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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 $ZnSO_4 \cdot 7H_2O$) 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,

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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.

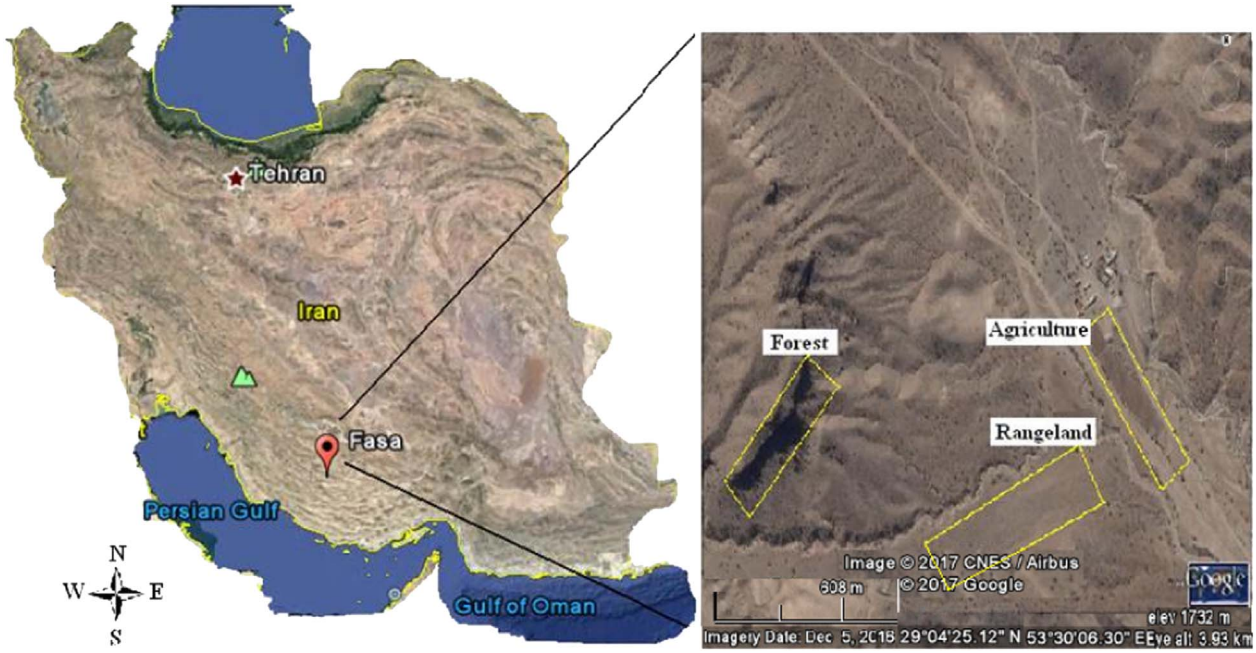

Fig. 1. The location of the study area and the location of the sampling sites where samples were taken from different land use types.

Table 1
Some physic-chemical properties in soils of the studied land uses (values are averages over three replications, $n = 3$).

Soil properties	Land use		
	Agriculture	Rangeland	Forest
Clay (%)	23.6	22.9	13.3
Silt (%)	39.6	52.0	52.0
Sand (%)	36.7	25.1	34.7
Textural class	Loam	Silt loam	Silt loam
Bulk density (g cm^{-3})	1.47	1.23	1.11
Volumetric field capacity water content, FC (%)	16	18	20
pH of saturated paste	7.99	8.16	7.89
Electrical conductivity of saturated extract, EC (dS m^{-1})	0.47	0.50	0.66
Organic matter, OM (%)	0.24	3.93	4.44
Cation exchange capacity, CEC ($cmol_+$ kg^{-1})	12.0	18.9	15.4
Calcium carbonate equivalent, CCE (%)	36	46	38
DTPA-extractable element (mg kg^{-1} soil)			
Zn	0.85	0.92	1.33
Fe	5.65	5.86	6.52
Cu	1.38	1.42	1.55
Mn	5.33	4.37	5.63
$NaHCO_3$-extractable phosphorus, P (mg kg^{-1} soil)	8.78	6.50	3.58
Total nitrogen, N (%)	0.012	0.19	0.22
Total Zn (mg kg^{-1})	63.52	72.37	85.96

2.4. Incubation experiments

An incubation experiment was conducted as 500 g of each studied soils in separate plastic bags. Treatments consisted of three levels of biochar application (0, 1.5 and 3% wt as wheat straw biochar), two levels of Zn application (0 and 10 mg Zn kg^{-1} soil as $ZnSO_4{\cdot}7H_2O$ solution) and soil types of three land use types (agriculture, rangeland and forest). The experiment was carried out as a factorial experiment arranged in a completely randomized design of 3 × 2 × 3 with 54 plastic pots (3 land use types × 2 levels of Zn × 3 levels of biochar × 3 replications). The mentioned amounts of biochar and Zn were added to the studied soil types and mixed thoroughly. Subsequently treated soils were transferred to the cubical PVC pots of 10 × 10 × 6 cm. Samples were incubated in ambient temperature at laboratory conditions (25 ± 2 °C). Soil moisture content was maintained at 80% of field capacity, FC for a time period of 70 days. The pots were weighted every other day and the required amounts of distilled water were added. The soils in the pots were mixed thoroughly every 2 weeks. Maximum cares were also taken to avoid external contamination by using analytical grade chemicals and distilled water.

