Fractionation of Heavy Metals in the Sewage Sludge Applied Soil

Bülent Topcuoğlu

***Abstract*—** An incubation experiment was conducted to investigate the effects of sludge application to soil on heavy metal bioavailability, metal mobility and metal fractionation. A thermal stabilized sewage sludge was applied to the uncontaminated calcareous red Mediterranean soil, and after 6 months incubation period, soil heavy metals (Zn, Cu, Ni, Pb and Cd) were analyzed. Sludge application has significantly increased the DTPA extractable metals and all the metals in the water-soluble and exchangeable fractions. Sludge application significantly increased the mobility factor of all metals. Zn, Pb and Ni were the most increased metals in the soil by sewage sludge application.

***Keywords*—** Sludge, Metal Fractionation, Metal Bioavailability.

I. INTRODUCTION

Heavy Metals are considered to be one of the most important contaminants in soil due to their toxicity, large contributing sources, non-biodegradable properties and cumulative behavior in intensive agricultural areas. [1]. Today, heavy metal pollution in agricultural soils has become one of the most serious environmental problems and causes significant harm to human health. Nowadays, due to the intensive use of agrochemicals in agricultural soils, heavy metals have become widespread pollutants, especially in and near intensive agricultural soils. While some engineering techniques can be used efficiently to clean up contaminated soils, most of them are expensive and complex technologies and are used for small-scale contaminated sites [2].

Nowadays, due to the proliferation of wastewater treatment plants, large amounts of sewage sludge are produced daily in cities. Sewage sludge contains valuable plant nutrients and organic matter that can improve soil fertility. The phytonutritive capacity of sludge has often been demonstrated to be analogous to that of manure [3]. However, there is a rising concern over sludge often contains potentially toxic elements, that can cause soil contamination, phytotoxicity and undesirable residues in plant and animal products [4]. 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. Risk for human health may then occur through consumption of such crops and intake of contaminated waters.

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Nevertheless, the main risks associated with the use of organic wastes in agriculture cannot be evaluated directly through determination of the total contents of metals in those materials, since the chemical or physicochemical forms of metals strongly affect their mobility, reactivity and availability to plants [5].

The maximum allowable heavy metal concentrations in contaminated soils today are based on the total concentration of metals [6]. However, these criteria are not sufficient to comprehensively evaluate the effects of both environmental effects and applications on plants because metal mobility, environmental diffusion and bioavailability are largely dependent on the physico-chemical properties of the soil and the chemical forms of the metals [7]. In particular, the assessment and estimation of food contamination is closely related to the bioavailable fraction of heavy metals in the soil.

Although many experimental findings agree that sludge reduces metal mobility, there are conflicting findings regarding the metal forms of sludges and their effects on metal availability. The aim of this research is to determine the effects of sludge applied to soil on metal bioavailability, metal mobility and metal fractions.

II. MATERIALS AND METHODS

The soil used in this experiment was sampled from red mediterranean soil, which represents the main agricultural areas of Turkey Antalya Aksu (Table 1). It was evaluated that the main analytical properties of the experimental soil shows that the soil physical and chemical parameters are in acceptable levels for plant growth and contaminant limits are below the limits of EU legislation.

TABLE 1: THE ANALYTICAL CHARACTERISTICS OF THE EXPERIMENTAL SOIL BEFORE APPLICATIONS

Parameters	
Texture Grade	Loam
pH- H_2O (1:5 w/v)	7.35
$CaCO_3$, %	23
Organic matter, %	1,2
Clay,%	18
CEC, cmol kg^{-1}	28,2
EC, dS m^{-1} 25°C	0,88
Total Zn, mg kg^{-1}	77 (150-300)*
Total Cu, mg kg^{-1}	14 (50-140)*
Total Ni, mg kg^{-1}	12 (30-75)*
Total Pb, mg kg^{-1}	18 (50-300)*
Total Cd, mg kg^{-1}	0,01 (1-3)*

*: Metal limits in soil, mg kg^{-1} dry wt [8].

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The thermal stabilized sludge material used in the experiment was obtained from water treatment plant of Metropolitan Municipality in Konyaaltı, Antalya.

TABLE II. AVERAGE ANALYTICAL CHARACTERISTICS OF SEWAGE SLUDGE.

