Evaluating the Application of some Natural Amendments to Hinder the Pollution of Barley Plants by Heavy Metals

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ABSTRACT

The contaminated districts are grown continuously by the excessive consumption of chemical fertilizers. Reducing soil toxicity and producing beneficial healthy food free of agrochemical contaminates particularly heavy metals (HMs) are the main purposes of this research paper. A pot experiment was carried out to evaluate the effect of clay minerals, compost and the interaction between them (Zeolite = Z, Bentonite = B, compost = C, zeolite + bentonite = ZB, zeolite + compost = ZC and bentonite + compost = BC) as soil amendments and their effect on reducing heavy metals (HMs = Cd, Ni and Pb) accumulation in barley plant (*Hordeum vulgare* L. Var. Giza 132) and their mobility in two contaminated soils (Abou-Rawash, Giza Governorate and Kafr El-Sheikh Governorate). The previous soil amendments were added by two rates (1 and 2%) compared to control (without any addition). Barley plants were harvested at 90 days. All treatments led to increasing fresh and dry weight of barley plants as well as decrease its concentration and content of HMs compared with control. Zeolite produced the highest growth while the lowest accumulation of HMs was resulted by bentonite addition. Generally, clay minerals are able to improve the growth of plants in polluted areas in addition to decreasing HMs uptake by plants in absence or presence of compost.

Key Words: Bentonite, Cadmium, Lead, Nickel, Pollution, Zeolite

INTRODUCTION

The pollution of soil by HMs especially Pb, Ni and Cd is one of the most important problems that face plant growth and cause many hazardous effects on animals and human health. Heavy metals existence to the environment as a result of both natural and anthropogenic processes; 1) naturally: HMs occur in soils due to the weathering activities (Facchinelli *et al*., 2001, Mbah and Anikwe, 2010), 2) anthropogenic: sources of HMs for soils contain marketable fertilizers, pesticide, soil amendment, liming materials and repeated applications of sewage sludge can also be sources of large amounts of HMs (Chauhan and Yadav, 2015).

Clay minerals are also important inorganic components in soil. Zeolites, bentonite and montmorillonite are phyllosilicate minerals; they have high specific surface areas with a net negative charge. So they characterized by high cation exchangeable capacity (CEC) and ion adsorption (Konig *et al*., 2012). The addition of clay minerals, such as Na- and Ca-bentonite, declined the extractability of some HMs (Usman *et al*., 2004).

The adsorption capacity of HMs on the organic matter surface is 30 fold that of the clay minerals, so soils with high organic matter percentage had higher adsorption ability and may reduce the mobility of HMs (Sauve *et al*., 2003).

The aim of this research paper is assessing the status of two different contaminated Egyptian soils with HMs and the effect of adding various types of clay minerals and organic materials (compost) to improve the efficiency of clay to remove pollutants. As well as producing beneficial healthy food free of agrochemical contaminates especially HMs.

MATERIALS AND METHODS

A pot experiment was carried out in the greenhouse of the National Research Centre to evaluate the effect of some clay minerals, compost and the interaction between them (Zeolite = Z, Bentonite = B, compost = C, zeolite + bentonite = ZB, zeolite + compost = ZC and bentonite + compost = BC) as soil amendments and their effect on reducing HMs (Cd, Ni and Pb) mobility in two contaminated soils. The first selected soil was taken from Abou-Rawash, Giza Governorate, while the second one is located in Kafr El-Sheikh Governorate. Soil samples were air-dried, crushed and sieved to pass through a 2 mm sieve and preserved for analysis. Table (1) shows some physical and chemical characteristics of these soils as described by Page *et al.* (1982) and Klute (1986). Available nitrogen was determined by micro- Kjeldahl apparatus (Page *et al*., 1982) while available phosphorus was estimated calorimetrically in 0.5 M $NaHCO_3$ extract at pH 8.5, according to Watanabe and Olsen (1965). Available K and extractable Ni, Cd, Pb were extracted with NH_4HCO_3-DTPA according to Soltanpour (1985) and measured by a Flame photometer for K and atomic absorption spectrophotometer (AAS) apparatus (Perkin Elemer, Model A Analyst 400) for HMs.

Every pot received 1 kg of the soil. Barley seeds were sown on October 1st, 2016. Ammonium sulphate (20.6%N), calcium superphosphate (15.5% P_2O_5) and potassium sulfate (48.5% K_2O) were used in the fertilization process. The moisture content of all pots was kept near field capacity using tap water for irrigation. All agricultural practices were followed according to the recommendations of the Ministry of Agriculture. Plants were thinned and left four plants/pot. After 90 days from sowing, all plants were picked from each treatment, divided to root and shoot. Plant samples were cleaned, weighed and dried in an electric oven at 65°C.

In addition, accumulation and distribution of the HMs in different plant parts of barley (*Hordeum vulgare* L. Var. Giza 132) were investigated (Cottenie *et al*,. 1982). The previous soil amendments were added by two rates (1, 2%) compared to control (without any addition). Barley plants were harvested at 90 days. Total fresh weight (g/pot), total dry weight (g/pot), water content (%), HMs concentrations (ppm) and uptake (µg/pot) were determined.

