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EFFECT OF BIOCHAR AMENDMENT ON ZINC AVAILABILITY IN AN ARTIFICIALLY CONTAMINATED SOIL

36 pt

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SUMMARY: This study focuses on the effect of biochar on zinc availability in an artificially contaminated soil. The biochar was produced under oxygen-limited conditions at 700 °C, using dried olive pomace as feedstock. Incubation experiments were conducted in order to study the influence of biochar amendment rate (0, 5 and 10%, added biochar) on metal leaching from soil at two different zinc concentrations (1000 and 2000 mg/kg). Zinc availability was evaluated through single extractions using three different solutions, namely deionized water (DW), $CaCl_2$ and EDTA. Soil samples were analyzed regarding pH, redox potential and electrical conductivity, as well. According to the results, the concentrations for EDTA-extractable zinc reached much higher levels than those of $CaCl_2$- and DW-extractable zinc. Moreover, zinc extractability decreased with increasing biochar amendment rate, for both concentrations. Biochar addition to soil, generally led to increased pH and electrical conductivity values, as well as to reduced redox potential values.

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1. INTRODUCTION

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The presence of elevated concentrations of potentially toxic metals in soil environments is a major issue of concern with numerous negative consequences not only on soil ecosystems but also on animals and humans. In the majority of cases, industrial and agricultural activities, as well as waste disposal are responsible for this phenomenon. Traditional remediation strategies which include soil excavation and landfilling are often expensive, particularly when dealing with extensive contaminated areas (Huang and Hao, 2012; Lee et al., 2011). Immobilization of potentially toxic metals using soil amendments is a relatively less expensive technique, mainly due to its in situ application, which has been showing encouraging results lately (Tica et al, 2011). The amendments used for this purpose include a wide variety of materials (Abbaspour and Golchin, 2011; González et al., 2012), not only of inorganic (Huang and Hao, 2012; Tica et al, 2011), but also of organic nature (Chen et al., 2010).

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Much attention has lately been drawn to the use of biochar as a soil amendment for contaminated soil remediation, and for metal immobilization in particular (Ahmad et al., 2012; Park et al., 2013; Tang et al., 2013; Zheng et al., 2013). This type of material is produced through pyrolysis of biomass, such as municipal solid waste, sewage sludge, and manure, agricultural and agroindustrial residues. It has the ability to reduce nutrient leaching through soil, therefore most of the research related to biochar concerns its use for improving soil quality and fertility (Houben et al., 2013; Wagner and Kaupenjohann, 2014).

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The main objective of this study was to evaluate the effect of a biochar material, generated form dried olive pomace (DOP), on zinc availability in an artificially contaminated soil sample. For this purpose, incubation experiments were carried out, through which the effect of different biochar amendment rates (0, 5 and 10%, added biochar) and zinc concentrations (1000 and 2000 mg/kg) were studied. Zinc availability was evaluated through single extractions using deionized water, $CaCl_2$ and EDTA solutions.

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2. MATERIALS AND METHODS

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3. Soil and biochar preparation

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The soil used in the present study was obtained from an agricultural area in Chania, Crete. At first, the sample was air-dried and subsequently the soil lumps were manually ground and sieved (<2mm).

DOP was initially oven dried and ground to obtain a particle size lower than 500 μm. Subsequently, the material was pyrolyzed under oxygen limited conditions in order to produce the biochar. In brief, porcelain crucibles were filled to capacity with the ground material, covered with a fitting lid and introduced in a muffle furnace. The target temperature of 700 °C for biochar production was achieved within 1 hour and the duration of the pyrolysis process was of 2 hours. The resulting material was then washed with deionized water in a solid/liquid ratio of 1/15 g/mL, in order to remove excess ash. Then, the residue was separated by vacuum filtration, rinsed with deionized water and dried in an oven.

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3.1. Characterization

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The characterization of the soil and biochar samples was performed according to standard and/or previously published methods, as it is described in our previous study (Pellera and Gidarakos, 2012). Additionally, in this study cation exchange capacity (CEC) of the soil and biochar samples was determined, according to USEPA (United States Environmental Protection Agency) method 9081.