2.5. Procedure of fractionation analysis

At the end of incubation period, soil samples were air-dried. Chemical fractions of Zn in the incubated soil was determined according to the Singh's fractionation procedure (Singh et al., 1988) that is relatively a combination of Chao (1972), Tessier et al. (1979) and Shuman (1985) and has been recommended as a suitable procedure for our calcareous soils (Reyhani Tabar et al., 2006). The Singh sequential procedure categorized Zn into seven chemical fractionations: the exchangeable fraction (F1), bound to carbonate fraction (F2), the fraction bound to organic matter (F3), the fraction bound to Mn-oxides (F4), the fraction bound to amorphous-Fe-oxides (F5), the fraction bound to crystalline-Fe-oxides (F6) and residual fraction (F7). Outline of the method is presented in Table 2. Residual form (F7) is obtained by subtracting sum of other fractions from total Zn. For determining the total Zn concentration, based on the procedure followed by Iwegbue (2007), 1 g of soil samples were treated with a mixture 4 mL of hydrofluoric acid and 10 mL of aqua regia in a beaker and was heated to 120 °C for 2 h. The digested samples were filtered through Whatman No. 1 filter paper and diluted to 100 mL with distilled water. The total Zn concentrations were determined using atomic absorption spectrophotometer (WA 670 G, Shimadzu, Japan). Zinc concentrations in aforementioned soil fractions were also determined by atomic absorption spectrophotometer. It should be pointed out that the aforementioned chemical Zn fractions in the initial studied soils of different land use types were determined use the same procedure (Singh et al., 1988) before starting incubation experiment (Table 3).

2.6. Mobility factor and reduced partition index of Zn

In order to calculate the potential risk and mobility of Zn in the

Table 2
Chemical reagents and conditions for the sequential extraction procedure used in this study (after Singh et al., 1988).

Fraction	Reagents	Extractions conditions
F1: Exchangeable (Exch.)	1 M $Mg(NO_3)_2$, 10 g soil:40 mL solution	Shake 2 h
F2: Carbonate (Car.)	1 M NaOAc (pH = 5 CH_3COOH), 10 g soil:40 mL solution	Shake 5 h
F3: Organic matter (OM)	0.7 M NaOCl (pH = 8.5), 10 g soil:20 mL solution (two times extraction)	Shake 30 min in boiling water both
F4: Mn-oxide-bound (Mn-Ox)	0.1 M $NH_2OH{\cdot}HCl$ (pH = 2 HNO3), 5 g soil:50 mL solution	Shake 30 min in boiling water both
F5: Amorphous Fe-oxide-bound (AFe-Ox)	0.25 M $NH_2OH{\cdot}HCl$ + 0.25 M HCl, 5 g soil:50 mL solution	Shake 30 min at 50 °C in water bath
F6: Crystalline Fe-oxide-bound (CFe-Ox)	0.2 M $(NH_4)_2C_2O_4$ + 0.2 M $H_2C_2O_4$ + 0.1 M ascorbic acid, 5 g soil:50 mL solution	Shake 30 min in boiling water both
F7: Residual (Res.)	Residual form is obtained by subtracting sum of other fractions from total Zn.	

Table 3
Chemical Zn fractions (%) in the initial studied soils of different land use types (after Singh et al., 1988) before starting incubation experiment (values are averages over three replications, n = 3).

Zn fractions	Land use types		
	Agriculture	Rangeland	Forest
F1: Exchangeable (Exch.)	0.45	0.20	0.25
F2: Carbonate (Car.)	0.27	0.10	0.15
F3: Organic matter (OM)	0.56	0.64	0.80
F4: Mn-oxide-bound (Mn-Ox)	0.87	0.54	0.86
F5: Amorphous Fe-oxide-bound (AFe-Ox)	1.89	3.06	7.44
F6: Crystalline Fe-oxide-bound (CFe-Ox)	6.72	6.90	7.27
F7: Residual (Res.)	39.60	42.97	46.36

soils, the mobility factor, MF, was determined through dividing the mobile fractions weakly bound to soil particles by all fractions as follows (Kabala and Singh, 2001):

$$MF = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5 + F6 + F7} \times 100 \quad (1)$$

High mobility of HMs (e.g., Zn) in soil recommended the affinity entering simply to the food chain with high risk. According to MF value, the classification of stability and risk of HMs in soil as follows: If $MF \leq 1$ defined no risk, $1 \leq MF \leq 10$ defined low risk, $10 \leq MF \leq 30$ defined medium risk, $30 \leq MF \leq 50$ defined high risk and $50 \leq MF \leq 75$ defined very high risk.

To compare the relative binding intensity of Zn in the soils, the partition index of Zn, I, and the reduced partition index, I_R, were determined. These parameters are defined as follows (Han et al., 2003):

$$I = \sum_{i=1}^{k} (F_i \times (i^n)) \quad (2)$$

$$IR = \frac{I}{(k^n)} \quad (3)$$

where i is the extraction step number, F_i is the percentage (fractional content) of the element (i.e. Zn) in the solid-phase component i out of the total extracted and n is an integer ($n = 2$) and k is the number of extraction stages (in our case $k = 7$). Generally, I_R parameter is introduced to explain the relative binding intensity of metal in soils and to compare of the binding intensity of a given metal among soils and of different metals in the same soil. So, a low rate of I_R indicates the metal often distributes in the soluble and exchangeable forms, while a high rate represents the metal mostly bound in the residual fraction. The medium value show metal distributes among all solid-phase fractions.

2.7. Statistical analysis

Data were analyzed by Duncan's Multiple Range Test at the probability level of 0.05 using SPSS (SPSS Inc., Chicago, IL, USA), MSTATC (Michigan State University, East Lansing, MI, USA) and EXCEL (Microsoft, Redmond, WA, USA) software packages.

3. Results and discussion

3.1. Zn distribution in different soil fractions

Results indicated that in the initial (before incubation experiment) control (without any Zn or biochar addition) soils of different land use types Zn distributed in the following sequence (Table 3): in agricultural soil F7 > F6 > F5 > F4 > F3, F1 > F2 (40% and 0.3% for F7 and F2, respectively); in forest soil F7 > F5 > F6 > F4 > F3, F1 > F2 (46% and 0.2% for F7 and F2, respectively) and in rangeland soil F7 > F6 > F5 > F3 > F4 > F1 > F2 (43% and 0.1% for F7 and F2, respectively). Results also showed that within the control (without any Zn or biochar addition) incubated samples, Zn in the soils of different land use types was distributed in the following sequence (Fig. 2); in agriculture, F7 > F6 > F5 > F4 > F1 > F3 > F2 (80% and 0.31% for F7 and F2, respectively); in forest soil F7 > F5 > F6 > F4 > F3 > F1 > F2 (75% and 0.17% for F7 and F1, respectively) and in rangeland soil F7 > F6 > F5 > F4 > F3, F1 > F2 (79% and 0.22% for F7 and F2, respectively). Comparison of Zn fractions between the incubated and un-incubated control soils revealed that generally in all studied soil types OM fractions reduced over incubation period probably due to increased decomposition of soil OM due to suitable moisture, air and temperature conditions for decomposer microorganisms; whereas, exchangeable fractions increased during incubation period probably due to ceased Zn uptake by plant in laboratory incubated conditions as compared to natural conditions. Changes in the other Zn fractions were not considerable (Tables 3–6).