All obtained data were statistically analyzed through analysis of variance (ANOVA) and least significant difference (LSD) at 0.05 probability level was calculated using the CoStat program to make comparisons among treatment means according to Gomez and Gomez (1984).

Table 1: Physical and chemical properties of the used soils.

Soil property	Abou-Rawash (AR)	Kafr El-Sheikh (KE)
pH (1:2.5)	6.83	7.64
EC dSm^{-1}(1:5)	0.20	0.89
Organic matter %	1.2	1.41
CEC $cmol_c$/kg soil	8.36	36.14
Soluble cations meq./ L		
Ca^{++}	1.00	2.42
Mg^{++}	0.25	1.46
Na^+	0.7	4.84
K^+	0.2	0.10
Soluble anions meq. / L		
HCO^-	0.33	2.87
CO_3^{--}	-	-
Cl^-	1.5	3.11
SO_4^{--}	0.32	2.84
Particle size distribution		
Fine sand %	71.5	12.5
Coarse sand %	3.3	3.0
Silt %	16.0	34.1
Clay %	9.2	50.4
Textural class	Sandy loam	Clayey
Available elements		
N%	0.20	0.31
P%	0.05	0.07
K%	0.13	0.13
Cd (mg Kg^{-1})	0.50	0.50
Ni (mg Kg^{-1})	4.63	3.14
Pb (mg Kg^{-1})	15.91	6.02
Total HMs (mg kg^{-1} soil)		
Cd	34.55	38.46
Ni	43.80	43.20
Pb	58.40	38.60

RESULTS AND DISCUSSION

Total fresh, dry weight and water content of barley

The efficiency of different amendments; zeolite (Z), bentonite (B), compost (C) and its mixtures (ZB, ZC and BC) that were applied to clayey and sandy textured soils by two different rates compared to control on barley growth parameters were illustrated in Fig. (1). The fresh and dry weights were increased by 11.48 and 29.93%, respectively in clayey soil compared with sandy one. The reasons for that are attributed to the superiority of clayey in its chemical, physical, hydrological and biological properties. For example, the high exchange capacity of clayey soil and its ability to sustain nutrients led to increasing nutrient uptake consequently enhancing plant biomass.

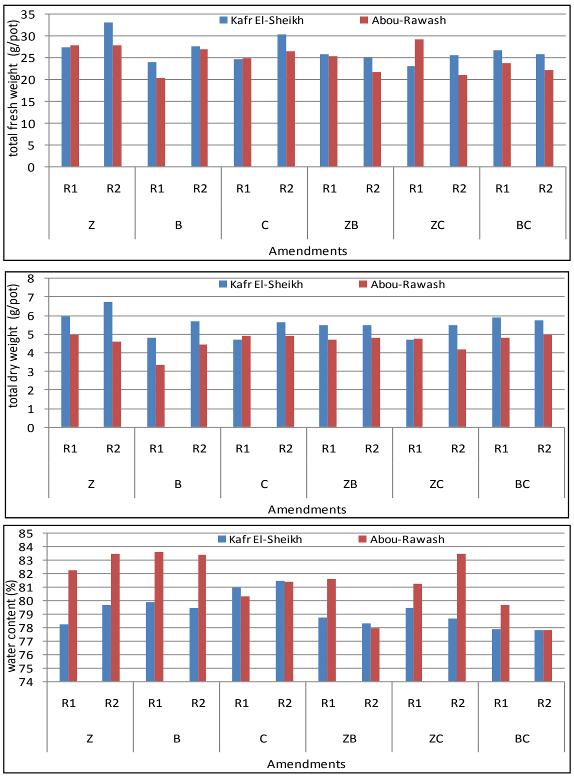

Fig. (1): Total fresh, dry weight (g/pot) and water content (%) of barley plants as affected by soil texture, amendment types and their rates.

Total fresh and dry weights of barley plants were significantly affected with different amendments. Total fresh weight followed the order; Z>C>B>ZC>BC>ZB, and total dry weight ranked in Z>BC>ZB>C>ZC>B without significant difference between them. The relative increasing percentages of zeolite treatment were 12.18 and 27.74 for fresh weight and 14.77 and 25.31% for dry weight compared with bentonite and control treatments, respectively. The variance between these two trends may be refering to the water content of barley which follows contradicts line to dry weight and follow the order: B>C> Z>ZC>ZB>BC.

Irrespective of the kind of amendments, the second application rate (R2) raised barley biomass more than the first one (R1) and the next is the control treatments with significant difference. The highest values of both fresh and dry weights were produced by the second rate of zeolite in clayey soil followed by its second rate in the same soil with significant difference between them, while, the lowest value was recorded by the low rate of bentonite in sandy soil.

Other studies have shown that addition of clay minerals raised the biomass production of carrot, lettuce by 3–5 fold (Cao and Ma, 2004), white lupin (Castaldi *et al*., 2005), ryegrass and subterranean clover (Rate *et al*., 2004) compared with the untreated soils. Many investigators reported that added of zeolites to either normal or contaminated soils improved the plant growth, fresh and dry weight of shoots and roots consequently, increased yield (Abdi *et al*., 2006 and Liu *et al*., 2009) by; 1) reducing the water-extractable metal ion concentrations (Lepp, 1998), 2) improving soil quality (Noori *et al*., 2006), 3) increasing net photosynthetic rate, stomatal conductance water use efficiency (Abdi *et al*., 2006).