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2.2.1 Incubation experiments

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Incubation experiments were conducted in 400 mL capacity polyethylene cups. Each cup contained 250 g of soil and the appropriate amount of biochar, in order to obtain two different amendment rates (5 and 10%) of added biochar. The soil-biochar mixtures were then spiked with Zn^{2+} solution to 70% of the soil water holding capacity. The concentration of the metal solution was calculated, so as to achieve values of 1000 and 2000 mg/kg of soil. Blank trials, i.e. non- contaminated soil-only cups, contaminated soil-only cups and non-contaminated soil-biochar (5 and 10) cups, were also conducted. All cups were loosely covered with a transparent membrane to limit evaporation, and finally incubated at 23±2°C.

0.5cm Incubation lasted for a period of 30 days for all assays, during which soil samples (two from each cup) were taken on a regular basis, i.e. on days 1, 10, 20 and finally on day 30. These samples were used to perform pH, electrical conductivity (EC), Redox potential determination, as well as one-stage metal extractions with different extractants:

- Deionized water (DW), **3 pt**
- $CaCl_2$ (0.01 M) and
- EDTA (0.05 M). **3 pt**

The pH of the soil samples was measured in two different suspensions with DW and KCl 1N,

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respectively, with a solid/liquid (g/mL) ratio of 1/2.5. EC and Redox potential were measured only in the DW suspensions.

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Table 1. Soil and biochar characterization.

Properties	Samples	
	Soil	Biochar
pH		
Deionized Water	7.95	10.14
KCl	7.12	9.50
pH_{PZC}	8.8	10.2
Pseudo-total concentration (mg/kg)		
Cd	< Detection Limit	< Detection Limit
Ni	25.48	7.58
Moisture (%)	20.69 [a]	2.8 [b]
Volatile matter [c] (%)	-	8.2
Ash [c] (%)	94.31	11.8
Fixed carbon [c] (%)	-	77.3
Organic Matter [c] (%) ($LOI_{@440\ °C}$)	5.69	-
SSA_{BET} (m^2/g)	12.04	72.81
C (%)	-	72.5
N (%)	-	10.1
Mineralogy	Quartz Calcite Kaolinite Illite	Quartz Calcite

[a] as received, [b] after production and storage, [c] dry basis

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For metal extractions, 1 g of soil sample was weighed in 50 mL centrifuge tubes, in which 10 mL of extractant solution were added. The tubes were then agitated at 250 rpm for a determined time period, which corresponded to 1 h, 3h and 1 h, for DW (Cao et al., 2009), $CaCl_2$ (Tica et al., 2011) and EDTA (Rao et al., 2010), respectively. Afterwards, the contents of the tubes were separated by centrifugation at 3,900 rpm for 15 min and finally, the supernatants were filtered (Whatman 589/3), acidified (pH < 2) and stored at 4 °C. It is worth mentioning that the samples obtained from the EDTA extractions were filtered once more through nylon membrane filters (0.45 μm). Zn^{2+} concentrations in the liquid samples were determined using an Atomic Absorption Spectrometer (AAS) Perkin-Elmer AAnalyst, 100A.

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Table 2. CEC of soil, biochar and soil-biochar mixtures 3 pt

Sample	CEC ($cmol_c$/kg)
Soil	0.037
Biochar	0.051
Soil-BC5%	0.051
Soil-BC10%	0.160

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4. RESULTS AND DISCUSSION

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4.1. Characterization

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The main properties of the soil sample and the produced biochars are presented in Table 1, while Table 2 shows the CEC values of Soil, Biochar and the soil-biochar mixtures, obtained after adding biochar to soil at two different rates, namely 5 and 10%.

It is obvious that the biochar used in this study has a higher CEC than soil. Moreover, biochar addition to soil has a positive effect on this parameter, especially at the highest amendment rate (10%), for which CEC is three times higher than the value for the 5% amendment rate. These results are comparable to those of Kloss et al. (2014), who in their study also observed that increasing biochar amendment rates led to increasing CEC. The effect of biochar addition to soil on its CEC has previously been noticed. Although the duration of this effect is doubtful, it is probably caused by leaching of hydrophobic compounds from the biochar or by increasing carboxylation of C via abiotic oxidation (Verheijen et al., 2010).