Application of 1.5 and 3% biochar changed this trend and resulting in: F7 > F6 > F5 > F4 > F3 > F1 > F2 for agriculture and forest land (81% and 79% after application of 1.5% biochar for F7 and 0.31% and 0.24% for F2 vs. 81% and 83% after application of 3% biochar for F7 and 0.14% and 0.19% for F2 in agriculture and forest soils, respectively); F7 > F6 > F5 > F4 > F3, F1 > F2 (79% and 0.89% for F7 and F2, respectively) and F7 > F6 > F5 > F4 > F3 > F1 > F2 (80% and 0.2% for F7 and F2, respectively) for rangeland after adding 1.5 and 3% biochar, respectively. Formentini et al. (2015) showed that the labile Zn fractions (adsorbed and exchangeable Zn) increased after applying pig slurry.

The Zn partitioning order in agricultural soil was F7 > F6 > F5 > F4 > F1 > F3 > F2 (74% and 0.42% for F7 and F2, respectively) after application of 10 mg Zn kg^{-1} soil without biochar application. This trend was similar to that of control. In forest and rangeland soils, Zn fractions respectively changed as the following orders: F7 > F6 > F5 > F4 > F3 > F2 > F1 (74% and 0.44% for F7 and F1, respectively) and F7 > F6 > F5 > F4 > F2 > F1 > F3 (74.90% and 0.58% for F7 and F3, respectively). The Zn partitioning follows the order F7 > F6 > F5 > F4 > F3 > F1 > F2 (77% and 0.42% for F7 and F2, respectively) and F7 > F6 > F5 > F4 > F1 > F3 > F2 (74% and 0.39% for F7 and F2, respectively) in agricultural soil after application of 1.5 and 3% biochar with 10 mg Zn kg^{-1} soil, respectively. Results showed that the variation trend in Zn fractions of agricultural soil treated with high level of applied biochar (3%) was the same as the control. The variation trend in Zn fractions of forest soil treated with 1.5 and 3% biochar and 10 mg Zn kg^{-1} was similar to that of conditions that only Zn was applied. This trend was F7 > F6 > F5 > F4 > F3 > F2 > F1 (77% and

