Agrotechnology
ISSN: 2168-9881

AlKhader, Agrotechnol 2015, 5:1
DOI: 10.4172/2168-9881.1000137

Research Article | Open Access

The Impact of Phosphorus Fertilizers on Heavy Metals Content of Soils and Vegetables Grown on Selected Farms in Jordan

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Abstract

A survey was conducted to investigate the levels of Cd, Pb and As heavy metals in soils, leafy vegetables (lettuce plant), and irrigation water in areas characterized by intensive agricultural activities in Jordan. Thirteen farms from three locations (Jordan Valley, Alyadoda, and Jarash) were selected for this purpose. Ten P fertilizers that are most widely used by farmers were also collected and analyzed for heavy metals content. The results indicated that the lettuce, used as an indicator plant for possible vegetables contamination with heavy metals, was within allowable levels of Cd and Pb of 0.2 and 0.3 mg kg^{-1} of fresh weight for leafy vegetables, respectively. The plant was, also, safe with respect to As as the level of this metalloid was much less than the established acceptable concentration of 1 mg kg^{-1} fresh weight. The results suggested that the most probable sources of the heavy metals (Cd and Pb) and metalloid (As) in the collected samples of soils and plant from the selected farms were soil parent materials and pesticides application. Long term P fertilizers additions are, also, likely sources of heavy metals in agricultural soils and crops. This implies a risk to the human health and environment in the future is expected.

Keywords: Heavy metals; Lettuce; Phosphorous; Fertilizers; Contamination; Fresh weight

Introduction

Phosphorous (P), which is supplied mainly through chemical fertilizers application, is considered an essential nutrient element for growth and development of plant crops. Its deficiency constitutes a major limiting factor in the crop production of the world [1]. Heavy metals like cadmium (Cd), lead (Pb) and arsenic metalloid (As) have been found in P fertilizers and are considered the most important of health concern [2]. These elements are regarded toxic [2,3] and classified as carcinogenic [2,4,5]. For example, Galadima and Garba [6] and Agwaramgbo et al. [7] reported that poisoning by Pb in Nigeria killed more than 500 children, and left thousands in severe health conditions in 2010. Recent studies, also, have demonstrated that As and other toxic heavy metals like Cd and Pb were responsible for causing a chronic kidney disease, known as toxic nephropathy, in contaminated areas in Siri Lanka [8]. Moreover, it was pointed out that P fertilizers (triple super phosphate) and pesticides were the main source of the heavy metals. Cadmium is a highly mobile metal and found to accumulate in plants in large amounts without showing phytotoxic symptoms. It is, therefore, considered as one of the most serious heavy metals to human health [9-11]. Moreover, Cd tends to accumulate in vegetables more than other heavy metals; for this reason Cd can enter the food chain by ingestion of vegetables [12]. In order to protect human health from food contaminants, JECFA (1989) [13] set provisional tolerable weekly intakes (PTWI) for inorganic As and Cd at 15 and 7 µg kg^{-1} body mass, respectively, while PTWI for Pb was established at 25 µg kg^{-1} body mass [14]. Lettuce (*Lactuca sativa* L.) showed a high capability to absorb Cd from the soil and considered an accumulator for heavy metals in its leave tissues [15,16]. Moreover, Wrobel [17] reported that lettuce plant (cv. Loreto) grown on a contaminated soil from a copper smelting plant showed Cd and Pb levels of up to 0.14 and 0.8 ppm (on fresh mass basis), respectively, compared with 0.02 and 0.2 ppm for vegetation grown on uncontaminated soil. Similarly, Mausi et al. [18] indicated that the permissible level of Pb (0.3 mg/kg) in oranges and mangos fruits was exceeded as they recorded mean values of 0.65 and 0.61 mg/kg, respectively. These high levels were attributed to the use of pesticides, fertilizers and wastewater. However, the levels of Cd in both fruits were within the recommended level of 0.2 mg/kg, where the recorded concentrations were 0.089 mg/kg in mangos and 0.057 mg/kg in oranges. Maalem, et al. [19] also found that P fertilization of *Atriplexes* induced higher levels of Cd in their leaves than control plants and even exceeded the standards. They suggested that phosphates raise the levels of Cd in the soil and, thus, its bioavailability for the plant is increased. However, the rate of transfer of the Cd from soil to the plant varied from 3 to 6, depending on the plant species. Actually, *Atriplexes*, used as fodder, are regarded as hyper-bioaccumulaters for toxic heavy metals like Cd and constitute a potential risk of contamination of the food chain [19]. Moreover, Wagesho and Chandravanshi [20] confirmed the reliance of the metals levels (Cd among them) in the plant (ginger) on their relevant levels in the soil where it has been grown. On the other hand, local research works have indicated that heavy metals like Cd (9.2-10.9 ppm) and Pb (1.2-32.5 ppm) are found in phosphate rock of Jordan which is used primarily in the production of P fertilizers [21,22]. In Addition, Alkhader and Abu Rayyan [22] investigated some P fertilizers like di ammonium phosphate (DAP), mono ammonium phosphate (MAP) and single super phosphate (SSP) and reported that Cd (0.5-7.9 ppm), Pb (1.8-2.2 ppm) and As (2.8-43.0 ppm) were contained as contaminants. Moreover, Ghrefat et al. [23] pointed out that fertilizers application induced high levels of Cd (4.6 ppm) and Pb (58.4 ppm) in soils located beside the Zerqa River. Therefore, the objective of this study is to investigate the possible contamination of soils, vegetable plants, and irrigation water in intensively cultivated