Total heavy metals content in barley plants

Total Pb and Ni content were higher in plants grown on KE soil than those grown on AR soil with significant difference for Pb and without significant difference for Ni. These results indicate that the ability of KE soil to supply Pb and Ni is higher than that of AR soil. In contrast, total Cd content was increased in plants grown on AR than those grown on KE with significant difference (Table 2).

Data also showed that, all added materials caused a reduction in the total Cd content, except C, ZB, BC. This may be due to Cd content was affected by yield increase and the reduction in Cd concentration of C, ZB, and BC treatments compared to control. The highest reduction in total Cd content occurred by bentonite up to 40.52% compared to the control. The addition of Z and ZC reduced the total Cd content by 8.45, 10.34% compared to control, respectively. Among the tested materials, additions of bentonite had a strong reduction effect on the Cd content compared with the other additives. This is because bentonite has a higher content of montmorillonite (more than 60%) compared to zeolite (10%), so, bentonite is well known as good adsorbent for Cd compared with the control (Stockmeyer and Kruse, 1991). The other amendments (C=ZB< BC) increased the content of Cd by 3.53, 3.53 and 17.67%, respectively. In another study, addition of zeolite at 1% decreased the Cd content of tobacco leaves significantly (Keller *et al*., 2005).

As shown in these results, both of total Pb and Ni content produced higher value under control treatment and all amendments deceased the ability of barley to absorb Pb and Ni. Total Pb content followed the order of: control>BC>ZC> Z >ZB>C>B, while total Ni content followed the order of: control>C>Z>BC>ZB>ZC>B. The highest reduction in total Pb content occurred after addition of bentonite up to 59.34% compared to the control. The amendments significantly diminished total Ni content in barley by 48.14, 30.96, 30.89, 20.93, 17.44 and 10.12% with addition of B, ZC, ZB, BC, Z, C compared to control, respectively. The reduction in Ni absorption was greater due to the addition of B and ZC than the other amendment.

The effects of soil amendments on heavy metal content of barely may be refer to 1) ion exchange is the main adsorption mechanism of HMs onto zeolite. 2) The zeolite attracts HMs and creates a stable complex that has strong chemical bonds (Mozgawa *et al*., 2009 and Khachatryan, 2014). 3) Addition of clay minerals reduced water soluble and exchangeable HMs. The decline in the extractable HMs was superior due to bentonite application than that zeolite (Usman *et al*., 2005 and 2006). 4) Innocuous exchangeable ions (Na, Ca and K) make zeolite particularly suitable for removing undesirable HMs (Khachatryan, 2014). The most promising clay minerals in interacting with HMs and reclaiming contaminated soils are zeolites and bentonites (Inglezakis *et al*., 2007).

Table (2) Total Cd, Pb and Ni content in barley plants as affected by soil texture, amendment types and their rates.

Amend-ments (AM)	Rate (R)	Total Cd content (µg/pot)			Total Pb content (µg/pot)			Total Ni Content (µg/pot)		
		Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR		KE	AR	
Control		9.82	14.00	11.60	49.62	10.55	30.10	64.78	42.90	53.84
Z	R_1	2.65	17.34	10.62	33.74	5.37	17.08	25.18	63.06	44.45
	R_2	7.00	12.94		n.d.#	5.05		20.37	49.85	
B	R_1	1.06	7.62	6.90	5.69	0.84	12.24	1.25	14.72	27.92
	R_2	0.66	9.00		1.40	5.34		19.68	24.18	
C	R_1	6.08	15.33	12.01	16.17	3.93	14.62	50.32	39.78	48.39
	R_2	13.71	13.86		7.42	n.d.		58.85	33.71	
ZB	R_1	10.83	15.83	12.01	8.03	21.33	15.82	45.34	29.58	37.21
	R_2	7.52	14.82		4.68	0.69		25.28	15.37	

Table (2), cont.

Amend-ments (AM)	Rate (R)	Total Cd content (µg/pot)			Total Pb content (µg/pot)			Total Ni Content (µg/pot)		
		Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR		KE	AR	
ZB	R_1	10.83	15.83	12.01	8.03	21.33	15.82	45.34	29.58	37.21
	R_2	7.52	14.82		4.68	0.69		25.28	15.37	
ZC	R_1	0.62	15.70	10.40	4.33	32.61	18.78	n.d.#	45.20	37.17
	R_2	8.39	14.60		1.18	14.38		30.32	39.79	
BC	R1	9.97	15.38	13.65	5.22	25.68	19.31	38.29	30.22	42.57
	R_2	14.20	19.25		5.15	19.63		41.42	37.83	
S mean		7.97	13.89	-	21.57	11.04	-	41.22	38.02	-
R mean	R_1	5.20	14.53	9.87	12.20	14.96	13.58	32.08	37.09	34.58
	R_2	8.58	14.08	11.32	3.97	9.02	6.50	32.65	33.46	33.05
$LSD_{0.05}$	S=***1.29 Am=***2.23 R=ns SxAmxR=ns				S=***4.36 Am=ns R=***5.35 SxAmxR=ns			S=ns Am=**9.87 R=***6.98 SxAmxR=ns		

(#) n.d.: not detected

The effect of different two rates on total Pb and Ni content were significant and not significant for total Cd content and the effect of the interaction between treatments (S X Am X R) on total content of Cd, Pb and Ni in barley plant were not significant.

