Fractionation of Heavy Metals in the Biochar Applied Soil

Bülent Topcuoğlu

Abstract— An incubation experiment was conducted to investigate the effects of biochar on heavy metal availability, metal mobility and metal fractionation in metal-contaminated soil. Heavy metals (Zn, Cu, Ni, Pb and Cd) were added to the uncontaminated calcareous red Mediterranean soil, and then 0% (control) and 2% biochar was applied to these soils. Soils were analyzed after a total of 6 months of incubation under greenhouse conditions. Biochar applied to the soil significantly decreased the DTPA extractable metals and all the metals in the water-soluble and exchangeable fractions. Biochar application significantly increased the organic bound and residual metal fractions in the soil and decreased the mobility factor of all metals. The results showed that biochar can be used as a soil conditioner to reduce metal availability in polluted soils.

***Keywords*—**Biochar, Metals, Soil Metal Fractionation

I. INTRODUCTION

IN recent years, heavy metals have become a major concern in soils due to their toxicity, large contribution resources, non-biodegradable properties and cumulative behavior in intensive agricultural areas [1]. Heavy metal pollution of agricultural soils is one of the most serious environmental problems and has significant harm to human health. Due to the intensive use of agricultural chemicals in agricultural soils, heavy metals are becoming common pollutants in agricultural soils and the environment. 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]. In this respect, alternative and economical solutions are needed to remove non-point pollutants or to reduce their effects.

Maximum heavy metal concentrations allowed in contaminated soils are based on total concentration [3]. However, these criteria are not sufficient for a comprehensive assessment of environmental impacts, as mobility, environmental diffusion and bioavailability are highly dependent on the physico-chemical properties of the soil as well as the chemical forms of metals [4]. In particular, the assessment and estimation of food contamination is closely related to the bioavailable fraction of heavy metals in the soil. The bioavailability of metals in the soil is affected by many factors such as texture, cation exchange capacity, pH value, soil colloids, organic matter and chelator, and the soil gives different responses according to the applications.

Biochar is a porous and high carbon product obtained by high temperature pyrolysis of organic materials. Many materials, including high-carbon organic substances, various plant wastes and organic fertilizers, can be used as raw materials for biochar production. Typically, biochars have high cation exchange capacity and alkaline chemical character. Among the most important features of biochars are their large surface areas and their ability to adsorb heavy metals [1]. Although Biochar applied to the soil does not cause a decrease in the total heavy metal content of the soil, it can reduce the availability and mobility of heavy metals [3] and therefore reduce the transport of heavy metals to the plant and the heavy metal concentration in the plant [4].

Although many experimental findings agree that biochar reduces metal mobility, there are conflicting findings regarding the metal forms of biochars and their effects on metal availability. The aim of this research is to determine the effects of biochar applied to soil contaminated with metals (Zn, Cu, Ni, Pb and Cd) on metal availability, metal mobility and metal fractions.

II. MATERIAL AND METHODS

Soil Sampling: The soil used in this experiment was sampled from red mediterranean soil, which represents the main agricultural areas of Turkey. Antalya Aksu. Greenhouse soil samples were taken from a depth of 0 to 30 cm and they were air dried, sieved (< 2 mm).

Preparation of Biochar for Experiment: The biochar material used in the experiment was obtained from orchard pruning waste. Biochar production was obtained by pyrolysis of 0.5-1 cm ground waste biomass and then pyrolysis and regrinding at 550 °C in an oxygen-free environment. The C/N ratio of the biochar used in the research was determined as 185/1 and the pH value as 7.4. The particle size of the material was less than 1 mm.

Experimental Design: Two levels of Biochar (control treatment and 4 % Biochar treatment) and 2 levels of heavy metals (control treatment and Zn, Cu, Ni, Pb and Cd at 300, 140, 75, 300 and 3 ppm concentrations respectively) with 5 replications. Ten kilograms of air-dried and sieved soil were filled into plastic containers. A pot plate was placed under each pot to prevent leakage. Heavy metals Zn, Cu, Ni, Pb and Cd were added to the experiment soil as metallic salt solutions (as $Zn(NO3)2$, $CuSO4$, $Ni(NO3)2$, $Pb(NO3)2$, $Cd(NO3)2$, respectively). Metal concentrations are designed to meet the European Union's maximum metal limits [5]. A homogeneous application was obtained by homogenizing the soil. The soil was then incubated in the greenhouse for 6 months before the

Bülent TOPCUOĞLU is with the Akdeniz University Vocational School of Technical Sciences, 07058 Antalya TURKEY

experiment. 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 the below-mentioned analyses.

Soil Characterization: The main analytical properties of the test soil are shown in Table 1, which also shows the soil contaminant limits allowed by EU legislation. It was evaluated that the properties of the experimental soil were suitable for general plant cultures and that it did not contain heavy metals at a level that would adversely affect plant growth.

