Effects of Leonardite Material on Soil Metal Fractions and Plant Growth in Soil Contaminated with Cadmium

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Abstract— In this experiment, the effects of Leonardite (LEO) material applied to soil contaminated with Cadmium (Cd) metal on the soil metal fractions, and its effects on the growth and metal concentration of Corn plant were studied. Regarding the Cd applications to the soil, the Cd content of the plant increased and the dry matter yield decreased significantly. In LEO applications, higher Cd values were determined in the organic bound fraction. LEO applied to the soil significantly decreased mobility factor of Cd , Cd concentration of the plant and the metal transfer factor. The amount of plant dry matter was determined relatively higher in LEO applications. The findings show that LEO material can be used as an alternative soil conditioner and environmental improvement material to support plant growth in soils contaminated with heavy metals.

Keywords— Soil pollution, Cadmium, Leonardite

I. Introduction

LEO, a low rank coal between peat and sub-bituminous, rich in humic acids is defined as eutrophic deposits with low oxygen content, in the lake bottoms, plastic structure, containing high organic matter and organism residues due to the abundance of vegetation in regions with heavy rainfall. These organic deposits may contain significant amounts of fulvic and humic acid derivatives. Fulvic acids (FA) and humic acids (HA) constitute an important part of soil organic matter and their binding capacity plays an important role in the mobility of metal ions [1]. Defined as an organic product, LEO can regulate the physical, chemical and biological properties of the soil with its natural quality and has been known as an important agricultural fertilization material in recent years.

The importance of using organic fertilizers in soil fertility is known in terms of ensuring sustainable use of soils and minimizing environmental pollution. In agricultural regions where organic matter resources are limited, LEO material has an important effect on increasing the soil carbon level. In addition, it helps in the rehabilitation of problematic soils in terms of chemical properties. It is also known that the chelating effects of humic and fulvic acids, which are released as a result of the decomposition of LEO material in the soil, affect the mobility of nutrients and metals in the soil.

In this study, the effects of LEO material, which is accepted as one of the current organic materials, on soil metal binding characteristics and plant growth in soil contaminated with cadmium metal were investigated. It is hypothesized that LEO application might enhance plant growth and reduce Cd uptake in Cd contaminated soil.

II. Material And Methods

In the study, unpolluted red Mediterranean soil in the natural ecosystem was used, apart from agricultural use. At 50 m above sea level, the soil sample under the influence of the Mediterranean climate developed on the calcareous parent material. There are natural vegetation grasses and maquis plants on the soil.

Greenhouse soil were taken at a depth of 0 to 20 cm for experiment and some were air-dried, sieved (< 2 mm) and stored in polyethylene bags sealed awaiting for soil analysis. Physical and chemical characteristics of greenhouse soil studied (Table 1) before the experiment are well within the accepted normal range of agronomic values, and the Cd concentration are below the levels indicated by the EU [2].

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

Parameters	Values	Evaluation
Sand, %	32	Clay Loam
Silt, %	38	
Clay, %	30	
pH- H_2O (1:5 w/v)	7.5	Slightly alkaline
$CaCO_3$, %	9,5	Calcareous
Organic matter, %	1,05	Low
CEC, cmol kg^{-1}	22	Medium
EC, dS m^{-1} 25°C	0,57	Salt-free
Total N, %	0,09	Low
P (ex), mg kg^{-1}	5,3	Low
K (ex), mg kg^{-1}	74	High
Ca (ex), mg kg^{-1}	1335	High
Mg (ex), mg kg^{-1}	115	Low
Total Cd, mg kg^{-1}	0,01 (1-3)*	Low

*: Metal limits in soil, mg kg^{-1} dry wt [2]

Plastic pots with 2.5 kg soil were used in the experiment. LEO and Cd metal applications were made to the soil sample according to the applications in Table 2 and it was left to incubate in the soil at the field capacity water level for 1 year.

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TABLE II. EXPERIMENTAL DESIGN OF LEO AND CD METAL LEVELS APPLIED TO THE SOIL

Cd treatments, Control (-L)	LEO + Cd treatments (+L)
0 ppm Cd	0 ppm Cd + LEO
10 ppm Cd	10 ppm Cd + LEO
20 ppm Cd	20 ppm Cd + LEO
40 ppm Cd	40 ppm Cd + LEO

Cd metal was applied to the soil in the experimental pots in the form of $Cd(NO_3)_2$. The amounts of N added to the soil with $Cd(NO_3)_2$ applications were equalized by adding NH_4NO_3 to be equal in all applications. After the LEO material was washed with distilled water and dried before the application, it was applied to all pots except the control at a level of 40 g/kg. After incubation, soil samples were taken from the pots and analyzed.