Dry shoot and root of barley

The highest shoot weight was produced in KE soil; in contrast the highest root biomass was resulted in AR soil (Table. 3). This may be due to KE soil more fertile than AR one and led to increase shoot while in AR soil, plants tend to increase root length to search on nutrients.

Plants grown in control and enriched amendment were expressed by the dry root and shoot biomass. The differences between studied soils, amended and unamended treatments, the rate of application and the interaction between them were significant ($p<0.05$). Dry shoot of barley increased by adding amendments compared to control as follow Z>BC>ZB>C>ZC>B by increase percentages 18.57, 15.43, 13.43, 12.30, 9.43, and 6.86, respectively compared to control. There are no significant differences between Z, BC, ZB, C, ZC in their effect on shoot dry weight of barely. The weight of dry root follows the same trend approximately; Z>BC >ZB≥C>ZC>B where no significant differences between B, ZC. The greatest dry weight produced by zeolite application compared to control.

Table (3) Dry shoot and root of barley as affected by soil texture, amendment types and their rates.

Amend-ments (AM)	Rate (R)	Dry shoot			Dry root		
		Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR	
Control		4.25	2.75	3.50	0.51	0.57	0.54
Z	R_1	5.27	3.68	4.15	0.70	1.29	0.90
	R_2	5.70	3.30		1.03	1.29	
B	R_1	4.37	2.75	3.74	0.46	0.61	0.66
	R_2	5.07	3.30		0.65	1.17	
C	R_1	3.96	3.70	3.93	0.73	1.23	0.78
	R_2	5.07	3.87		0.58	1.06	
ZB	R_1	4.81	3.62	3.97	0.68	1.05	0.78
	R_2	4.73	3.70		0.76	1.11	

Table (3), cont.

Amend-ments (AM)	Rate (R)	Dry shoot			Dry root		
		Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR	
ZC	R_1	4.26	2.91	3.83	0.47	0.82	0.70
	R_2	4.74	3.07		0.73	1.10	
BC	R_1	5.03	3.68	4.04	0.90	1.14	0.87
	R_2	4.85	3.73		0.87	1.22	
S mean		4.69	3.20	-	0.64	0.92	-
R mean	R_1	4.62	3.39	4.08	0.66	1.02	0.84
	R_2	5.03	3.50	4.26	0.77	1.16	0.96
$LSD_{0.05}$	S=***0.08 Am=***0.14 R=***0.10 SxAmxR=***0.35				S=***0.03 Am=***0.04 R=***0.03 SxAmxR=***0.11		

Irrespective of soil texture, kind of amendments, the increasing rates of all amendments successively increased dry shoot and root values. The second rate increased shoot and root dry weight by 4.41 and 14.29% compared to first application rate.

Cadmium concentration (ppm) and content (µg/pot) in shoot and root

The Cd concentrations and contents of barely shoots and roots growing in AR soil were significantly higher than that grown on KE soil; except for soil effect on Cd concentration of roots was not significant (Table 4). This may be attributed to the dilution effect, whereas, the plant growth values were higher in clayey soil (KE) than that in sandy one (AR). Cd concentration and content in shoots of barely plants grown on KE were lower than that grown on AR by 172.1 and 79.7% respectively.

Table (4) Cadmium concentration (ppm) and content (µg/pot) in shoot and root of barley as affected by soil texture, amendment types and their rates.

Amend-ments (AM)	Rate (R)	Shoot						Root					
		Concentration (ppm)			Cd Content (µg/pot)			Cd Concentration (ppm)			Cd Content (µg/pot)		
		Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR		KE	AR		KE	AR	
Control		2.00	4.73	3.37	8.88	11.86	10.44	2.50	1.83	2.17	1.30	1.02	1.16
Z	R_1	0.20	4.10	2.57	1.05	15.07	8.95	2.27	1.77	1.83	1.58	2.27	1.54
	R_2	1.03	3.33		5.85	10.96		1.07	1.53		1.09	1.98	
B	R_1	0.10	2.50	1.97	0.46	6.84	6.04	1.30	1.23	1.38	0.60	0.78	0.86
	R_2	0.07	2.40		0.34	7.87		0.50	0.93		0.31	1.11	
C	R_1	1.23	3.60	2.87	4.76	13.49	10.64	1.80	1.50	1.85	1.32	1.84	1.37
	R_2	2.47	3.17		12.58	12.27		1.95	1.50		1.13	1.60	
ZB	R_1	2.07	3.63	2.85	9.76	13.14	10.38	1.57	2.55	2.04	1.07	2.68	1.63
	R_2	1.33	3.33		6.35	12.29		1.53	2.27		1.17	2.52	
ZC	R_1	n.d.	3.90	2.71	n.d.	15.26	9.30	1.33	0.53	1.66	0.62	0.44	1.11
	R_2	1.43	4.20		6.81	12.9		2.23	1.53		1.58	1.69	
BC	R_1	1.90	3.37	3.11	9.61	12.71	11.73	0.40	2.60	2.10	0.36	2.97	1.92
	R_2	2.67	4.00		12.68	14.93		1.73	3.53		1.52	4.32	

Table (4), cont.