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 N, %	0,125
P (ex), mg kg^{-1}	2,8
K (ex), mg kg^{-1}	120
Ca (ex), mg kg^{-1}	1280
Mg (ex), mg kg^{-1}	255
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 [5]

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 [6].

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 [7] 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 total, bioavailable and sequentially extracted metal concentrations, soil samples were digested in aqua regia (1:3 HNO3/HCl) and HCLO4 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).

Metal Mobility Factor: 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 [8].

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 [5]. DTPA extractable metal concentrations of experimental soil after biochar and metal applications are presented in Figure 1 and the proportional changes of metals in applications are presented in Figure 2 and Figure 3.

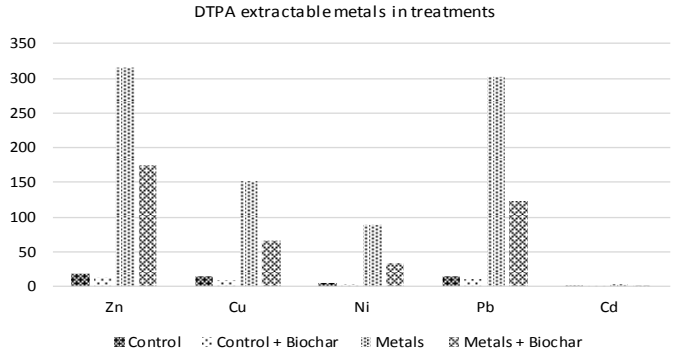

Fig. 1. DTPA extractable metal concentration in control soil and biochar treated soil

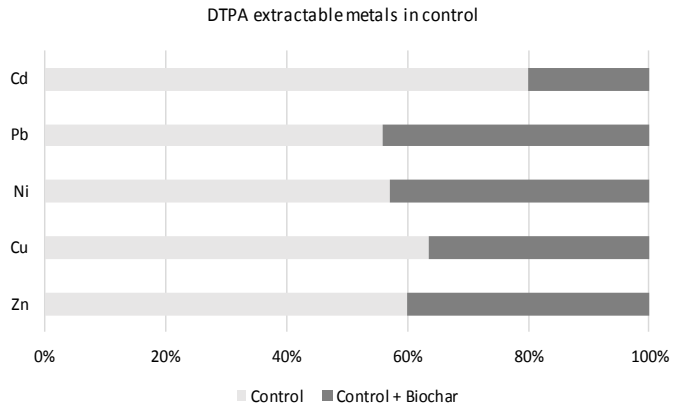

Fig 2. DTPA extractable metal rates in control soil and control+biochar treated soil

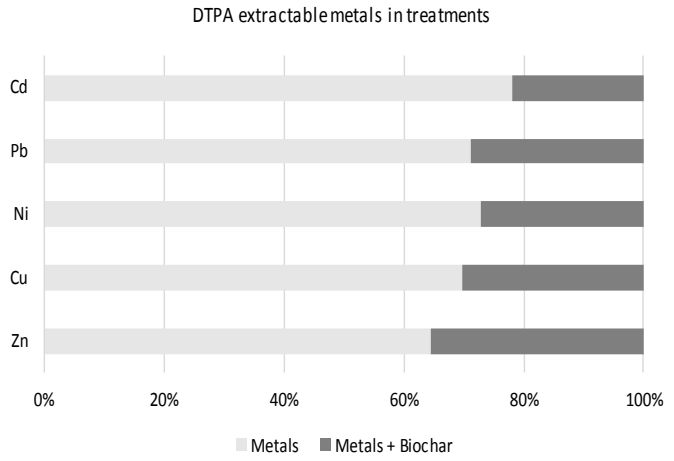

Fig 3. DTPA extractable metal rates of soil in metal and metal+biochar treatments

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. Metal applications to the soil significantly increased the amount of metals extractable with DTPA (Figure 1). Biochar applications resulted in significant reductions in DTPA extractable Zn, Cu, Ni, Pb and Cd concentrations in both control and metal-treated soil (Figure 2 and Figure 3). The effect of biochar on DTPA extractable metals in metal-applied soil was higher than that of the control. Biochar significantly reduced metals in soluble form applied to the soil and easily taken up by plants. In this regard, it has been reported that biochar applied to soil significantly reduces CaCl2-extractable metals [9].

Soil Metal Fractionation

The ratios of Zn, Cd, Ni, Pb and Cd in soil fractions are presented in Figure 4-8. 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. 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]. In the control process, the distribution of metals in the soil samples generally followed the following order for the metals studied: Zn: F1<F2<F3<F4<F5, Cu: F1<F2<F3<F4<F5, Ni: F1<F2<F4<F3<F5, Pb: F1<F2<F4<F3<F5, Cd: F1<F3<F2<F4<F5.