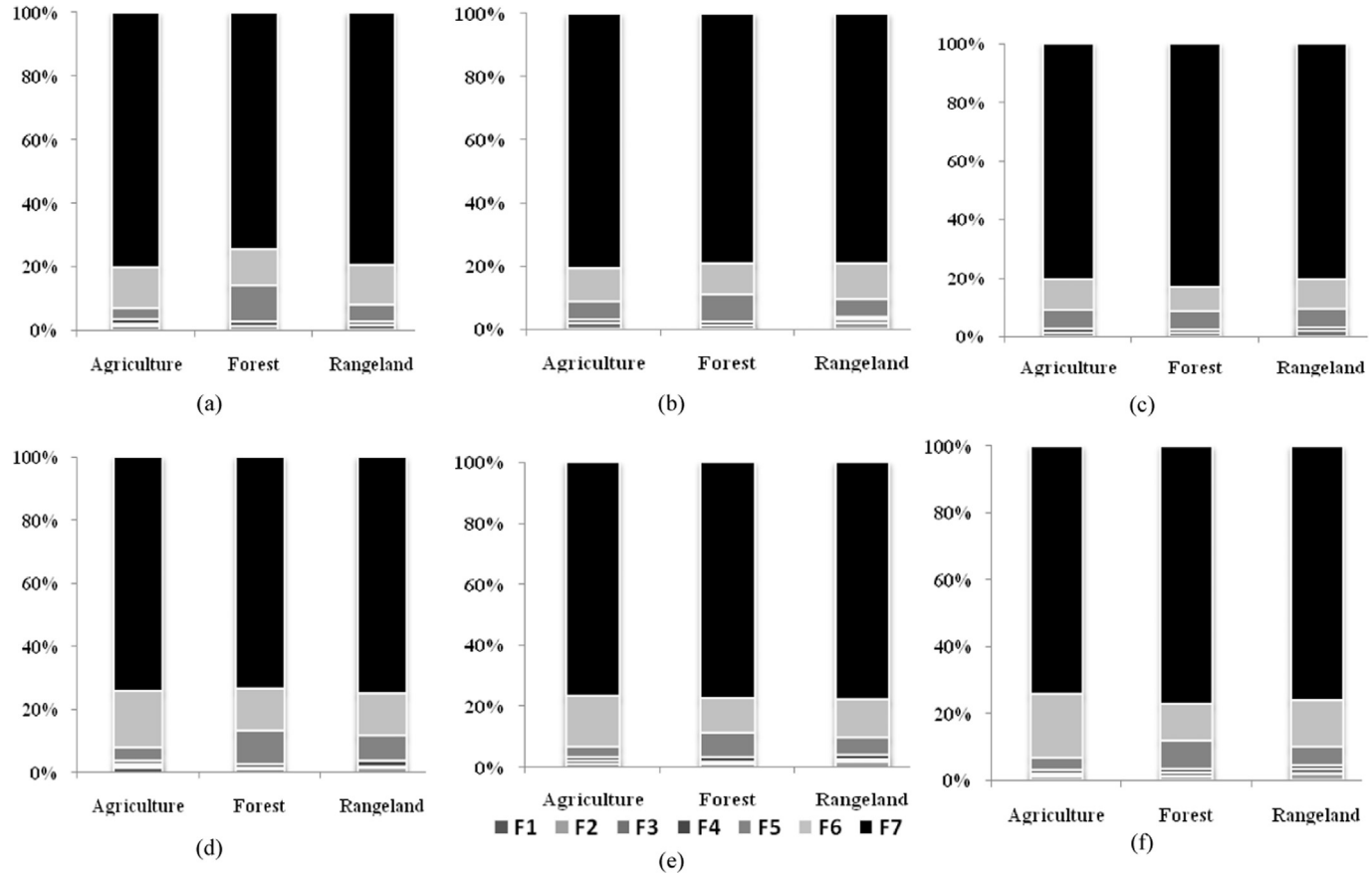

Fig. 2. The relative percentage of Zn fractions (F1 to F7 indicate exchangeable, bound to carbonate, bound to organic matter, bound to Mn-oxides, bound to amorphous-Fe-oxides, bound to crystalline-Fe-oxides and residual fractions, respectively) in agricultural, forest and rangeland soils (values are averages over three replications, $n = 3$) after application of biochar (B) and Zn, (a) B0Zn0 (control), (b) B1.5Zn0 (1.5%biochar without Zn), (c) B3Zn0 (3%biochar without Zn), (d) B0Zn10 (10 mg Zn kg^{-1} soil without biochar), (e) B1.5Zn10 (1.5%biochar with 10 mg Zn kg^{-1} soil) and (f) B3Zn10 (3%biochar with 10 mg Zn kg^{-1} soil).

Table 4
Effect of applied biochar and zinc (Zn) on the exchangeable fraction of Zn (F1) in the studies soil types (values are averages over three replications, $n = 3$).

Zn (mg kg^{-1})	Biochar (% wt)			Mean
	0	1.5	3	
Agricultural soil (mean = 0.45 A)				
0	0.67[1] a	0.40 abc	0.22 c	0.43 A
10	0.67 a	0.35 abc	0.39 abc	0.47 A
Mean	0.67 A	0.37 B	0.31 B	
Forest soil (mean = 0.34 A)				
0	0.37 abc	0.37 abc	0.34 abc	0.36 A
10	0.26 bc	0.30 abc	0.39 abc	0.32 A
Mean	0.31 B	0.33 B	0.36 B	
Rangeland soil (mean = 0.45 A)				
0	0.40 abc	0.64 ab	0.37 abc	0.47 A
10	0.43 abc	0.45 abc	0.44 abc	0.44 A
Mean	0.42 B	0.54 AB	0.41 B	

[1] Means in each row or column followed by the same capital letters and in the body of table followed by the same lowercase letters are not significantly different ($p < 0.05$) by Duncan's Multiple Range Test.

Table 5
Effect of applied biochar and zinc (Zn) on the carbonate fraction of Zn (F2) in the studies soil types (values are averages over three replications, $n = 3$).

Zn (mg kg^{-1})	Biochar (% wt)			Mean
	0	1.5	3	
Agricultural soil (mean = 0.17 B)				
0	0.16[1] cde	0.15 de	0.07 e	0.12 C
10	0.23 b–e	0.22 b–e	0.21 b–e	0.22 BC
Mean	0.19 B	0.18 B	0.14 B	
Forest soil (mean = 0.24 B)				
0	0.11 de	0.16 cde	0.14 de	0.14 C
10	0.31 a–e	0.30 a–e	0.42 a–e	0.34 B
Mean	0.21 B	0.23 B	0.28 B	
Rangeland soil (mean = 0.41 A)				
0	0.12 de	0.53 abc	0.11 de	0.25 BC
10	0.48 a–d	0.65 a	0.55 ab	0.56 A
Mean	0.30 B	0.59 A	0.33 B	

[1] Means in each row or column followed by the same capital letters and in the body of table followed by the same lowercase letters are not significantly different ($p < 0.05$) by Duncan's Multiple Range Test.

0.42% for F7 and F1 after application of 1.5% biochar and 10 mg Zn kg^{-1} soil and 77% and 0.59% for F7 and F1 after application of 3% biochar and 10 mg Zn kg^{-1} soil). In rangeland soil after application of 1.5% biochar and 10 mg Zn kg^{-1} soil, the Zn partitioning follows the order F7 > F6 > F5 > F4 > F2 > F3 > F1 (76% and 0.71% for F7 and F1, respectively). This trend showed little change when 3% biochar was applied. In this case, F7 > F6 > F5 > F3 > F4 > F2 > F1 (76% and 0.83% for F7 and F1, respectively). Results showed that application of 3% biochar caused that Zn distribution shift from exchangeable and carbonate fractions to the organic matter fraction. Hao et al. (2010) also showed that application of 5% bone char resulted in shifting Zn distribution from HOAC extractable fraction to reducible fractions, effectively reducing the mobility and bioavailability of Zn in soil.

Results showed that in all soil samples (control and treated) of

Table 6
Effect of applied biochar and zinc (Zn) on the organic fraction of Zn (F3) in the studies soil types (values are averages over three replications, $n = 3$).

Zn (mg kg^{-1})	Biochar (% wt)			Mean
	0	1.5	3	
Agricultural soil (mean = 0.36 B)				
0	0.30[1] d	0.42 cd	0.28 d	0.33 C
10	0.41 cd	0.41 cd	0.36 cd	0.39 BC
Mean	0.35 C	0.41 BC	0.32 C	
Forest soil (mean = 0.49 A)				
0	0.46 bcd	0.38 cd	0.35 cd	0.39 BC
10	0.38 cd	0.65 a	0.70 a	0.58 A
Mean	0.42 BC	0.51 AB	0.52 AB	
Rangeland soil (mean = 0.52 A)				
0	0.40 cd	0.62 ab	0.43 cd	0.48 AB
10	0.39 cd	0.54 abc	0.73 a	0.56 A
Mean	0.39 BC	0.58 A	0.58 A	

[1] Means in each row or column followed by the same capital letters and in the body of table followed by the same lowercase letters are not significantly different ($p < 0.05$) by Duncan's Multiple Range Test.

different land use types, most of the applied Zn is presented in residual fraction. In other words, the residual Zn ranged between 75 and 85%; 72 to 82% and 75 to 81% in agricultural, forest and rangeland soils, respectively. The residual fraction is as the most stable fraction and HMs related to the parent material instituted in this fraction. Our results were in agreement to those of Kabala and Singh (2001) who stated that the residual Zn fraction ranged between 45% in silty soils to 94% in the clay-loam soil. Furthermore, Ma and Rao (1997) reported that Zn to be strongly bound in the residual fraction. After that, among other forms, the oxide-bound fractions occurred in the highest percentage. Our results were also in accordance to those reported by Ma and Rao (1997). However, some other investigators showed that the Fe and Mn oxide-bound Zn fractions are of the most dominance (Ahumada et al., 1999). Ratuzny et al. (2009) stated that distribution of HMs between different fractions is dependent on the HMs source and soil characteristics. Weathering may mobilize HMs associated with this fraction (Filgueiras et al., 2002). Many studies reported that clay minerals have high adsorption attraction of exogenous Zn (Asada et al., 2012).