Amendments (AM)	Rate (R)	Shoot						Root					
		Concentration (ppm)			Cd Content (μg/pot)			Concentration of Cd (ppm)			Cd Content (μg/pot)		
		Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR		KE	AR		KE	AR	
S mean		1.47	4.00	-	6.85	12.31	-	1.82	1.80	-	1.12	1.69	-
R mean	R_1	1.1	3.52	2.22	4.27	12.75	8.51	1.45	1.70	1.57	0.93	1.83	1.38
	R_2	1.50	3.41	2.45	7.44	11.87	9.65	1.50	1.88	1.69	1.13	2.20	1.67
$LSD_{0.05}$	S=***0.30 Am=***0.50 R=***0.35 SxAmxR=ns				S=***1.30 Am=***2.25 R=ns SxAmxR=ns			S=ns Am=*0.44 R=***0.32 SxAmxR=ns			S=***0.23 Am=***0.41 R=**0.29 SxAmxR=ns		

The Cd concentrations in barley shoot were affected by adding amendments to soil significantly and follow the order: B<Z<ZC<ZB<C<BC, the decrease percentages were 41.54, 23.74, 19.58, 15.43, 14.84 and 7.72% compared to control, respectively. The same trend was observed in Cd content of shoot (B<Z<ZC<ZB), the decrease percentages were 42.15, 14.27, 10.92 and 0.57%. There is one exception where Cd content in shoot increased by the addition of BC>C by 12.36 and 1.92% compared to control. It can be observed that compost application only or in combination with clay minerals led to increase Cd concentration and content more than the addition of minerals individually, this may be refer to 1) the organic acids that produced by compost degradation in soil increased the solubility of Cd 2) adding of Z to compost (ZC mixture) may be controlled releasing Cd to plant roots. In this regard, Geebelen *et al*. (2002) showed that enrichment of compost with zeolite or bentonite could give long-term immobilization of the HMs because these minerals won't be corrupted thus will bind the metals for much longer and decreasing soil toxicity by immobilization of the HMs.

Although, the effect of amendments on Cd concentration in root was not significant, the same trend was observed, whereas, Cd concentrations in barely roots decreased significantly by adding amendments compared to control as follows: B< ZC< Z<C <ZB <BC with decrease percentages; 36.41, 23.50, 15.67, 14.75, 6.00 and 3.23% compared to control respectively. Also, Cd content of root reduced by 25.86 and 4.31% with addition of B and ZC but increased by 18.10, 32.76, 40.52 and 65.52% with addition of C<Z< ZB<BC without significant differences between them. Generally Mengel and Ernest (2001) reported that Cd was taken up and transferred from the root to the shoot. Zornoza *et al*. (2002) showed that the Cd taken up by the plants accumulated mainly in the roots,

The third interaction (SxAmxR) effect on Cd concentration and content in both barley shoot and root was not significant. The lowest value resulted by addition of the 1st rate of zeolite compost mixture to KE soil.

Similar results were shown by Usman *et al*. (2006) they reported that, a strong reduction of HMs concentrations in wheat shoots with decrease percentages 36% and 20% for Cd, 56% and 65% for Ni by addition of Na-bentonite and Ca-bentonite compared with control treatment, respectively.

Lead concentration (ppm) and content (μg/pot) in shoot and root

Lead concentrations and contents in the shoot and root were higher significantly in plants grown on KE than that grown on AR soil with increase percentages 78.6 and 145.0 for shoot and 21.13 and 0.79% for root, respectively, except for Pb content in root the differences were not significant (Table 5).

The concentration and content of Pb in barley shoot were affected by amendments and decreased as follow: B≤C<ZB<Z<ZC<BC with decrease percentages; 66.67, 66.67, 57.72, 50.77, 38.12 and 36.26% for concentration and 66.48, 66.48, 58.31, 47.27, 41.65 and 39.10 for content, compared with control, respectively.

In contradict line, addition of compost and bentonite mixtures (C and ZB) increased Pb concentration by 40.9 and 6.9% as well as addition of C, ZB and B increased Pb content in root by 75.0, 44.8 and 1.54%, respectively. This opposite trend in the root may be due to the addition of these amendments reducing Pb transfer from root to shoot compared to control that expresses of normal condition. The other amendments were decreased both of Pb concentration and content as follow: Z<BC<ZC with decreasing percentages 39.53, 30.57 and 11.82 for concentration and 7.4, 5.86 and 1.54% for content compared to control, respectively. The absorbed Pb by the plants mainly accumulated in the roots, this result is closed with that obtained by Zornoza *et al*. (2002). Generally, total concentration values of Pb were 12.4, 6.77, 7.55, 10.5, 9.07, 9.23 and 8.24 ppm for control, Z, B, C, ZB, ZC and BC, respectively. It can be observed that, zeolite was able to decrease the concentration of lead in barley followed by bentonite and the next is the mixture between them, this result is confirmed by Baltrėnas and Kazlauskienė, (2007) and Hasanabadi *et al*. (2015). Zeolite and compost decreased the HMs uptake by white lupin compared with the control and compost was the most efficient at reducing Pb uptake, while zeolite was the most efficient at reducing Cd uptake by the plants (Castaldi *et al*., 2005).

