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Sequential extraction of zinc in the soils of different land use types as influenced by wheat straw derived biochar

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ABSTRACT

Heavy metals distribution between different phases of soil influence their bioavailability and mobility. Fractionation techniques, unlike total content of metals, can provide facts about their mobility and transformation. Also, heavy metals mobility in biochar amended soils has been a recent subject of research. This paper represents the effect of biochar and zinc (Zn) in different land uses on Zn fractionation. In the present study an incubation experiment was carried out to evaluate the influence of three wheat straw biochar levels (0, 1.5 and 3% wt) and two Zn levels (0 and 10 mg Zn kg^{-1} soil as ZnSO$_4$·7H$_2$O) on Zn fractionations of agricultural, rangeland and forest soils. Applications of 3% biochar shifted the Zn distribution from exchangeable and carbonate fractions to the organic matter fraction. Furthermore, in all treatments most of Zn belonged to residual fraction. The concentration of exchangeable Zn was decreased significantly by nearly 60 and 54% with application of 1.5 and 3% biochar to agricultural soil, respectively. In rangeland soil these results are contrary to organic Zn fraction. Zinc concentration associated with carbonate showed a statistically significant increase (about 49%) as 1.5% biochar was applied to rangeland soil. Nevertheless, carbonated Zn concentration decreased significantly (about 44%) after 3% biochar was applied. Based on the results, in all land use types the Zn bound to carbonate, organic matter and crystalline iron oxide were increased significantly after application of 10 mg Zn kg^{-1} soil. The organic Zn concentration of biochar and Zn amended forest and rangeland soils were significantly more than that of agricultural soil. The reduced partitioning index values for all the soil types were high and close to 1 resulting from a high ratio value of the Zn strongly bounded in the residual fraction. The mobility factor gave values not higher than 10% for all treatments and land use types. The calculated mobility factor values showed that the bioavailability of Zn was relatively low. The influence of biochar on Zn mobility/bioavailability was different in the various land use types that can be considered in management of Zn polluted soils and their remediation or in the soil fertility management of agricultural soils.

1. Introduction

Since the existence of heavy metals (HMs) in soil to supply sufficient nutrients for plant growth and also determining the risk of environmental pollution with HMs are associated to their concentrations in soil, studies of the nature and amount of HMs can give beneficial information. Knowledge of the total contents of HMs in soil gives little information for their bioavailability and behavior. In order to better understanding plant availability of HMs, knowledge about their mobility, chemistry and distribution among soil fractions is necessary. Fractionation method can provide adequate information about HMs behavior and mechanisms in soil and highlight the relationship between soil and HMs. In this way, different chemical extractants at each stage can extract the amount of HMs which band with inorganic specific fraction of the soil. This technique differs in the number of fractions extracted, as well as the order and kind of reagents used. The weakest

extractant at the first and the strongest at the end are extracted. There are several methods for ranking fractionations of HMs. According to Tandy et al. (2009) and Wang et al. (2009) in addition to total amounts of HMs, their toxicity and mobility are influenced by chemical fractionations. Singh's fractionation procedure (Singh et al., 1988) that is used to determine various forms of HMs in soil, classified HMs into seven fractions: exchangeable, carbonate, organic, manganese-oxide (Mn-Ox), amorphous-iron (Fe)-oxide (AFe-Ox), crystalline-Fe-oxide (CFe-Ox) and residual. Water soluble and exchangeable fractions are readily mobile and available to plants but HMs combined with crystalline networks of clays is relatively inactive. The fraction of precipitated as carbonate, occluded in Fe, Mn and aluminum (Al) oxides, or complexes with organic matter could be considered relatively active or tightly bound, depending upon the actual combination of physical and chemical properties of soil (Sposito et al., 1982).