3.2. Changes in the exchangeable fraction

Comparison of mean values showed that the concentration of exchangeable Zn (F1) were decreased significantly by nearly 60 and 54% with application of 1.5 and 3% biochar, respectively in agricultural soil (Table 4). This effect was not observed in forest and rangeland soils. The aforementioned opposite responses of exchangeable Zn fraction in agricultural soil as compared to that of the two other soils may correspond to the significantly low native OM content in the agricultural soil (0.24%) as compared to the high OM contents in the rangeland (3.93%) and forest (4.44%) soils (Table 1). Chelating groups of organic fertilizer can complex by HMs which reduces the concentration of soil exchangeable fractions. In addition, application of biochar increased soil alkalinity and high pH results in an increased negative charge and Zn^{+2} hydrolysis (Weng et al., 2002). It has been also reported that applying pig manure and green waste compost in tropical soils increased exchangeable Zn fraction due to decrease in pH (Doelsch et al., 2010). These results are in contradiction with our findings. Shuman (1999) reported that some organic waste materials such as spent mushroom compost and humic acid decreased the potential availability of Zn by redistributing it form the exchangeable to the less soluble fractions like manganese oxide or organic matter fractions. Dvorak et al. (2003) documented that application of 9.4 t/ha of dry matter sludge prompted only minor changes in exchangeable Zn content in all soils. But they concluded that higher rate of sludge (28.2 t/ha of dry matter) resulted in a significant increase in the exchangeable Zn fraction. Application of 10 mg Zn kg^{-1} soil did not affect F1concentration, significantly. The maximum F1 concentration was obtained for control in agricultural soil while the minimum concentration of F1 was observed after application of 3% biochar to agricultural soil. The mean exchangeable Zn concentration did not changed significantly by altering land use (Table 2). Puga et al. (2016) showed that application of biochar decreased the metal concentration such as Zn in leachate. In other words, biochar addition reduced metal mobility. Tan et al. (2015) stated that many mechanisms such as ion exchange, electrostatic attraction, physical adsorption and carbonate precipitation control the metal retention by biochar in soils.

Organic fertilizer with great content of humus and carboxyl, hydroxyl, carbonyl and amino groups can complex or chelate with heavy metal ions as a result decline the HMs mobility from the exchangeable fraction to other stable fractions (Rijkenberg and Depree, 2010; Bolan et al., 2003). Of course, sometimes application of manure and compost increased Zn exchangeable fraction, significantly. Chen et al. (2013) stated that during incubation the concentration of exchangeable Zn fraction were increased due to releasing this Zn fraction into the soil system. Hao et al. (2010) showed that the most labile Zn fractions (CH_3COOH extractable and reducible fractions) increased in the top soil as the applied pig slurry dosage increased. Chen et al. (2013) showed that the percentage order of Zn fractions in control sample was residual > reducible > exchangeable > oxidizable. After biogas residue application, the concentration of exchangeable Zn fraction was increased, significantly. Their results showed that the most Zn was bound to Fe and Mn oxides and crystalline structures of the minerals. Application of organic fertilizer decreases the HMs mobility from the exchangeable fraction to other stable fractions (Bolan et al., 2003).

3.3. Changes in the carbonate fraction

Results showed that application of 1.5% biochar increased carbonate Zn fraction significantly by 49% in rangeland soil. While this concentration decreased significantly (about 44%) after 3% biochar was applied (Table 5). In the other soil types significant changes in carbonate Zn fraction was not found. Based on the results in all soil types the carbonate Zn fraction were increased significantly after application of 10 mg Zn kg^{-1} soil (about 46, 59 and 55% for agricultural, forest and rangeland soils, respectively). The minimum carbonate Zn concentration was obtained with application of 3% biochar without Zn addition for agricultural soil while the maximum concentration was obtained with application of 1.5% biochar and 10 mg Zn kg^{-1} soil for rangeland soil (Table 5). Korolewicz et al. (2001) reported that compost process decreased the exchangeable Zn and increased the carbonate Zn fractions. Ross (1994) stated that metal bioavailability could restrict probably due to forming insoluble salts from release of phosphorus and organic matter mineralization during compost process.

Comparison of mean values showed that carbonate Zn fraction in rangeland and agricultural soils were respectively the maximum and minimum among the studied soil types (0.41 vs 0.17 mg Zn kg^{-1} soil, respectively).

3.4. Changes in the organic matter fraction

Table 6 shows the effect of applied biochar and Zn on the organic fraction of Zn in three soils of different land use types. Results showed that application of 1.5 and 3% biochar significantly increased organic Zn fraction for rangeland soil as compared to that of control (by nearly 34%). These findings are in agreement with Guan et al. (2011) who reported that addition of 1% livestock manure decreased exchangeable and weakly adsorbed fractions of Cu and increased organic matter Cu fraction. Likewise they stated that application of 3% livestock manure enhanced Cu mobility. According to Formentini et al. (2015) it is due to increment in the amount of soluble organic ligands as a result of Cu