	Sewage Sludge	Limit values [8], (mg kg^{-1} dry wt)
Moisture, %	38.6	
pH- H_2O (1:5 w/v)	6.45	
Ash, %	44.2	
Total N, %	1.88	
P_2O_5, %	2.14	
K_2O, %	0.48	
Total Zn, mg kg^{-1}	1660	2500-4000
Total Cu, mg kg^{-1}	236	1000-1750
Total Ni, mg kg^{-1}	54	300-400
Total Pb, mg kg^{-1}	443	750-1200

Before the experiment, the sludge material was air dried and ground to 2 mm particle size. Ten kilograms of air-dried and sieved (< 2 mm) soil were filled into plastic containers. A pot plate was placed under each pot to prevent leakage. Two levels of sludge (control treatment and 2 % sludge treatment as an oven-dry basis; equal to about 50 ton ha^{-1} agronomic application level) were applied experimental soil with 5 replications. A homogeneous application was achieved by carefully mixing the soil with the sludge. The soil was then incubated in the greenhouse for 6 months. Experimental soils were irrigated with deionized water 1-2 times a week for 6 months to maintain field water capacity. After incubation, soil samples were taken from each pot for bioavailable metal and fractionation analyses.

Electrical conductivity (EC) and pH were measured at a 1:2 soil:water ratio. Cation exchange capacity (CEC) was determined by extraction of 0.1 M NN4AoC; The CaCO3 content was determined by calcimetry; organic carbon was measured by wet oxidation; and tissue were determined by the Bouyoucos hydrometer method. To determine the 'total' heavy metal concentrations, the soil was digested in aqua regia (1:3 HNO3/HCl) according to the international standard [10]. The bioavailable metal fractions were extracted from the soil with diethylenetriaminepentaacetic acid-CaCl2-triethanolamine adjusted to the pH 7.3 (DTPA) procedure. The main analytical properties of the metal-free experimental soil are shown in Table 1, which also shows the soil pollutant limits allowed by EU legislation.

Sequental extraction method [11]. was applied to soil samples to identify metal fractions. The heavy metal sequential extraction procedure had the following steps:

F1. 1 M MgCl2 (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.

To determine the bioavailable and sequentially extracted metal concentrations, soil samples were determined according to the international standard. Zn, Cu, Ni, Pb, and Cd concentrations of greenhouse soil samples were analyzed using ICP-MS under optimized measurement conditions and values adjusted for oven-dried material (at 105 °C for 12 h).

The mobility of the soil metal was calculated based on the theoretically mobile fractions in the sequential extraction procedure in which the metals were softly bonded to the solid phases. The relative metal mobility index was calculated as a "mobility factor" (MF) based on the following equation:

$$MF: \frac{(F_1 + F_2 + F_3)}{(F_1 + F_2 + F_3 + F_4 + F_5)} x100$$

This equation is largely describes the potential mobility of metals [12].

A one-way ANOVA test ($p \leq 0.05$) calculated using the SPSS-16 statistical package for Windows program was applied to compare the differences in heavy metal concentrations and evaluation parameters in the soils.

III RESULTS AND DISCUSSION

DTPA extractable metal content and proportional variation of the soil

Before applications, the experimental soil generally has slightly alkaline reaction, moderate CEC, low EC values and high lime content. The physical and chemical properties of the experimental soil are within the accepted range of normal agronomic values, and the heavy metal concentrations are below the EU-specified levels [9]. DTPA extractable metal concentrations of experimental soil after sludge applications are presented in Figure 1 and the proportional changes of metals in treatments are presented in Figure 2.

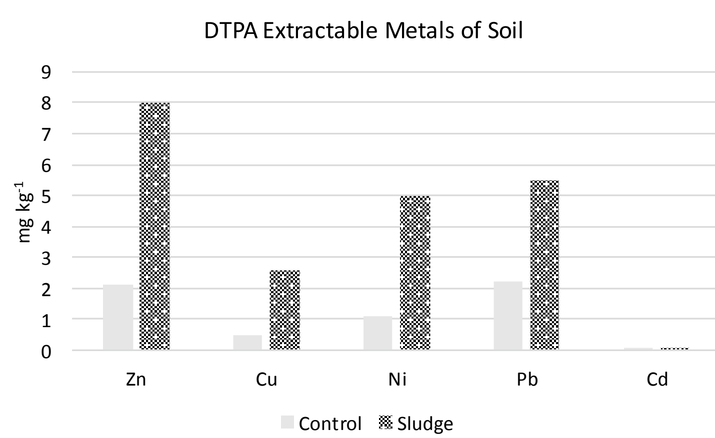

Fig. 1. DTPA extractable metal concentration in control soil and sludge treated soil