After incubation, 100 ppm N, 40 ppm P_2O_5 and 100 ppm K_2O were applied to all pots as basic fertilization and 4 corn seeds were planted. After the germination of the corn seeds, it was reduced to 2 pieces in each pot. In the experiment, the water level in the pots was adjusted to the field capacity and after the vegetation period of 2 months, the plants were harvested by cutting from the pot surface. Soil samples taken were prepared for analysis by drying and sieving processes.

Sequental extraction method [3] was applied to soil samples to identify metal fractions. The heavy metal sequential extraction procedure 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 NH_2OH/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 HNO_3+5 ml 30 % H_2O_2 (pH 2) for 3 h at 85 °C; metals associated with organic matter.

F5. HNO_3-HCl digestion; residual fraction.

Harvested fresh Corn plant samples were washed through with tap water and rinsed with deionized water. Plant samples were dried at 70 ºC in a forced-air oven, ground in an agate mortar and then digested in aqua regia (1:3HNO_3/HCl). After cooling to the room temperature, residue was diluted with deionized water and analysed for total Cd metal.

For the determination of ‘total’ and fractional Cd concentrations in digested and extracted soil and plant samples were analysed by using ICP-MS under optimised measurement conditions, and values were adjusted for oven dried (12 h at 105 °C) materia laccording to the international standard [4].

Selected environmental pollution indexes for soil samples ‘Mobility of Metals’ [5], as for plant samples ‘Heavy Metal Transfer (Bioconcentration) Factor’[6] were used for integrated evaluation of parameters.

Analysis of variance was used to evaluate the effects of different factors. Statistical analyses were performed by using SPSS-16 for Windows program.

III. RESULTS AND DISCUSSION

A. *Soil metal fractions after incubation*

Findings regarding the distribution of metal fractions in the soil left to incubation for 1 year depending on Cd and LEO applications in the soil are presented in Figure 1, Figure 2, Figure 3, Figure 4 and Figure 5.

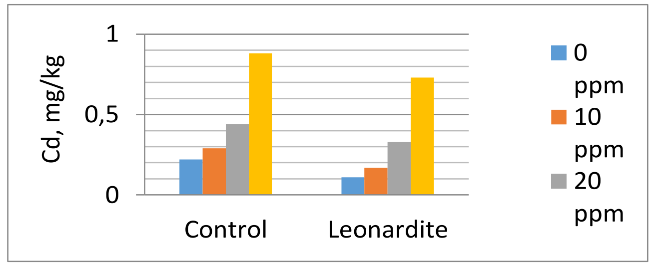

Fig 1. Water-soluble and exchangeable form of Cd (F1)

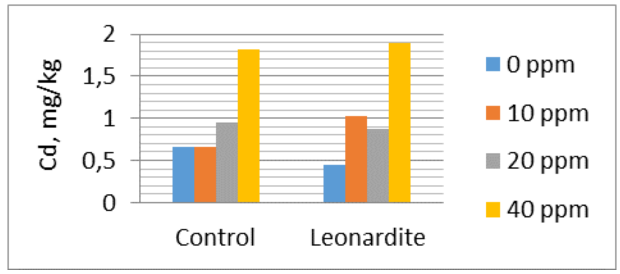

Fig 2. Cd form bound to carbonates (F2)

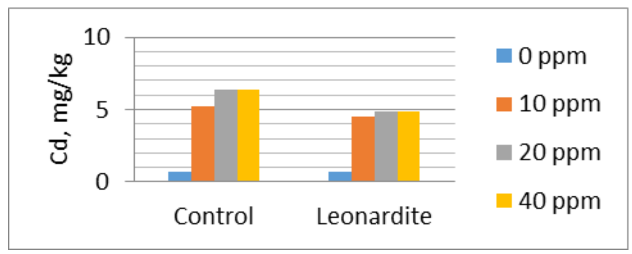

Fig 3. Cd form bound to iron and manganese oxides (F3)