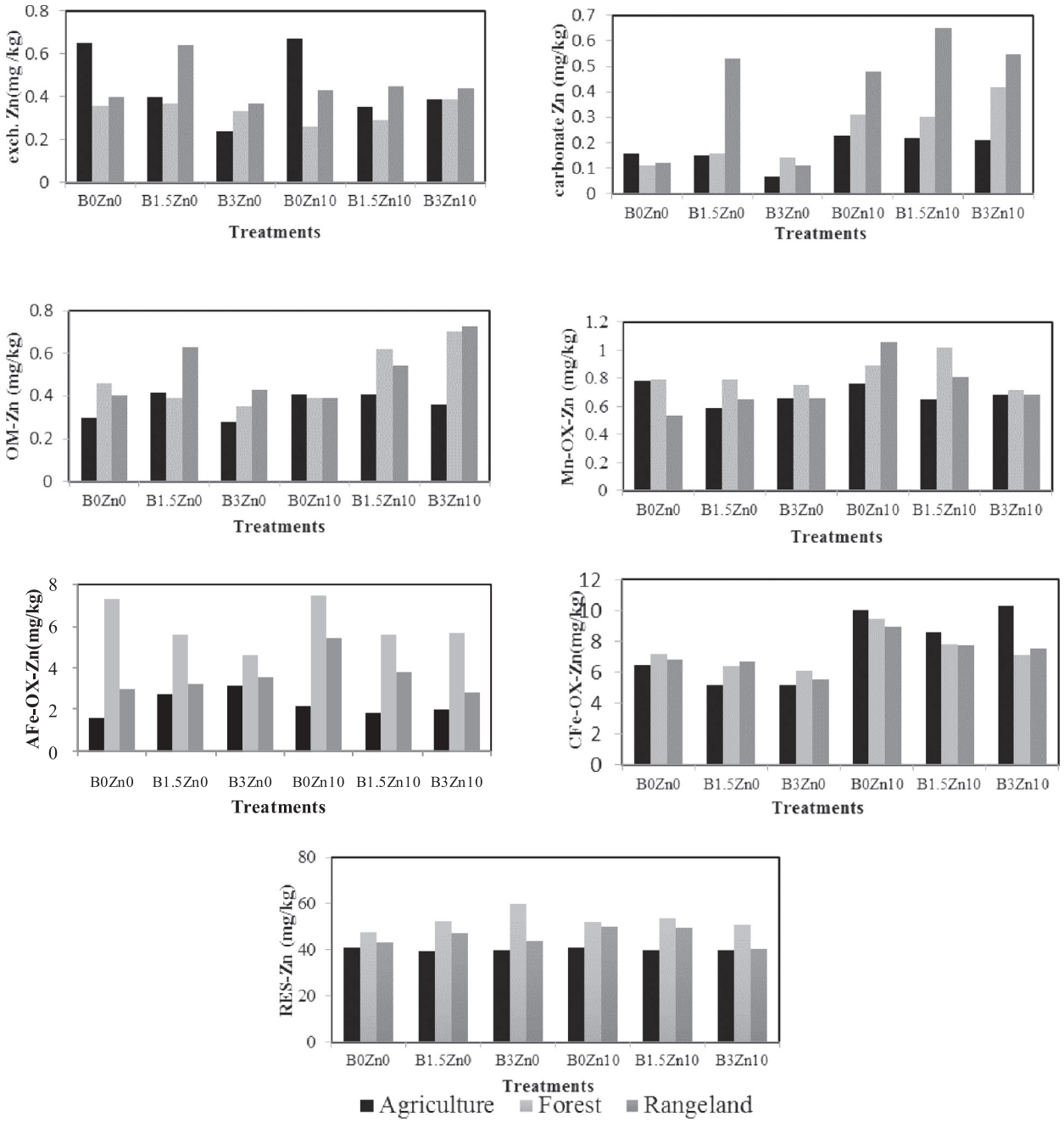

Fig. 3. Zn distribution in different fractions of agricultural, rangeland and forest soils after application of biochar and Zn (values are averages over three replications, $n = 3$).

Table 7
Correlation coefficients between different Zn fractions in the studied agricultural soil (values are averages over three replications, $n = 3$).

	$Zn_{Res.}$	$Zn_{Exch.}$	$Zn_{Car.}$	Zn_{OM}	$Zn_{Mn\text{-}Ox}$	$Zn_{AFe\text{-}Ox}$	$Zn_{CFe\text{-}Ox}$
$Zn_{Res.}$	1	0.83*	0.48	− 0.08	0.94**	− 0.65	0.52
$Zn_{Exch.}$		1	0.50	0.14	0.91*	− 0.64	0.33
$Zn_{Car.}$			1	0.70	0.51	− 0.74	0.86*
Zn_{OM}				1	0.85	0.76	0.43
$Zn_{Mn\text{-}Ox}$					1	− 0.77	0.50
$Zn_{AFe\text{-}Ox}$						1	− 0.58
$Zn_{CFe\text{-}Ox}$							1

* and ** are statistically significant at the probability levels of 0.05 and 0.01, respectively.

Table 8
Regression equations between Zn fractions in the studied soils of different land use types and biochar (% wt) and applied Zn (mg kg^{-1}) treatments along with their determination coefficients (Zn_t).

Regression equations	Determination coefficient (R^2)
Agricultural soil	
$Zn_{Exch.}$ = 0.631–0.118 Biochar	0.78**
$Zn_{Car.}$ = 0.127–0.009 Zn	0.72*
$Zn_{CFe\text{-}Ox}$ = 0.5.633–0.403 Zn	0.90**
Forest soil	
$Zn_{Car.}$ = 0.14–0.02 Zn	0.86**
$Zn_{AFe\text{-}Ox}$ = 7.143–0.747 Biochar	0.80*
Rangeland soil	
$Zn_{CFe\text{-}Ox}$ = 7.031–0.458 Biochar + 0.175 Zn	0.95**

* and ** are statistically significant at the probability levels of 0.05 and 0.01, respectively.

Table 9
Effect of applied biochar and zinc (Zn) on reduced partition index (I_R) in the studies soil types (values are averages over three replications, $n = 3$).