Zinc is defined as essential micronutrient for plant growth. However,

Zn deficiency in soils has been recognized as a worldwide problem that is increasing especially in arid and semi-arid regions. Mandal and Mandal (1986) reported that effectiveness of Zn fertilizer is low, even with Zn addition, deficiency does not solve. Soil conditions, plant species, climate conditions and agronomic practices are the significant factors affecting on Zn availability to plants and behavior in soil (Alloway, 1990). Soil pH, organic matter content, clay minerals, cation exchange capacity and sesqui-oxides are the main factors affecting the binding capacity of soils for Zn (Baghernejad et al., 2015, 2016). Zinc availability in soil is increased with decreasing pH values. In acid soils adsorption by clay minerals control the circulation of Zn while in alkaline soils chemi-sorption on sesqui-oxides and bonds on organic ligands are dominant processes (Kabata-Pendias and Pendias, 1992). Soil Zn is distributed into different forms. Water soluble beside exchangeable, organically bound, manganese oxide bound, amorphous oxide bound, crystalline oxide bound and residual fractions are Zn storages in soils (Mandal and Mandal, 1986).Water soluble and exchangeable forms of Zn are readily available to plants. Zinc in other forms is potentially plant available (organically bound, bound in oxides and sulfides) or residual form is unavailable to plant (Adriano, 2001). Waterlot et al. (2013) showed that Zn associated with the exchangeable, carbonate and Fe-Mn oxides/hydroxides fractions were the main Zn fractions. Ma and Rao (1997) reported that clay content, pH, organic matter and Fe-Mn oxides are the most important soil properties and components influencing the HMs bioavailability.

Increasing organic matter as soil amendment can be effective for HMs bioavailability. Biochar, pyrolysed of different organic substances, has considered in much research recently because of its potential ability and specific properties such as strong alkalinity, large surface area and organic matter content, porous structure and low cost (Dai et al., 2016). Furthermore, biochar as a practical remediation agent is effective sorbents for controlling HMs in the soil although this behavior is controlled by type of biochar and production method. Several previous studies have shown that biochar reduced HMs mobility and bioavailability in soil (Jiang et al., 2012). For instance, Dai et al. (2013) showed that functional oxygen groups and minerals on the biochar surfaces can form the complexes and precipitates with Zn^{+2}. Hao et al. (2010) showed that the concentration of HOAC extractable lead (Pb) and Zn were decreased by application of 1, 2 and 5% bone char as soil amendment after 3 months incubation. Their results highlighted the potential of bone char amendments to reduce the bioavailability of Pb and Zn in contaminated soil. By adding amendments HMs mobility in soils are reduced due to form chemical mechanisms such as absorption, complexation, precipitation and co-precipitation (Raicevic et al., 2005). Hodson et al. (2000) reported that the addition of bone char to soil increase soil pH and the formation of Zn phosphate precipitates as a result the concentration of acetic acid (HOAC) extractable Zn was decreased.

Organic substances like biochar can alter the distribution of different metal fractions in soils. As a consequence, on one hand their influences can be considered in remediation and management practices of polluted soil or ecosystems. On the other hand, their influences can be considered in soil fertility management practices and in agricultural/plant nutrition issues. Since the influence of biochar on the distribution of metal fractions may be different in the soils of different land use types. Therefore, the purpose of this study was to determine chemical fractions of the native or added Zn to agricultural, forest and rangeland soils in response to application of various wheat straw derived biochar levels.

2. Material and methods

2.1. Site description

Area of study (nearly 56,528 ha) is located in Mian Jangal region of Fasa (Fig. 1), Fars province, Iran (28° 55′ 45″ to 29° 13′ 15″ N, 53° 15′ 35″ to 53° 38′ 15″ E). The study area with the mean annual