Table (5) Lead concentration (ppm) and content (µg/pot) in shoot and root of barley as affected by soil texture, amendment types and their rates.

Amend-ments (AM)	Rate (R)	Shoot						Root					
		Pb Concentration (ppm)			Pb content (µg/pot)			Pb Concentration (ppm)			Pb content (µg/pot)		
		Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR		KE	AR		KE	AR	
Control		10.75	2.20	6.48	45.78	6.04	26.70	2.83	9.00	5.92	1.43	5.04	3.24
Z	R_1	6.20	n.d.#	3.19	32.66	n.d.	14.08.	1.53	4.20	3.58	1.07	5.37	3.00
	R_2	n.d.	n.d.		n.d.	n.d.		n.d.	3.90		n.d.	5.05	
B	R_1	n.d.	n.d.	2.16	n.d.	n.d.	8.95	12.50	1.40	5.39	5.69	0.85	3.29
	R_2	n.d.	n.d.		n.d.	n.d.		2.07	4.57		1.40	5.33	
C	R_1	n.d.	n.d.	2.16	n.d.	n.d.	8.95	22.13	3.20	8.34	16.18	3.92	5.67
	R_2	n.d.	n.d.		n.d.	n.d.		12.90	n.d.		7.42	n.d.	
ZB	R_1	n.d.	3.43	2.74	n.d.	12.84	11.13	11.47	8.07	6.33	8.02	8.49	4.69
	R_2	n.d.	0.07		n.d.	0.25		6.20	0.40		4.68	0.45	
ZC	R_1	n.d.	6.67	4.01	n.d.	26.10	15.58	9.30	7.93.	5.22	4.33	6.52	3.19
	R_2	n.d.	4.43		n.d.	13.71		1.67	0.60		1.18	0.66	
BC	R_1	n.d.	6.97	4.13	n.d.	25.67	16.26	5.78	n.d.	4.11	5.22	n.d.	3.05
	R_2	n.d.	4.87		n.d.	18.17		5.82	1.20		5.15	1.47	
S mean		3.93	2.20	-	17.74	7.24	-	6.02	4.97	-	3.83	3.80	-
R mean	R_1	1.03	2.85	1.94	5.44	10.77	8.11	10.45	4.13	7.29	6.75	4.19	5.47
	R_2	0.00	1.56	0.78	0.00	5.36	2.68	4.77	1.78	3.27	3.31	2.16	2.73
$LSD_{0.05}$		S=***0.88 Am=*1.52 R=***1.08 SxAmxR=*3.73			S=***4.37 Am=ns R=***5.35 SxAmxR= ns			S=***0.53 Am=***0.92 R=***0.65 SxAmxR=***2.26			S=ns Am=***0.95 R=***0.67 SxAmxR=***2.33		

(#) n.d.: not detected

Irrespective of control values in barley shoot that led to increase the mean values of the two application rates (1, 2% and control), lead concentration and content in shoot of treated barley with Z, B and C were not detected. The addition of amendments at R2 (2%) was more efficient than R1 (1%) and significantly decreased Pb concentrations and content by 59.8 and 67.0 for shoot and 55.1 and 50.1% for root compared to R1, respectively.

These results agree with other researchers have demonstrated similar effects Li *et al*. (2009) reported that adding zeolite (20 g/kg) reduced Pb concentration in rape shoots up to 30%. Mohsen *et al*. (2010) showed that the concentrations of $Cd^{2+}$and Pb^{2+} in the corn roots and shoots grown in the enriched bentonite–sand culture were higher than those planted in the enriched zeolite–sand culture significantly. This may be confirming the immobilization of Cd^{2+} and Pb^{2+} was occurred by the zeolite. Mamdouh *et al*. (2014) reported that the roots of barley contained higher Pb concentrations compared with the shoots.

Nickel concentration (ppm) and content (µg/pot) in shoot and root

The addition of amendments reduced Ni concentration and content in plants that grown on both of different soil than grown on un-amended soil (Table 6). Barley shoot grown on sandy soil AR had Ni concentration higher than plants grown on clay one KE (30.3%), while shoot content of Ni takes the same trend of dry weight and increased in clayey soil than sandy one by 14.1%. As for the effect of different soils on Ni concentration and content in root, it took the same line of Ni concentration in shoot and increased in plants that grown on AR compared to KE by 28.9 and 69.7%, respectively.

Table (6) Nickel concentration (ppm) and content (µg/pot) in shoot and root of barley as affected by soil texture, amendment types and their rates.