Zn (mg kg^{-1})	Biochar (% wt)			Mean
	0	1.5	3	
Agricultural soil (mean = 0.913 A)				
0	0.919[1] b	0.917 bc	0.922 ab	0.919 A
10	0.900 f	0.912 cd	0.905 ef	0.906 D
Mean	0.910 B	0.914 A	0.914 A	
Forest soil (mean = 0.904 B)				
0	0.891 g	0.912 cd	0.926 a	0.910 C
10	0.892 g	0.904 ef	0.901 f	0.899 E
Mean	0.891 D	0.908 B	0.914 A	
Rangeland soil (mean = 0.903 B)				
0	0.917 bc	0.908 de	0.921 ab	0.915 B
10	0.895 g	0.905 ef	0.876 h	0.892 F
Mean	0.906 B	0.906 B	0.898 C	

[1] Means in each row or column followed by the same capital letters and in the body of table followed by the same lowercase letters are not significantly different ($p < 0.05$) by Duncan's Multiple Range Test.

complexation with ligands instead of adsorption onto soil organic matter.

Addition of 10 mg Zn kg^{-1} soil significantly increased organic Zn fraction in the soils of all land use types (about 15, 34 and 14% for agricultural, forest and rangeland soils, respectively). The comparison of mean values showed that the organic Zn fraction, with biochar and Zn application, in forest and rangeland soils were significantly more than agricultural soil. It is probably due to the higher organic matter content of forest and rangeland soils than that of agricultural soil (4.44 and 3.93 vs. 0.24% OM for forest, rangeland and agricultural soils, respectively). The maximum organic Zn concentration was observed after application of 3% biochar beside 10 mg Zn kg^{-1} soil for rangeland soil (about 0.73 mg Zn kg^{-1} soil). But the minimum organic Zn concentration was obtained with application of 3% biochar in agricultural soil (0.28 mg Zn kg^{-1} soil).

3.5. Changes in the Mn/Fe oxide (inorganic) fraction

Results showed that application of biochar has no significant effect on Mn-Ox-Zn fraction in the soils of all land use types; while application of 10 mg Zn kg^{-1} soil increased the Mn-Ox-Zn fraction of rangeland soil, significantly by 54% as compared to that of control (Fig. 3). Based on the results, the higher input of Zn into the soils usually caused a higher Zn amount retained by soil Fe-Mn oxides (Waterlot et al., 2013). The maximum concentration of Mn-Ox-Zn fraction (2.07 mg Zn kg^{-1} soil) was observed when 3% biochar and 10 mg Zn kg^{-1} soil were added. Our findings showed that application of biochar and Zn did not affect concentration of AFe-Ox-Zn fraction, significantly (Fig. 3). Comparison of mean values showed that the concentration of AFe-Ox-Zn fraction for the forest soil was significantly more than that of agricultural and rangeland soils (about 62% and 40% more than agricultural and rangeland soils, respectively). It may correspond to the lower pH value (Table 1) and as a consequence more AFe oxides contents in the forest soil than those of agricultural and rangeland soils. The maximum concentration of AFe-Ox-Zn fraction (about 7.43 mg Zn kg^{-1} soil) was observed with addition of 10 mg Zn kg^{-1} soil without biochar application for forest soil; while the minimum concentration (1.63 mg Zn kg^{-1} soil) was observed in control (without any Zn or biochar application) agricultural soil. Results showed that application of biochar has no significant effect on concentration of CFe-Ox-Zn fraction in the soils of all land use types (Fig. 3). Concentration of CFe-Ox-Zn fraction were increased by application of 10 mg Zn kg^{-1} soil by nearly 42, 19 and 22% in agricultural, forest and rangeland soils, respectively. The maximum and minimum concentration of CFe-Ox-Zn fraction (about 10 and 5 mg Zn kg^{-1} soil respectively) were obtained after application of 3% biochar and 10 mg Zn kg^{-1} soil and 3% biochar alone for agricultural soil. Dvorak et al. (2003) showed that Zn application to soils led to increase in Fe-Mn oxides Zn concentration. According to the results of Morera et al. (2002), Fe-Mn oxides markedly contributed in the soil sorption capacity for sludge and inorganic Zn.

3.6. Changes in the residual fraction

Results showed that application of biochar and Zn fertilizer did not change significantly in all soil types. Comparison of the mean values showed that concentration of the residual Zn fraction for forest soil was more than agriculture and rangeland soils (i.e., the concentration of residual Zn fraction were about 53, 40 and 46 mg Zn kg^{-1} soil in forest, agricultural and rangeland soils, respectively). It is maybe due to the more initial Zn concentration in forest soil than the other studied soil types. Gao et al. (2001) showed that in uncontaminated soil, residual fraction is mainly fraction while in contaminated soil, with increasing available HMs fraction increased. Torri and Lavado (2008) showed that sewage sludge application increased exchangeable, water soluble, organic, carbonate and/or Fe and Mn oxide of Zn fractions, significantly. They showed that at the beginning of the experiment, the residual Zn fraction was the dominant fraction but after the application of the

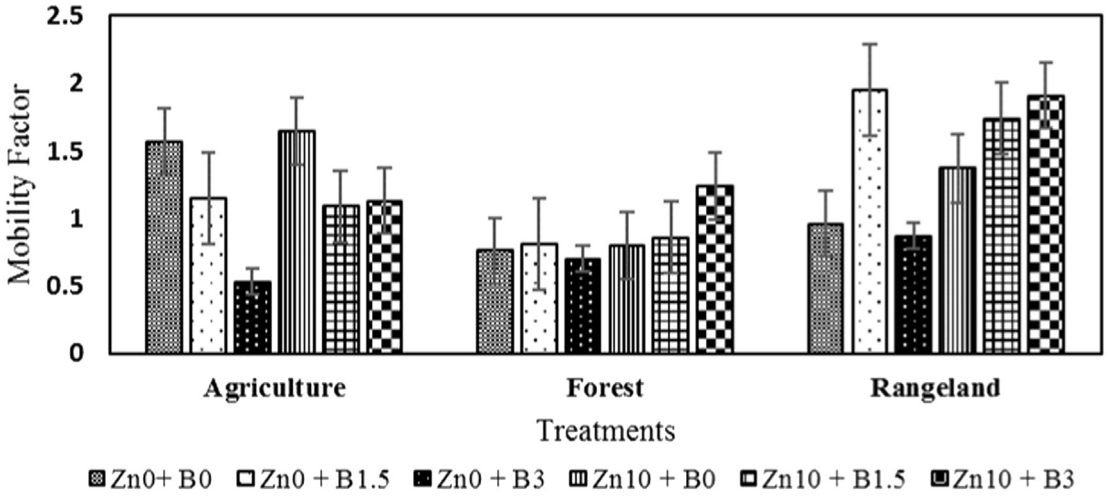

Fig. 4. Effect of biochar and Zn treatments on Zn mobility factor (MF) in the soils of different land use types (values are the averages over three replications, $n = 3$ and error bars indicate the standard errors of each mean value).