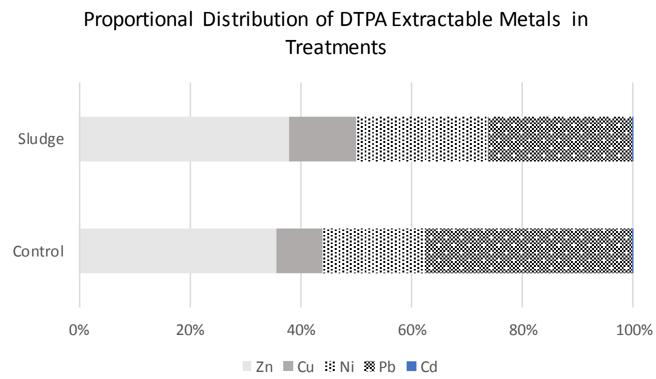

Fig. 2. Proportional distribution of DTPA extractable metals in control and sludge treated soil

In this study, the bioavailability of metals was expressed in terms of DTPA extractable concentrations, meaning that the metals can be easily taken up by plants. Sludge applications resulted in significant increase in DTPA extractable Zn, Cu, Ni, Pb and Cd concentrations sludge-treated soil. DTPA extractable Cd concentration was increased slightly by the sludge treatments (Figure 1). Depending on the sludge treatments, Zn was the metal whose DTPA extractable concentration increased the most, followed by Pb and Ni (Figure 2). These results indicate that the application of sewage sludge to the soil significantly increased the plant-available metal contents.

Soil Metal Fractionation

The concentrations and proportional distributions of Zn, Cd, Ni, Pb and Cd in control and sludge treated are presented in Figure 3-12. The distribution of metals in the metal-free natural agricultural soil (control) showed that the largest percentage of all metals was found in the residual fraction, followed by organic-bound fraction (F4). The residual phase represents metals largely embedded in the crystal lattice of the soil fraction, showing that these metals cannot move under normal conditions [8].

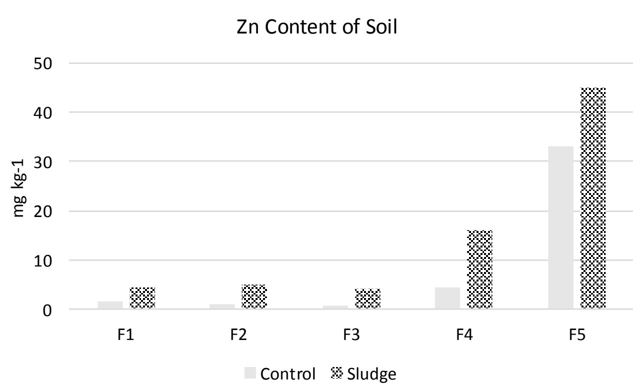

Fig. 3. Distribution of Zn fractions in control and sludge-treated soil

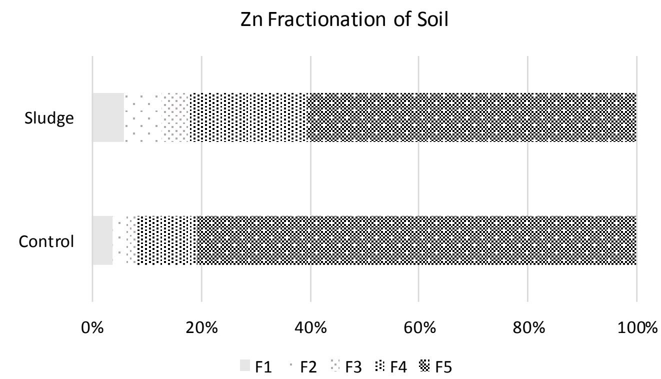

Fig. 4. Proportional distribution of Zn fractions in control and sludge treated soil

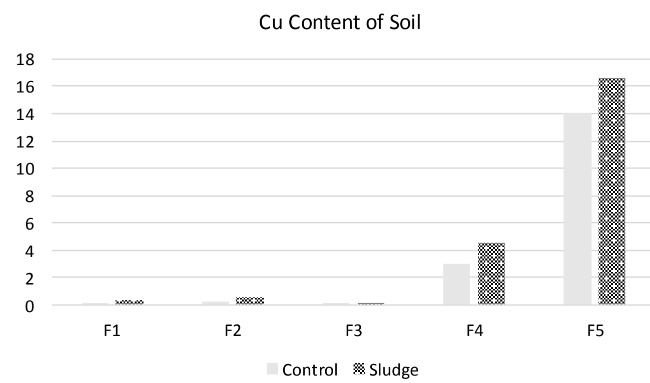

Fig. 5. Distribution of Cu fractions in control and Cu-treated soil by sludge applications