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4.2. Soil parameters variation

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Figure 1 shows the variation of pH during the incubation period for non-contaminated (Fig. 1a and b), as well as for contaminated (Fig. 1c and d) assays. In all cases, the values obtained for KCl suspensions are lower than the ones obtained for DW suspensions.

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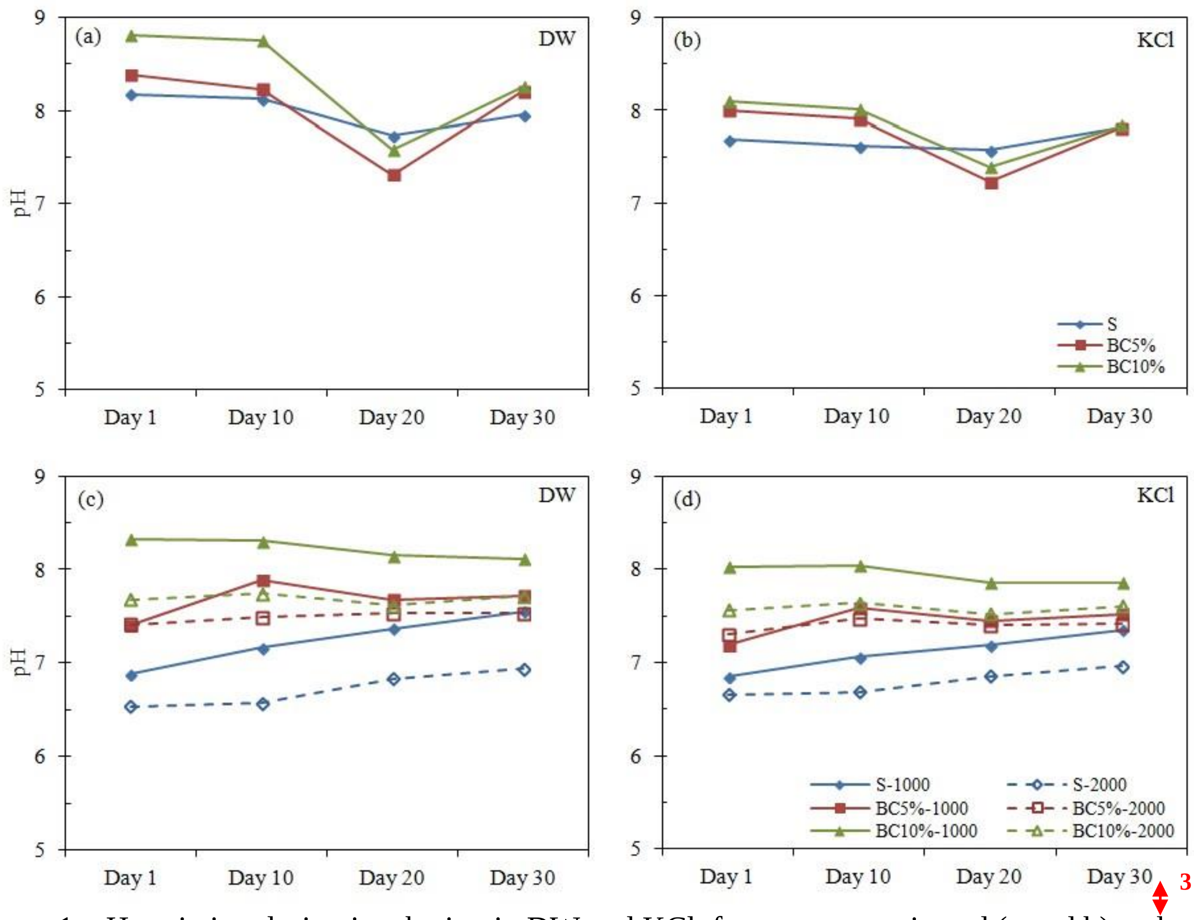

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Figure 1. pH variation during incubation in DW and KCl, for non-contaminated (a and b) and contaminated (c and d) assays