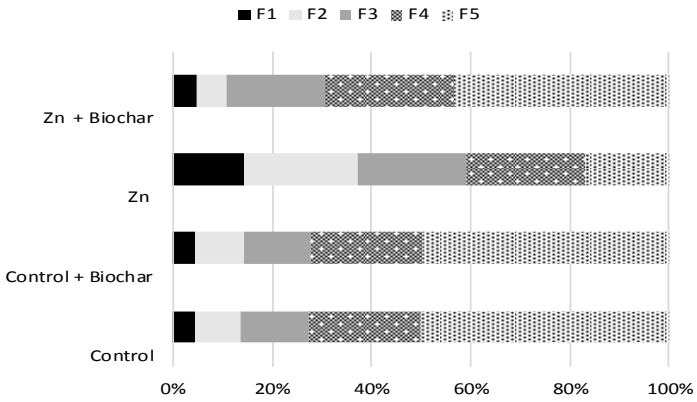

Fig 4. Distribution of Zn fractions in control and Zn-treated soil by biochar applications

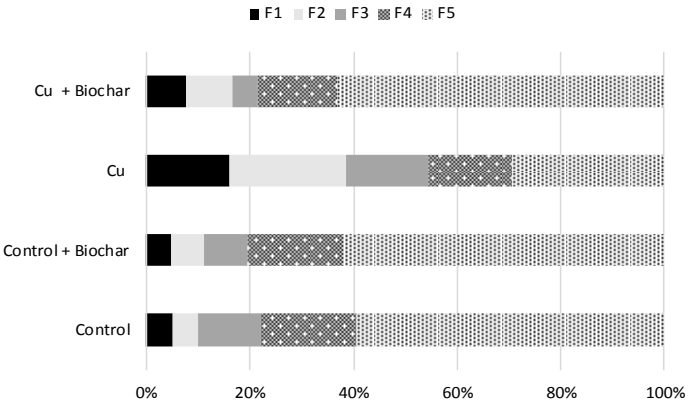

Fig. 5. Distribution of Cu fractions in control and Cu-treated soil by biochar applications

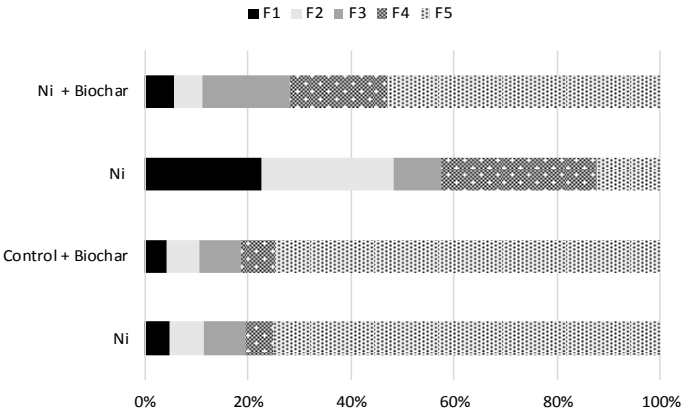

Fig. 6. Distribution of Ni fractions in control and Ni-treated soil by biochar applications

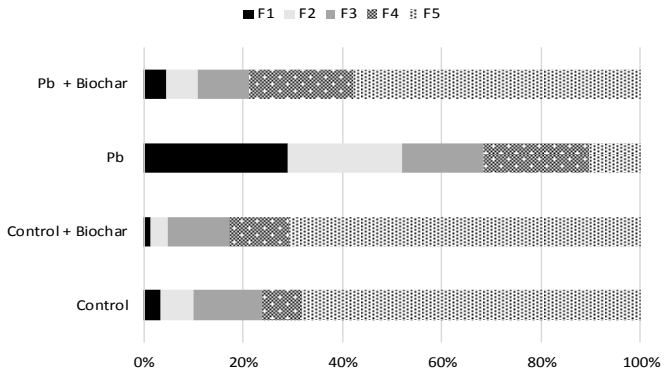

Fig. 7. Distribution of Pb fractions in control and Pb-treated soil by biochar applications

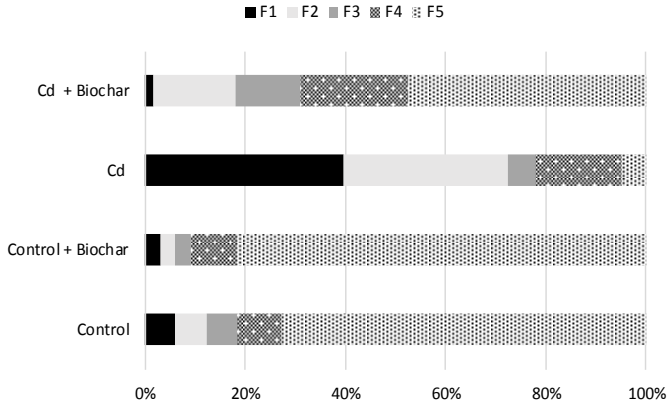

Fig. 8. Distribution of Cd fractions in control and Cd-treated soil by biochar applications