Amendments (AM)	Rate (R)	Shoot						Root					
		Ni Concentration (ppm)			Ni Content (µg/pot)			Ni Concentration (ppm)			Ni Content (µg/pot)		
		Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR		KE	AR		KE	AR	
control		13.70	15.17	14.43	58.19	41.65	49.70	7.10	8.73	7.91	3.48	4.92	4.20
Z	R_1	4.23	14.13	10.57	22.30	51.43	39.02	4.10	8.61	6.20	2.88	11.11	5.43
	R_2	2.93	13.23		16.55	43.51		3.73	4.90		3.82	6.34	
B	R_1	n.d.#	4.07	6.97	n.d.	10.92	24.38	2.75	6.26	5.35	1.25	3.79	3.54
	R_2	3.70	5.20		18.77	17.30		1.40	5.88		0.91	6.90	
C	R_1	12.70	8.33	11.58	50.32	31.17	45.10	n.d.	7.01	4.23	n.d.	8.60	3.29
	R_2	11.60	8.00		58.85	30.98		n.d.	2.53		n.d.	2.72	
ZB	R_1	8.87	8.00	9.12	42.62	28.39	34.78	4.00	1.13	4.00	2.72	1.19	2.43
	R_2	4.83	4.17		23.01	15.37		3.00	n.d.		2.27	n.d.	
ZC	R_1	n.d.	11.47	9.93	n.d.	44.88	35.71	n.d.	0.40	2.70	n.d.	0.32	1.46
	R_2	6.37	12.90		30.32	39.80		n.d.	n.d.		n.d.	n.d.	
BC	R_1	6.90	8.20	10.38	34.00	30.22	40.04	4.75	n.d.	3.90	4.29	n.d.	2.53
	R_2	8.17	10.13		38.94	37.83		2.83	n.d.		2.48	n.d.	
S mean		8.47	11.04	-	38.91	34.10	-	3.84	4.95	-	2.31	3.92	-
R mean	R_1	5.45	9.03	7.24	24.87	32.84	28.90	2.60	3.90	3.25	1.86	4.17	3.01
	R_2	6.27	8.94	7.60	31.07	30.80	30.93	1.83	2.22	2.02	1.58	2.66	2.12
LSD0.05		S=***1.22 Am=**2.11 R=***1.49 SxAmxR=ns			S=ns Am=**9.76 R=***9.25 SxAmxR=ns			S=***0.33 m=***0.58 R=***0.41 SxAmxR=***1.41			S=***0.18 Am=***0.32 R=***0.22 SxAmxR=***0.78		

(#) n.d.: not detected

The addition of amendments also caused caused a reduction in Ni concentration and content of shoot and root as follow: B<ZB<ZC<BC<Z<C by 51.70, 36.80, 31.19, 28.06, 26.75 and 19.75% for Ni concentration in shoot, B<ZB<ZC<Z<BC<C by 50.95, 30.02, 28.15, 21.50, 19.44 and 9.26% for Ni content in shoot, ZC<BC<ZB<C<B<Z by 65.87, 50.70, 49.43, 46.52, 32.36 and 21.62% for Ni concentration in root and ZC<ZB<BC<C<B by 65.24, 42.14, 39.76, 21.67 and 15.71% for Ni content in root compared to control, respectively. There is one exception, Z increased Ni content in root by 29.29% compared to control.

These results indicated that the application of bentonite was the highest efficiency in reducing Ni concentration on the shoot. Addition of compost may initially increase plant growth by increasing the nutrient availability, but after degradation of the organic matter, the adsorbed HMs might be released and become available again to the plants.

Although the second application rate increased the concentration and content of Ni in the shoot, it decreased Ni concentration and content in root and both of two different rates decreased Ni concentration and content in shoot and root compared to control. This could be attributed to increasing the application rate led to increasing plant growth and its ability to absorb most elements.

The results are in conformity with the finding of Giordani *et al*. (2005) and Mamdouh *et al*. (2014) where they showed that increasing Ni level in soil improved Ni concentration in plant roots and shoots, but the barley roots contained more Ni than shoots. Usman *et al*. (2006) showed that adding Na-bentonite and Ca-bentonite (2% w/w) led to significantly reduction by 56% and 65% for Ni, respectively compared with the control. This is due to the sorption of Ni by bentonite reaches 80% of its CEC. The selectivity depends entirely on the hydrated radii of the ions. Nickel has a small size, so it is more effective than Cd and Pb in the reacting with the bentonite particles (Gregg and Sing, 1982).

Extractable metals from soils after barley

For all the treatments, DTPA-extractable Cd, Ni and Pb concentrations decreased with amendments than untreated soil (Table 7). DTPA extractable Cd and Pb were increased in AR than extracted from KE by 54.54 and 141.85%, respectively. In contrast Ni extractable from clay soil higher than from sandy soil by 31.87% compared to sandy one AR.

Extractable HMs from amended soil was decreased than unamended one as follow: C<BC<B<ZC<Z<ZB by 18.75, 18.75, 12.5, 12.5, 6.25 and 6.25% for Cd, ZC<ZB<B<C<Z<BC by 9.54, 8.21, 6.88, 6.88, 5.00 and 2.55% for Pb and ZC<C<ZB<BC<Z<B by 9, 8.12, 6.76, 4.50, 3.15 and 3.15%, compared with control, respectively.

It was observed that the highest efficient amendments on decreasing extractable Cd was compost treatment and compost that mixed with zeolite for both Ni and Pb. In this concern, Khachatryan (2014) reported that, zeolite consists of three-dimensional framework of SiO^{+4} and AlO^{+4} tetrahedral. The aluminum ion is small enough to occupy the central position of the tetrahedron, and the isomorphous replacement of Al^{3+} for Si^{4+} raises a negative charge in the lattice. The negative charge is balanced by K, Na and Ca which exchanged with HMs.