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In both non-contaminated and contaminated assays, it is noticed that biochar addition causes an increase in soil pH, with the 10% amendment rate leading to higher values than the 5% rate. This is attributed to the alkaline nature of the biochar, which is a result of the transformation of K and Ca ions into oxides, hydroxides and carbonates, through pyrolysis of DOP (Houben et al., 2013). However, pH decreases with increasing metal concentration in the assays. The behaviour of pH throughout the incubation period varies among samples. More specifically, for non-contaminated (both non-amended and amended) assays, pH has a decreasing trend with time, while for contaminated non-amended assays, pH seems to increase throughout incubation. On the other hand, for contaminated amended assays, pH is maintained generally stable with slight variations. EC and Redox variations are presented in Figure 2. Soil amendment with biochar at increasing rates seems to generally cause an increase in EC for all contamination levels, with similar observations having been made by Hossain et al. (2010). It is also noticed that for metal contaminated assays, EC values are higher than for non-contaminated ones. However, EC profiles do not show a clear trend throughout incubation. For what concerns Redox potential, it decreases as the biochar content of the samples increases, although the assays contaminated with 2000 mg Zn^{2+}/kg of soil tend to differ in some cases. It is generally observed that the Redox potential range for all assays is maintained between +100 and +350, therefore biochar did not cause any dramatic changes in this specific parameter.

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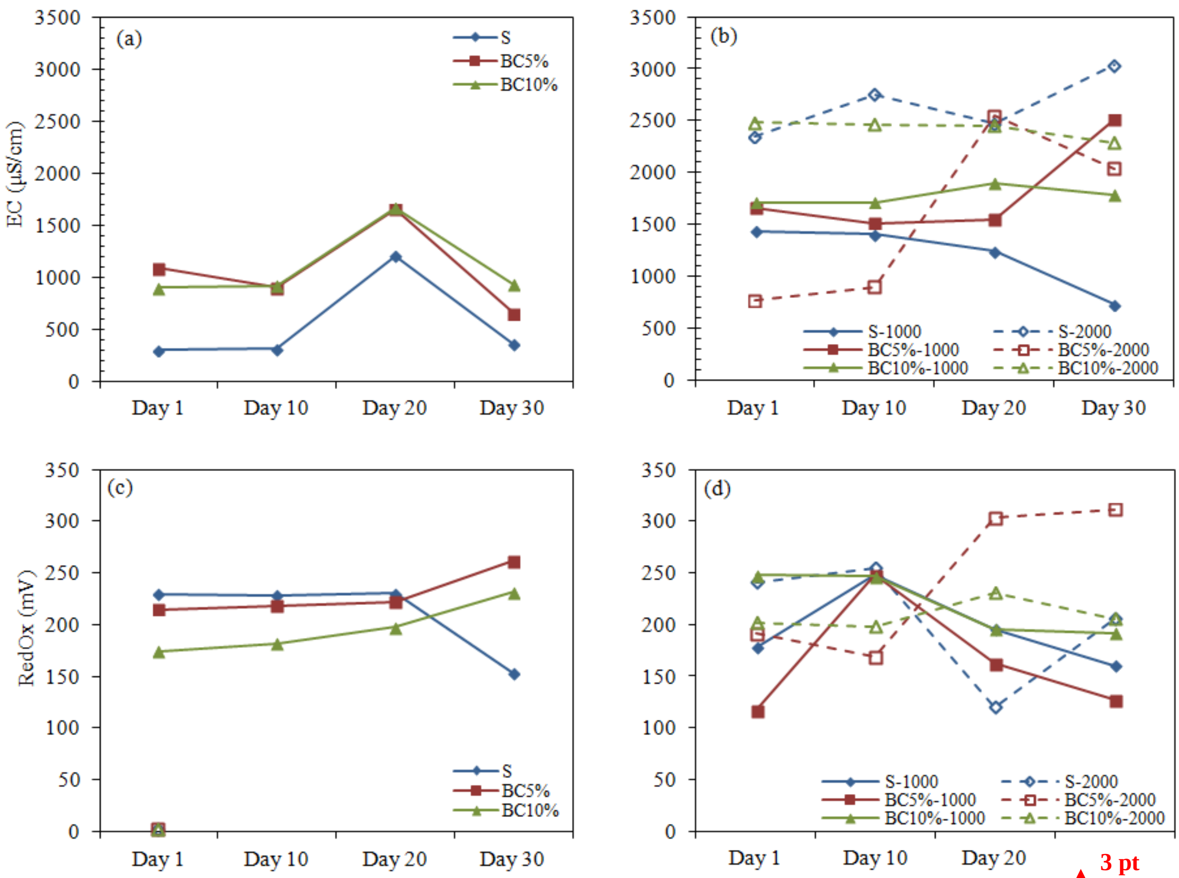