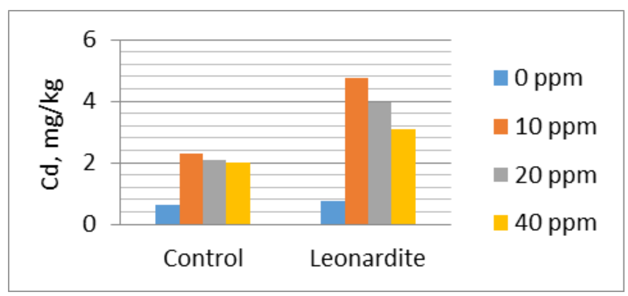

Fig 4. Cd form bound to organic substances (F4)

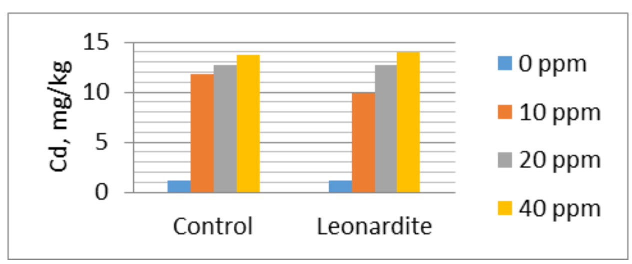

Fig. 5. Residual form of Cd (F5)

Depending on the Cd metal applications to the soil, the Cd concentration was found to be high in all fractions in the soils with and without LEO applied, and the Cd concentration increased in the F1, F2, F3 and F5 fractions depending on the increasing Cd concentrations. Although the Cd concentration in F4 fraction, which is an organic bound metal form, was higher than the control, a relative decrease was determined due to increasing Cd applications. In LEO applications, a statistically significant decrease was determined in the F1, F2, F3 fractions, while an increase was detected in the F4 fraction. These results show that LEO applications significantly reduce the water-soluble and exchangeable forms of metals, which are easily available, and their bonds to oxidized metal forms. Bioavailability and toxicity of some metals in natural surface waters are reduced by complexation with dissolved organic matter [7]. The fact that LEO, which is a natural organic structure, increases the organic-bound metal forms, is considered to have an important effect on the stability of Cd metal in the soil. Several studies have found that Cd has affinity for organic matter [8]. It was determined that LEO applications did not have a significant effect on the residual metal fraction (F5). The fractional distribution of Cd metal in the soil followed the order of 'F5> F3> F4> F2> F1'. Cd was found in the soil mostly in residual form and bound to iron and manganese oxides. This result also shows the mainly chemical binding site of Cd metal in soil.

B. Effect of LEO applications on metal mobility (MF)

The effect of LEO applications on metal mobility in Cd metal applied soil is presented in Figure 6. Metal mobility factor was found to be relatively high in soils where LEO was not applied to the soil. Similar results were reported with LEO applications [9,10] and potassium humate rich in humic acids [11]. These findings show that the Cd element is chemically adsorbed by the LEO material to a large extent, the LEO material significantly reduces the metal mobility in the soil and in a sense provides stability against the metal elements in the soil. The metal mobility factor was found to be higher in the treatments that did not apply Cd to the soil. It is considered that this is probably due to the relatively low F4 and F5 fractions of the available Cd metal in the soil.

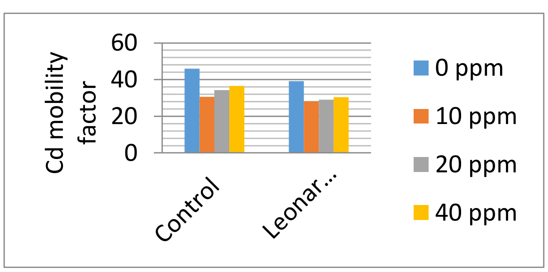

Fig. 6. Metal mobility factor of Cd

C. Effects of Cd and LEO applications on the growth and metal uptake of Corn plant.

The effects of Cd metal and LEO applied to the soil on the above-ground biomass (dry matter) value, Cd content and metal transfer factor of the Corn plant are presented in Figure 7-1, Figure 7-2, Figure 8 and Figure 9.