Table (7) Extractable metals from soils after barley as affected by soil texture, amendment types and their rates.

Amend-ments (AM)	Rate (R)	Cd			Pb			Ni		
		Soil texture (S)		Mean	Soil texture (S)		Mean	Soil texture (S)		Mean
		KE	AR		KE	AR		KE	AR	
control		0.13	0.19	0.16	5.49	12.52	9.01	2.59	1.85	2.22
Z	R_1	0.12	0.18	0.15	5.27	11.73	8.56	2.46	1.83	2.15
	R_2	0.11	0.17		5.17	11.18		2.40	1.76	
B	R_1	0.10	0.17	0.14	4.85	12.44	8.39	2.31	1.89	2.15
	R_2	0.10	0.17		4.77	11.12		2.26	1.67	
C	R_1	0.11	0.11	0.13	4.85	11.68	8.39	2.47	2.18	2.04
	R_2	0.10	0.11		4.44	13.53		2.32	1.79	
ZB	R_1	0.11	0.18	0.15	4.65	11.78	8.27	2.31	1.77	2.07
	R_2	0.10	0.17		4.06	10.66		1.99	1.71	
ZC	R_1	0.10	0.17	0.14	4.40	11.88	8.15	2.22	1.75	2.02
	R_2	0.10	0.16		3.78	10.80		1.97	1.72	
BC	R_1	0.12	0.16	0.13	5.23	12.45	8.78	2.49	1.70	2.12
	R_2	0.11	0.16		4.96	12.03		2.44	1.66	
S mean		0.11	0.17	-	٤,٩٧	12.02	-	2.40	1.82	-
R mean	R_1	0.11	0.16	0.14	4.87	11.99	8.43	2.38	1.85	2.11
	R_2	0.10	0.16	0.13	4.53	11.55	8.04	2.23	1.72	1.97
$LSD_{0.05}$	S=***0.01 Am= ns R=ns SxAmxR=*0.03				S=***0.27 Am=*0.46 R=ns SxAmxR=ns			S=***0.05 Am=***0.08 R=ns SxAmxR=***0.20		

Without significant difference, the extractable Cd, Pb and Ni were decreased by application of second rate of all amendments irrespective of its kind than the first one by 7.14, 4.63 and 6.64% compared to first rate, respectively.

Immobilization of heavy metals was affected by adding zeolites, bentonite, and compost through different mechanisms such as sorption, desorption, cation exchange and complexity (Simon, 2001, Geebelen *et al*., 2002, Roman *et al*., 2003, Castaldi *et al*., 2005). The effect of clay minerals amendments may be attributed to the formation of strong bonds between the metals and the adsorbing surface in the zeolite-soil and compost-soil (Lombi *et al*., 2002).

CONCLUSION

Using clay minerals might be beneficial in providing healthy barley free of HMs; it can help plants to live with heavy metal. This advantage based on plant type and its mechanism of absorption, kind and concentration of HMs as well as physical, chemical and biological characteristics of contaminated soil. Further studies are required to confirm the results of this work and investigate of the efficiency of clay minerals application to different plant species under natural field condition.

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تقييم إضافة بعض محسنات التربة الطبيعية للحد من تلوث نبات الشعير بالعناصر الثقيلة

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الملخص

تنمو المناطق الملوثة بشكل مستمر بسبب الاستهلاك المفرط للأسمدة الكيميائية، لذلك فإن الحد من سمية التربة وإنتاج الغذاء الصحي المفيد الخالي من الكيماويات الزراعية خاصة العناصر الثقيلة من أهم أهداف هذا البحث. أجريت تجربة أصص لتقييم تأثير معادن الطين والسماد العضوى (الكمبوست) والتفاعل بينهما (الزيوليت = Z والبنتونيت = B والكمبوست = C والزيوليت + البنتونيت = ZB والزيوليت + الكمبوست = ZC والبنتونيت + الكمبوست = BC) كإضافات أرضية وتأثيرها على الحد من تراكم المعادن الثقيلة (Ni, Cd, Pb) في نبات الشعير في نوعين من التربة الملوثة (محافظة الجيزة ومحافظة كفر الشيخ). أضيفت المواد السابقة بثلاثة معدلات (0 و 1 و 2 %)، تم حصاد نباتات الشعير بعد 90 يومًا. أدت جميع المعالجات إلى زيادة الوزن الطازج والجاف للشعير، وكذلك تقليل التركيز والمحتوى الكلي من العناصر الثقيلة مقارنة بمعاملة الشاهد. وقد نتج عن الزيوليت أعلى نمو، في حين أن أقل تراكم للعناصر الثقيلة نتج عن إضافة البنتونيت. وبصفة عامة، فإن المعادن الطينية قادرة على تحسين نمو النباتات في المناطق الملوثة بالإضافة إلى خفض امتصاص النباتات للعناصر الثقيلة.

الكلمات المفتاحية: بنتونيت، تلوث، رصاص، زيوليت، كادميوم، نيكل.