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Figure 2. EC and Redox variation during incubation, for non-contaminated (a and c) and contaminated (b and d) assays.

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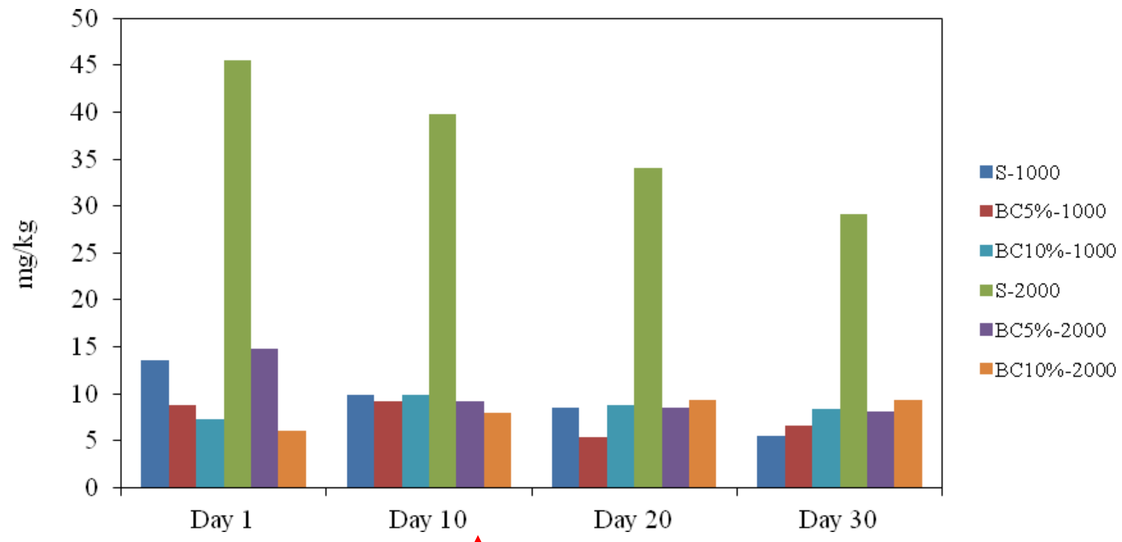

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Figure 3. One-stage extractions with DW

4.3. Metal extractions

Figures 3, 4 and 5 depict the results of the one-stage extractions that were performed on soil samples, with the figures referring to DW, $CaCl_2$ and EDTA, respectively. These three extractants were used in order to evaluate the extractability of zinc from different soil fractions. More specifically, DW extracts water-soluble zinc, $CaCl_2$ helps release the exchangeable portion, while when using EDTA, sorbed and organically bound zinc is extracted.

For both tested concentrations (1,000 and 2,000 mg/kg of soil), zinc extractability is noticed to decrease as the biochar amendment rate increases from 0 to 10%. The effect of biochar on zinc mobility may be attributed to the fact that this type of materials often causes changes in soil pH and CEC. More specifically, due to its alkaline nature (pH usually between 7 and 9) biochar addition leads to increased soil pH, which in turn enhances metal immobilization (Beesley et al., 2011; Houben et al., 2013; Lucchini et al., 2014). Moreover, as it can be seen in the figures, longer incubation periods allowed higher zinc retention on soil samples, for their majority, with the exceptions manifesting an almost stable behavior with time.