precipitation and evaporation of about 352 and 3200 mm, respectively and a cold semi-arid mountain climate is located about 90 km far from the Shiraz-Fasa road. The studied soils of different land uses were developed on a relatively similar calcareous alluvium parent materials and Aghajari geological formations. At the studied area fine marl, silty and gypsiferous stones of Razak geological formation located on the Asmari-Jahrom formation. Furthermore, sandstone, siltstone and marl of the Aghajari formation located on the Razac formation and under conglomeratic formation of the Bakhtiari formation (Geological Survey and Mineral Exploration of Iran, 2017). The soils consisted of different land uses including agriculture with agricultural plants of wheat, barley, corn, cotton, and canola; rangeland with rangeland plants of *Artemisia L.*, *Thymus L.*, *Peganum harmala L.*, *Astragalus L.*, *Acantholimon L.*, *Ephedra L.* and *Ferula L.* and forest with trees and bushes including *Juniperus excelsa* M.Bieb., *Pistacia khinjuk* Stocks, *Amygdalus scoparia*, *Amygdalus lycioides* Spach and *Amygdalus erioclada* Bornm. According to Soil Taxonomy (Soil Survey Staff, 2014), the soils in land use of agriculture and rangeland belong to Inceptisols (Fine-loamy, carbonatic, Fluventic Xerochrepts) and those of forest land use belong to Entisols (Fine-loamy, carbonatic, termic, Typic Xerofluvents).

2.2. Soil sampling, preparation and analysis

In order to provide the uniform samples of each land use type, 10 subsamples of 1 kg weight from 0 to 20 cm depth were collected from the certain points which located on the main diameters of the studied area with the same distance in June 2015. The subsamples were then mixed thoroughly to obtain about 10 kg of composite samples for each land use type. All soil samples were air-dried and sieved to < 2 mm. Some physic- chemical properties were measured with three replications by common standard methods (similar to those used by Arthur et al., 2017; Moosavi et al., 2015 and Zahedifar et al., 2017): sand, silt and clay fractions by hydrometer method (Gee and Bauder, 1986) and textural class by soil texture triangle (NRCSS, USDA); bulk density by core method; pH of saturated paste by glass electrode pH-meter (EDT RE 357, Microprocessor pH-meter, Series 3, UK); electrical conductivity (EC) of saturated extract by EC-meter (METROHM 644, Conductometer, Swiss); OM content by wet oxidation method (Nelson and Sommers, 1996); cation exchange capacity, CEC by displacement cations with ammonium acetate (Sumner and Miller, 1996); calcium carbonate equivalent, CCE by titration with hydrochloric acid (Loppert and Suarez, 1996); Available, diethylene-triamine-pentacetic acid (DTPA)-extractable zinc (Zn), iron (Fe), copper (Cu) and manganese (Mn) fractions were extracted using DTPA buffered at pH 7.3 (Lindsay and Norvell, 1978) and their concentrations were determined using atomic absorption spectrophotometer (WA 670 G, Shimadzu, Japan); the sodium bicarbonate extractable phosphorus (P) by Olsen et al. (1954) method and total nitrogen (N) concentration by Bremner (1996) methods. Aforementioned properties of the studied soils were summarized in Table 1.

2.3. Biochar production and characterization

Dried wheat straw was used as biochar which provide in a poor oxygen conditions (pyrolysis process). After air drying at 35 °C for about 48 h and grinding into small parts, packed into aluminum bags of about 20 × 10 × 10 cm (2 L volume) and pyrolysed in an electrical furnace at poor oxygen conditions. Pyrolysis temperature was continuously increased to the maximum of 400 °C with a rate of 5 °C min^{-1}. Heating at this temperature for 4 h lasted. Then prepared biochar was cooled at room temperature. Finally biochar was mixed carefully, ground and sieved to pass through 2 mm sieve and some properties were measured using the common standard methods. The EC (dS m^{-1}), pH (in suspension of 1:10 biochar:water ratio), nitrogen (%), phosphorus (%), Fe, Mn, Zn and Cu (mg kg^{-1} biochar) values were 14.13, 7.65, 0.66, 129, 372, 51, 9, and 5, respectively.