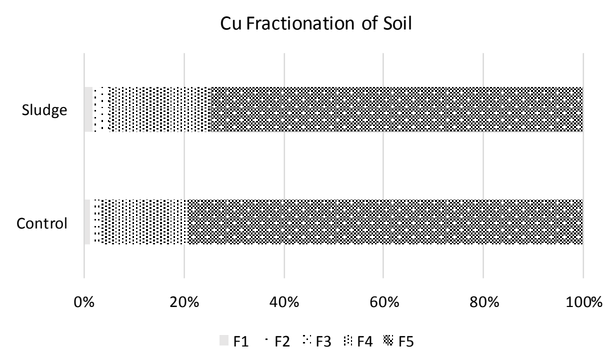

Fig.6. Proportional distribution of Cu fractions in control and sludge treated soil

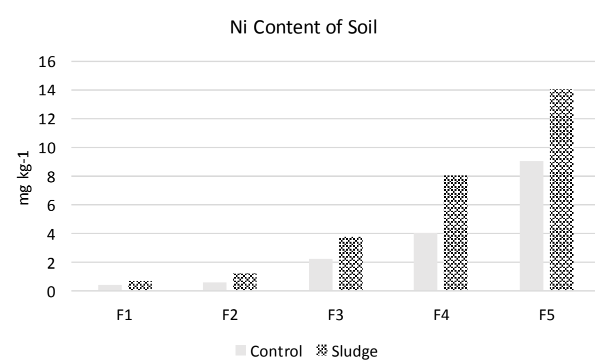

Fig. 7. Distribution of Ni fractions in control and Ni-treated soil by sludge applications

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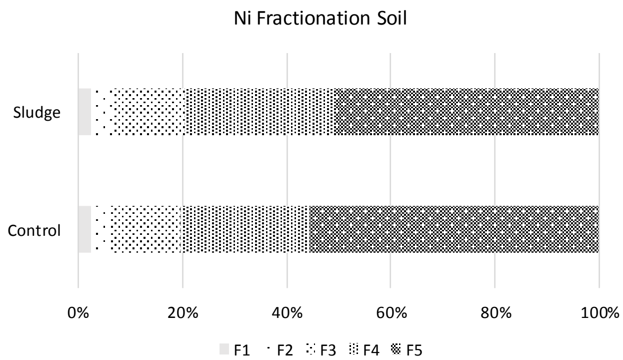

Fig. 8. Proportional distribution of Ni fractions in control and sludge treated soil

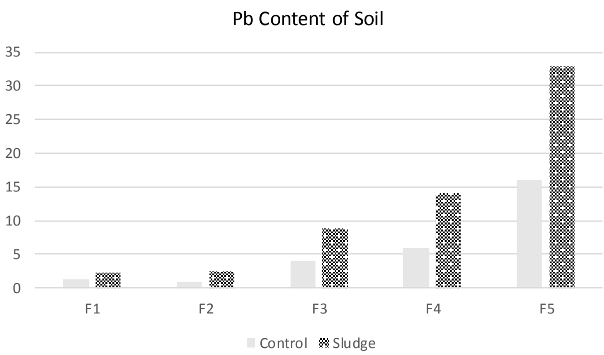

Fig. 9. Distribution of Pb fractions in control and Pb-treated soil by sludge applications

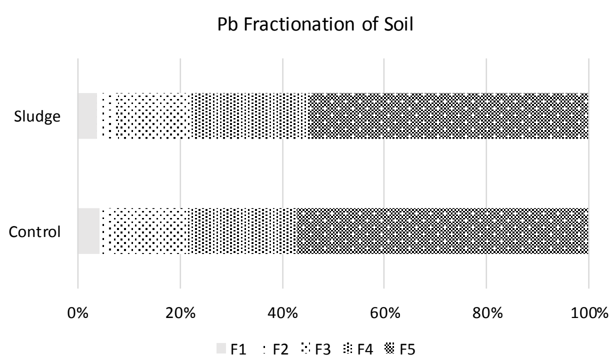

Fig. 10. Proportional distribution of Pb fractions in control and sludge treated soil