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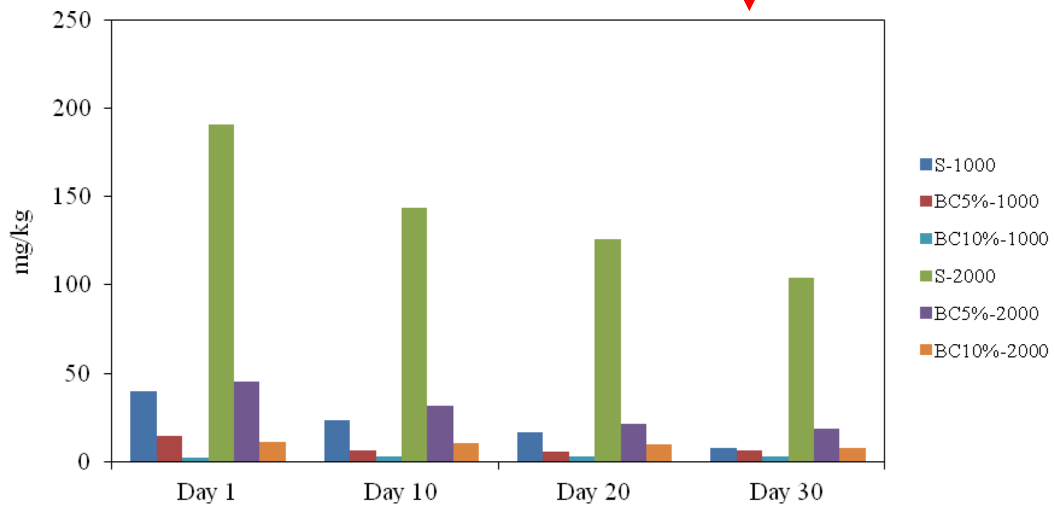

Figure 4. One-stage extractions with $CaCl_2$ (0. 01 M)

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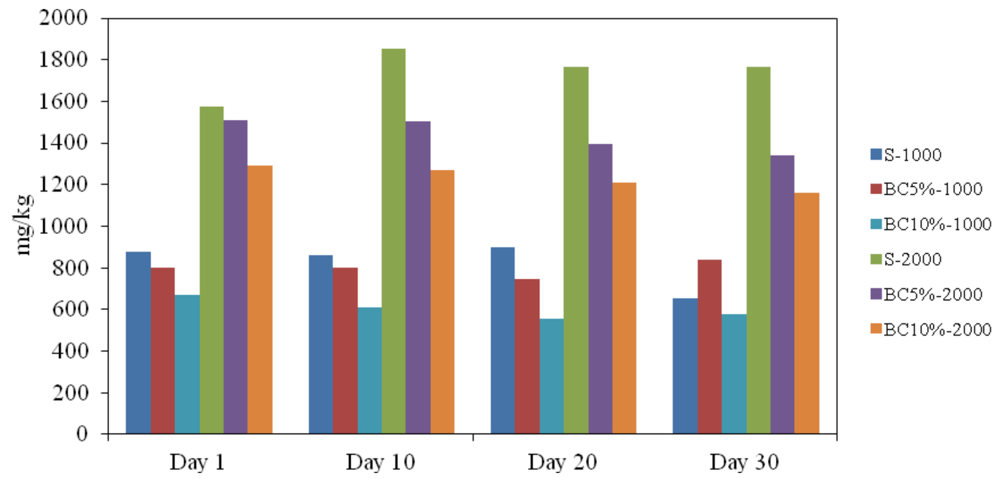

Figure 5. One-stage extractions with EDTA (0.05 M)

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Additionally, concentrations for EDTA-extractable zinc reached much higher levels than those of $CaCl_2$- and DW-extractable zinc. However, regarding the metal portion on which biohar had more effect on, this is the case for the exchangeable zinc, and since the highest extractability reduction was observed for the extractions with $CaCl_2$.

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5. CONCLUSIONS

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In this study dried olive pomace – generated biochar was evaluated as a soil amendment for reducing zinc mobility. Biochar was proved to have a positive effect for what concerns zinc immobilization, especially for the portion of the metal that is exchangeable and sorbed and organically bound to soil constituents. The increase in soil pH caused by biochar addition is most probably the reason for improved zinc retention to soil, with this theory being corroborated by the pH values of the assays during incubation.

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