and Cd were present in SS in greater concentrations than in the soil. The heavy metal concentrations of SS is below the levels indicated by the EU [7] for the agricultural use of waste organic material (SS).

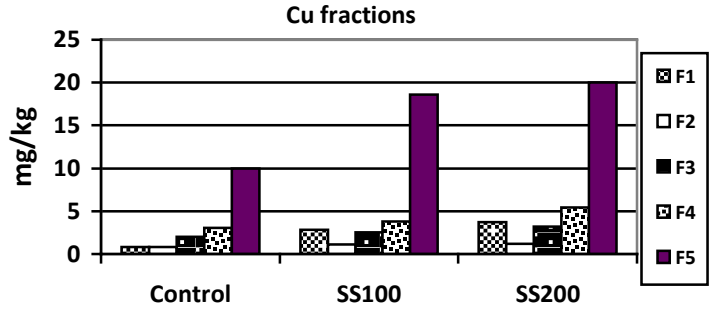
Successive applications of SS for 4-yr period led to a far greater introduction of the heavy metals examined and brought about a significant increase in their 'DTPA extractable' form in the soil when compared with the control (Figure 1). After 4 years of successive SS applications, significant changes in the 'DTPA extractable' contents of Zn, Cu, Ni, Pb and Cd in experimental soil were determined.

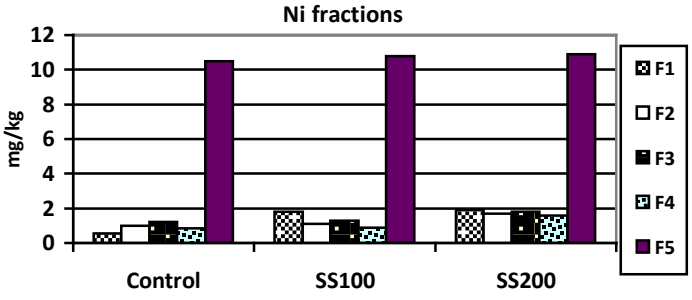
The total Zn, Cu, Pb, Ni and Cd contents of soil at the beginning of the experiment were 77, 17, 33, 14 and 0,001 mg kg^{-1}, respectively. The Zn, Cu, Pb and Cd variations were more marked with SS and consistent with the amounts of SS tested. Increasing soil-metal concentrations with increasing SS applications have been reported [11]. In spite of the important increases in Zn, Cu and Pb contents registered, the concentrations in the soil remained below the EU legislation [7] for soils.

All amounts of SS brought about significant increases in DTPA-extractable metal concentrations in comparison with the control (Table III). DTPA-extractable Zn, Cu, Pb, Ni and Cd also registered significantly higher values in 200 ton ha^{-1} than in 100 ton ha^{-1} application level of SS. DTPA extractable Cd concentrations of control treatment were always below the sensitivity of analytical method (0.02 mg kg^{-1}).









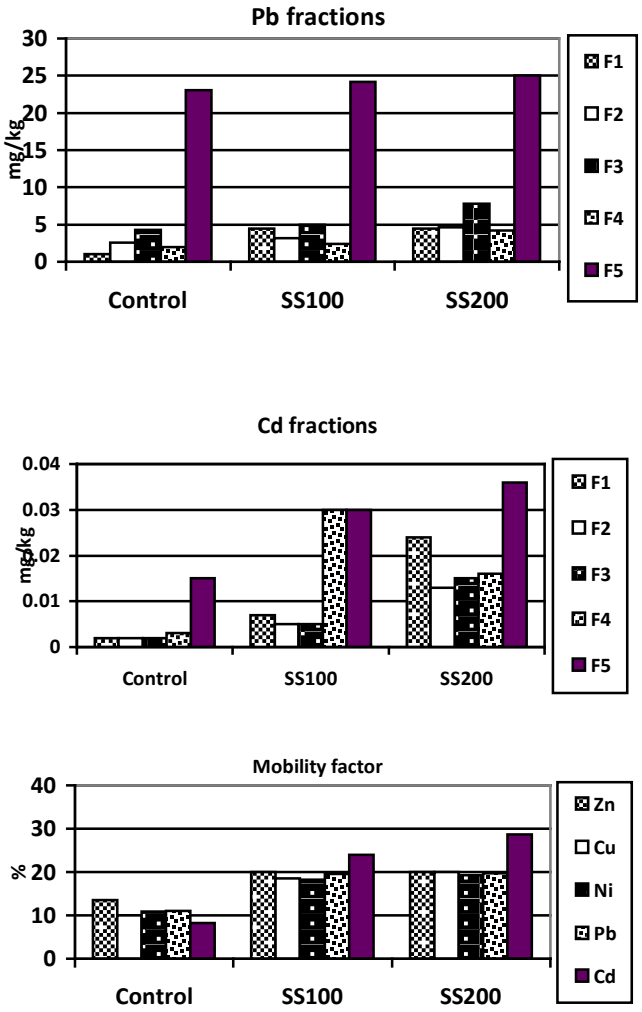


Fig. 2 Bioavailability (DTPA-extractable), fractionation and mobility factors of Zn, Cu, Ni, Pb and Cd in soils amended with sewage sludge over 2005-2009.

The exchangeable (F1) and acid-extractable fractions (F2) are considered to be easily soluble and available. Soil pH has a direct impact on the mobility of metals as it affects their solubility and their capacity to form chelates in soil [12]. It has been reported that [13] more than 50 % of the Pb fraction was residual fraction by the sewage sludge amendments, but the amount of exchangeable Pb increased over the course of the experiment. Present study showed that the bioavailability of metals in SS treatments increased over the incubation. Boucher et al. (2005) reported that increased proportions of extractable metals in soil may be due to reductions in pH and/or increases in soluble carbon.

The addition of SS led to soil metal fractions increase significantly (Figure 2). The mobility of metals in control and SS treated soils may be assessed on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was calculated as a ratio of sum of water soluble, exchangeable and carbonate fractions to sum of all fractions, and this described as a mobility factor [14]. SS amendments led to mobility factor of metals increase significantly. The results of the present study suggest that the mobility of metals declines in the following order:

Control soil: Zn>Pb>Cu>Ni>Cd

SS100 amended soil: Cd>Zn≥Pb>Cu>Ni

SS200 amended soil: Cd>Pb>Cu>Zn>Ni

In all treatments bioavailability (DTPA extractable) of metals declines in the following order: Zn>Pb>Cu>Ni

As can be seen, SS amendments cause a dramatically metal accumulation in soil. More than that metals sourced by SS were mostly in the mobile forms. The highest mobility factor was obtained in SS200 amendments and Cd was the most mobile element.

Although total concentrations of all metals were found below the pollutant limits, it can be seen that the increase in DTPA-extractable fractions was more marked than those of total concentrations. These results support the hypothesis [15] that metals added with SS or other organic wastes may be more mobile in soil than native metals.

IV. Conclusion

The results of the present study indicated that soil application of SS increased total and DTPA extractable levels of Zn, Cu, Pb, Ni and Cd in the soil compared with the control. Specially, these metals entering soil by SS were in mostly mobile fractions. The findings on the effects of heavy metal accumulation in the soil as a result of successive applications of SS to greenhouse soil could be thought a noticeable evidence for the safety reuse concerns of SS. In the future studies biosolid cleaning technologies involving phytoremediation technics should be taken into consideration for the composting and safety usage of SS and other biosolids.

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