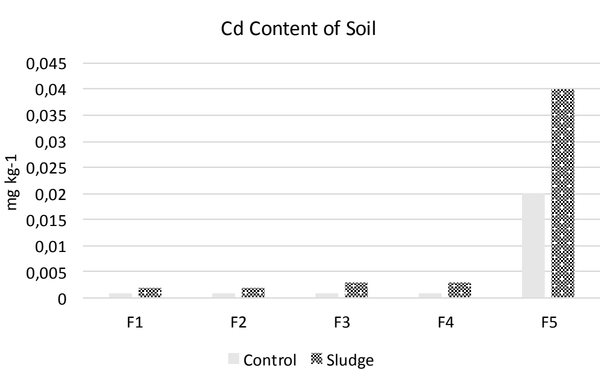

Fig. 11. Distribution of Cd fractions in control and Cd-treated soil by sludge applications

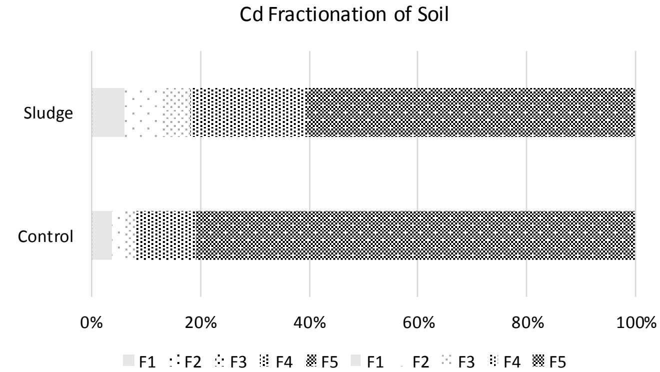

Fig. 12. Proportional distribution of Cd fractions in control and sludge treated soil

Similar to DTPA extractable metals, a significant increase in the F1, F2 and partially F3 fractions, which are considered as plant-available fractions of metals, was determined due to sludge applications. Proportionally, the increase in the F1, F2 and F3 fractions of Cu and Cd was less than the other metals. In the control and sludge treatments, the highest Cu and Cd metals were determined in the F4 and F5 fractions. In control treatment, the distribution of all metals in soil samples generally followed the order F1<F2<F3<F4<F5 with few exceptions. This also varied slightly for some metals depending on the sludge treatments. Studies on this subject [13, 14] reported that sludge applied to the soil significantly increased the metal concentration retained in the residual fraction.

Mobility of Metals

The metal mobility equation largely describes the potential mobility of metals. High MF values have been interpreted as indications of relatively high instability and bioavailability of heavy metals in soils (15). Sludge applications to soil increased the mobility factor value for all metals studied, especially Zn (Figure 13).

The findings are in contradiction with the literature reporting that sludge applications increase adsorbed metals in soil and decrease the concentration of bioavailable metals [15]. Based on the metal contents of sewage sludge in Table 2, metal content is expected to increase with sludge application to soil. However, the adsorption or mobility of these metals entering the soil may be affected by the physical and chemical properties of the soil and other properties of the sludge. However, in the study on the phyoremediation efficiency of sludge, the opposite results were also obtained, and results were reported that sludge increased available metals in soil and metal uptake in tobacco plants [16].

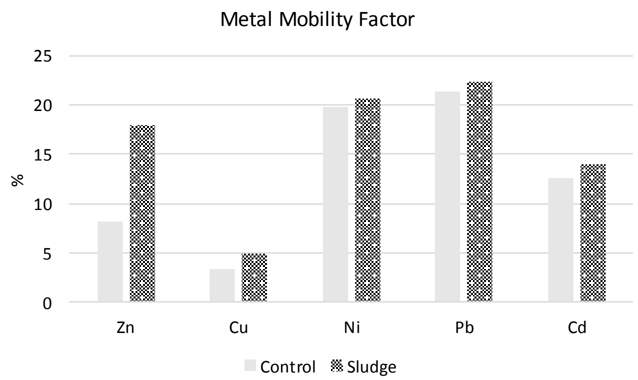

Fig. 13. Mobility factor (MF) value of metals in control and sludge treated soil.

III. Conclusion

The results of this study showed that the application of sludge to the soil increased the levels of DTPA-extractable/bioavailable metals in the soil. Also sludge treatments have increased the F1, F2 and F3 fractions of metals and increased the mobility of all metals. According to these results, in the long term, sewage sludge use can also lead to significant accumulation of Zn, Cu, Pb, Ni, Cd and Ni in soils and plants. In addition to the known risks of sewage sludge such as high metal content and other potential toxic effects, the fact that the metals contained in the sludge are mostly in plant-available, easily soluble and mobile forms in the soil is considered as an important parameter to be considered in agricultural applications.

Conflicts of Interest

The authors declare no conflict of interest.

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