Metal applications to the soil significantly increased the heavy metal concentrations and ratios in the soil fractions in both control and metal-treated soil, except for the F5 fraction. Metals in fractions F1, F2, F3, and F4 increased significantly with metal applications to soil. The exchangeable (F1) and acid-extractable fractions (F2) are considered to be readily soluble and usable and readily available to the plant. In metal applications to soil, the proportional distribution of metals in soil samples generally followed the following order; Zn: F1<F5<F3<F4<F2, Cu: F5<F2<F1<F3<F4, Ni: F1<F2<F4<F5<F3, Pb: F5<F3<F2<F4<F1, Cd: F5<F3<F4<F2<F1. As might be expected, the applications of soil metals were increasing, especially in the F1 and F2 metal fractions, due to the metal applications being in the form of soluble metal salts. At the same time, F3 and F4 metal fractions, which represent oxidisable and organic matter bound metals, increased with metal applications to the soil.

When the fractionation of metal applied soils after biochar incubation is examined, it is seen that the F1, F2 and F3 fractions decreased significantly, and especially the residual fraction (F5) increased significantly. In biochar applications to soil, the proportional distribution of metals in metal-treated soil samples generally followed the following order; Zn: F1<F2<F3<F4<F5, Cu: F1<F3<F2<F4<F5, Ni: F1<F2<F3<F4<F5, Pb: F1<F2<F3<F4<F5, Cd: F1<F3<F2<F4<F5. According to these data, it is seen that biochar applied to the soil significantly reduces the easily available metal fractions and significantly increases the ratio of metals retained in the F4 and F5 fractions relatively. Studies on this subject [9, 10, 11] reported that biochar applied to the soil significantly increased the metal concentration retained in the residual fraction and significantly reduced the metals in the easily soluble fraction.

Mobility of Metals

The metal mobility equation largely describes the potential mobility of metals. High MF values, expressed as the mobility factor (MF), have been interpreted as indications of relatively high instability and bioavailability of heavy metals in soils (15). Biochar applications to metal-free control soil decreased the mobility factor value for all metals studied, especially Cu, Ni, Pb and Cd (Figure 9). As metal applications to the soil naturally give soluble metal salts to the soil, MF values increased for all metals. Biochar applications significantly reduced MF values in metal-treated soil.

The decrease in the mobility of metals in biochar-treated soils can be explained by the adsorption of metals on the active surfaces of biochar. In this regard, it has been reported that biochar applications increase the metal adsorbed in the soil and the concentration of bioavailable metals decreases [11, 12]. However, in the study on the phyoremediation efficiency of biochar, the opposite results were also obtained, and results were reported that biochar increased metal uptake in tobacco plants [13].

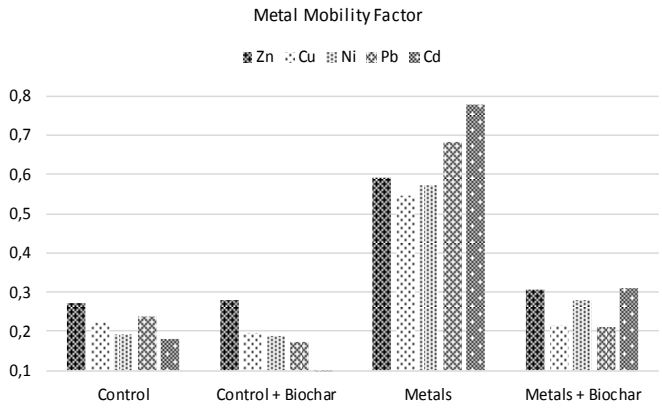

Fig 9. Change of metal mobility factor (MF) in control and metal treated soil by biochar applications

CONCLUSION

The results of this study showed that the application of Biochar to the soil reduced the levels of DTPA-extractable/bioavailable Zn, Cu, Ni, Pb and Cd in the soil. In addition, the application of biochar essentially increased the residual and organically bound metal fractions and significantly reduced the mobility of all metals. According to these results, biochar has the potential to be used as an alternative remediation agent with its reducing effects on

metal mobility in metal-contaminated soils. However, due to the different findings obtained in phytoremediation studies, differences in evaluations, the ability to obtain biochar from different sources, and the variability of its properties depending on the material obtained and the manufacturing method, there is a need for studies on this subject to be tested on biochars obtained with different materials and methods.

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