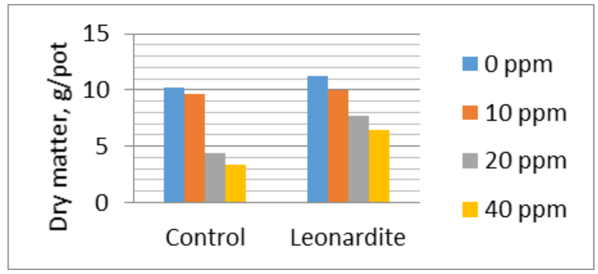

Fig. 7-1. Dry matter amount of Corn plant

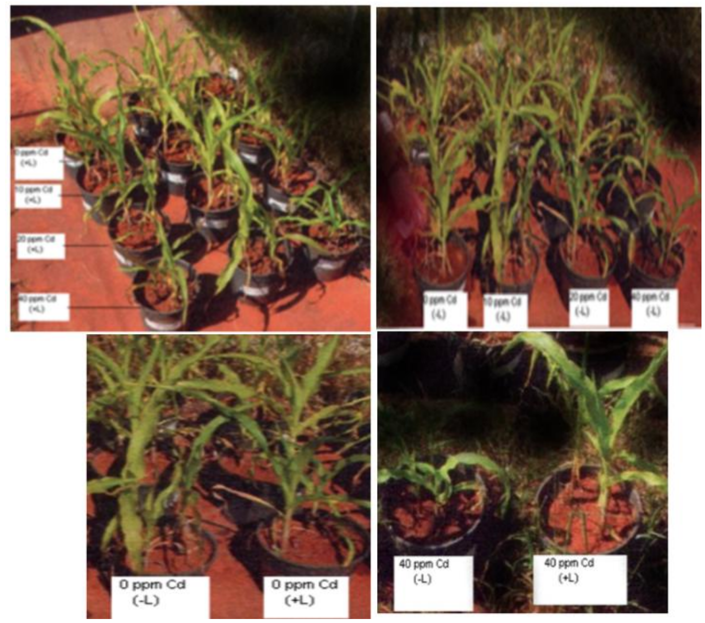

Fig. 7-2. Growth images of Corn plants in the experiment

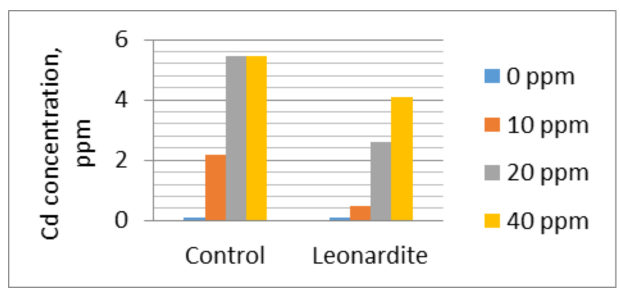

Fig. 8. Cd concentration of Corn plant

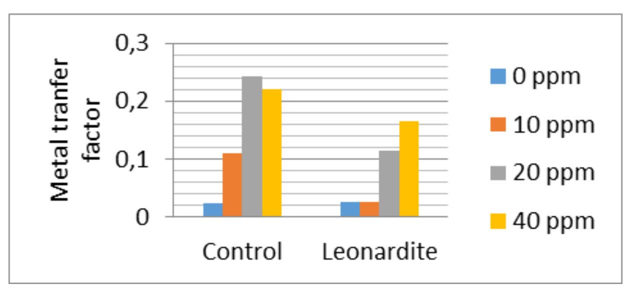

Fig. 9. Metal transfer factor of Corn plant

Cd metal applied to the soil negatively affected plant growth and significant decreases were determined in plant biomass due to increased Cd applications. In LEO applications, the decrease in plant biomass was determined less in increasing Cd applications than in control application (Figure 8). It is reported that humic acid applications were decreased plant toxicity in metal contaminated soil [7]. These findings show that LEO applications may have a significant effect on reducing metal mobility or on the plant being less affected by metal toxicity with another effect. Regarding the Cd metal applications to the soil, the Cd concentration in the plant increased in the control and LEO applications, but relatively less Cd concentration in the plant was determined in the LEO applications (Figure 8). Cd applications to the soil increased the metal transfer factor in the plant in all treatments. However, in LEO applications, the metal transfer factor value was determined to be lower by almost half (Figure 9). It is evaluated that the decreasing Cd concentration in the plant and the decreasing metal transfer factor are compatible with the decreased metal mobility in the soil due to LEO applications.

IV. Conclusion

The amount of Cd retained in different fractions in the soil increased with the Cd applied to the soil, and lower Cd values and lower mobility factor were determined in the soil metal fractions in LEO applications. The amount of dry matter of the plant decreased with Cd applications, and higher dry matter values were obtained in LEO applications. Lower Cd content and metal transfer factor were determined in the plant by the application of LEO. The findings show the inhibitory effect of LEO material on the absorption of heavy metals and show that it can be used as an alternative environmental improvement material for stabilization of polluted soils and growing healthy crops in achieving success in crop production in the future, this success depends on the sustainable management of soils and the preservation of soil quality.

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