amendment, Zn was mainly found in the inorganic fractions. They also stated that the exchangeable Zn fraction increased due to mineralization of sludge organic matter. He et al. (2007) showed that at the beginning of experiment, the distribution order of Zn fractions in a loamy soil was OM > Fe-Mn-Ox > Res. > Exch. > Car. They also reported that application of sludge increased Zn concentration in all fractions and the aforementioned order of fraction distribution was changed to: OM > Exch. > Car. > Res. > Fe and Mn-Ox in response to applied sludge. Yang et al. (2011) showed that the concentration of all Zn fractions increased after application of 1000 mg Zn kg^{-1} soil. They showed that application of Zn increased exchangeable, carbonate and Fe-Mn oxide fractionations significantly. While, organic matter fraction maintains without significant changes and residual fraction decreased significantly. Hao et al. (2010) also stated that addition of bone char effectively changed non-residual fractions of Pb and Zn to residual fraction and reduced their mobility and bioavailability in soil. It has been reported that metals bound to residual fraction are related to the parent material and may be mobilized due to weathering, causing long-term concerns (Filgueiras et al., 2002).

3.7. Correlation and regression relations between Zn chemical fractions

Statistical analysis was carried out in order to obtain the relationships between different chemical fractions of Zn in the studied soil types. Results showed that there were the significant correlations between residual fraction with Mn-Oxide and exchangeable fractions of Zn in agricultural soil (Table 7). Furthermore, the significant correlation was observed between exchangeable fraction and Mn-Oxide fraction of Zn. Moreover, the correlation between carbonate and crystalline-Fe fractions of Zn was statistically significant. Results revealed that there was not significant correlation between Zn chemical fractions for other studied soil types.

According to regression equations, in agricultural soil, application of biochar reduced concentration of exchangeable Zn fraction; while application of 10 mg Zn kg^{-1} soil increased carbonate and crystalline-Fe-Oxide Zn fractions. In the forest soil, concentration of carbonate Zn fraction was increased after application of 10 mg Zn kg^{-1} soil, whereas biochar decreased amorphous-Fe-Oxide fraction of Zn. Also, crystalline-Fe-Oxide fraction of Zn was increased when 10 mg Zn kg^{-1} soil was applied (Table 8).

3.8. Effect of biochar and Zn treatments on reduced partitioning index (I_R) and mobility factor (MF)

Results showed that the I_R values for all soils were high and close to 1. Theses high I_R values result from a high ratio of the Zn strongly bound in the residual fraction (Table 9). Han et al. (2003) showed that the I_R value for Zn was medium indicating that Zn was partitioned in all fractions. Our findings demonstrated that biochar decreased Zn bioavailability in agricultural and forest soils, significantly but it increased Zn bioavailability in rangeland soil. Unlike biochar, application of 10 mg Zn kg^{-1} soil increased Zn bioavailability in all experimental soils, significantly. The results are in agreement with the findings of Han et al. (2003) who reported that with increasing the total content of metals I_R values decreased. Comparison of the mean values indicated that the order of Zn bioavailability in the studied soil types is as: rangeland soil > forest soil > agricultural soil. The maximum Zn bioavailability was observed after application of 3% biochar and 10 mg Zn kg^{-1} soil.

Results indicated that the MF values for all applied treatments and studied soil types were not higher than 10%. Mobility factor values indicate that Zn is highly stable in our experimental soils. In other words, the calculated MF values show that the bioavailability of Zn is relatively low in the studied soils. Effect of biochar and Zn application on MF of experimental soil types was summarized in Fig. 4. Application of biochar decreased MF significantly while addition of 10 mg Zn kg^{-1} soil increased it in the agricultural soil. For forest soil the mentioned influences were not observed. Application of 1.5% biochar increased MF, significantly due to increased carbonate Zn fraction in response to application of 1.5% biochar (Table 5). On the other hand application of biochar and Zn increased MF values of the rangeland soil. Puga et al. (2016) showed that Zn had medium mobility with MF of 9–22%. Lopes et al. (2015) also classified Zn according to MF value from medium to high risk.

4. Conclusion

As Zn is existent in soil in numerous chemical forms, its total content does not give adequate information about its bioavailability. For this reason, application of fractionation technique is offered due to give information about actual and potential mobility of metals. Base on this result, the Zn fractions followed the different orders for the soils of different land use types and treatments. Results of this study indicated that wheat straw derived biochar reduced the concentration of exchangeable Zn significantly in agricultural soil. Chelating groups of organic fertilizer can complex by heavy metals which reduce the concentration of the soil exchangeable fractions. In addition, application of biochar increased soil alkalinity and high pH results in an increased negative charge and Zn^{+2} hydrolysis. Application of 1.5% biochar increased the carbonate fraction of Zn while at high level of applied biochar i.e., 3% it was decreased. Biochar increased organic Zn fraction significantly in rangeland soil. The high value of reduced partitioning index revealed that Zn strongly bound in the residual fraction. Our findings demonstrated that biochar amendment decreased Zn bioavailability in the agricultural and forest soils significantly; whereas, it increased Zn bioavailability in the rangeland soil. Unlike biochar, application of 10 mg Zn kg^{-1} soil increased Zn bioavailability in all the experimental soils, significantly. The calculated mobility factor values showed that the Zn bioavailability was relatively low and Zn in the experimental soils is highly stable. It is noteworthy that the influence of biochar on Zn mobility and bioavailability was altered by changing the land uses. This issue can be considered in management of Zn polluted soils and their remediation practices or in the soil fertility management of agricultural soils.

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