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Received August 13, 2015; **Accepted** September 24, 2015; **Published** September 30, 2015

Citation: AlKhader AMF (2015) The Impact of Phosphorus Fertilizers on Heavy Metals Content of Soils and Vegetables Grown on Selected Farms in Jordan. Agrotechnol 5: 137. doi:10.4172/2168-9881.1000137

areas in Jordan, with heavy metals (Cd and Pb) and As metalloid. Some widely used P fertilizers will also be investigated as prolonged fertilizers application might be one of the most probable reasons for the contamination. Lettuce was used as an indicator plant for potential heavy metals contamination of vegetables.

Materials and Methods

Farms selection

Thirteen farms from three locations characterized by intensive agricultural activities in Jordan (Jordan Valley, Alyadoda, and Jarash) were selected for soil, plant, fertilizers and irrigation water sampling during the spring/summer period of the 2010 year.

Soil

Three composite soil samples at 0-20 cm depth were collected from each selected farm for some chemical and physical analysis. The samples were air dried, crushed and passed through a 2 mm sieve. Soil pH and electrical conductivity (EC) for the paste extract were determined according to Bower and Wilcox [24], cation exchange capacity (CEC) according to Chapman [25], organic matter according to Allison [26], calcium carbonate (calcimeter method) according to Allison and Moodie [27], total N (Kjeldhal method) according to Bremner [28], available P (using spectrophotometer) according to Olsen and Dean [29] and available K (using flame photometer) according to Pratt [30]. Soil 0.005 M diethylenetriaminepentaacetic acid (DTPA)-extractable Cd and Pb, and 0.5 M $NaHCO_3$- extractable As were determined according to Lindsay and Norvell [31], and Shiowatana et al. [32], respectively. Atomic absorption spectrophotometer (AAS) (Model Varian, Spectr. AA-200, Australia) was used in these determinations, with instrument detection limits for Cd, Pb and As as 0.002 ppm, 0.01 ppm and 0.2 ppb, respectively. Soil texture (hydrometer method) was determined according to Day [33].

Fertilizer

Levels of nutrients (N, P and K), heavy metals (Cd and Pb) and metalloid (As) in ten P fertilizers which are widely used in the investigated farms were determined according to Horwitz and Latimer [34]. Cadmium, Pb and As were, also, determined using AAS.

Irrigation water

Chemical analysis for the irrigation water samples collected from the investigated farms was conducted to determine pH, EC, major cations and anions according to Chapman and Pratt [35]. Cadmium, Pb and As concentrations were measured using AAS.

Plant

Lettuce plant (iceberg type) samples were collected from only three farms (farms no. 11, 12 and 13) which were cultivated with this crop out of the 13 selected farms. Three plants from each farm were used to make representative samples. Plants were weighed firstly to have fresh weight and then rinsed with tap water followed with distilled water and dried in an oven at 65^0 C for 72 h and their dry matters were determined. After that they were ground by stainless steel grinder to pass a 1 mm stainless steel sieve for chemical analysis. Each plant sample of 1.0 g weight was transferred into a silica crucible and placed in a muffle furnace at 500^0C for 4 h in dry-ashing process. The crucible was left to cool and then 5 ml of 6 N HCl was added. After that, the crucible was placed on a hot plate and digested to obtain a clear solution. The residue was dissolved in 0.1 N HNO_3 and transferred to a 50 ml volumetric flask and completed to the mark with deionized water. Standard solutions of the elements (Cd, Pb, and As) were prepared from stock solutions (1000 ppm) by dilution with 0.1 N HNO_3 for linearity inspection. The plant contents of these elements were determined using AAS. Measurements were taken in triplicate and averaged. Total N, P and K in the plant samples were determined according to Chapman and Pratt [35].

Results and Discussion

Chemical and physical analysis for the soils

The results of some chemical and physical properties of the collected soil samples (0-20 cm depth) from the 13 selected farms are presented in Table 1. The investigated soils showed properties that ranged in their values as follows: pH (7.9-8.7), salinity (0.65-32.8 dS/m), total N (0.02-0.22%), available P (4.9-130.4 ppm), and K (275.4-730.9 ppm), DTPA-extractable Cd (0.01-0.22 ppm), and Pb (0.40-1.90 ppm), and $NaHCO_3$–extractable As (0.69-17.77 ppm). The values were averages of three composite soil samples collected from each farm. The soil samples had different textural classes, as shown in the table. The results indicated that uncultivated virgin soil (Farm no. 10) had relatively

Table 1: Average values for some chemical and physical properties of the soils (0-20 cm depth) from the selected farms in the survey.

Farm number	Location	pH	Salinity	Total N	Available		Extractable			Texture
					P	K	Cd	Pb	As	
			dS/m	%	(ppm)					
1	Middle Jordan Valley	8.1	2.76	0.08	23.1	572.9	0.028	0.62	9.04	Clay
2		8.0	1.26	0.22	130.4	730.9	0.066	0.78	7.45	
3		8.2	24.2	0.12	63.7	461.3	0.158	0.84	16.41	
4		8.1	3.47	0.14	98.4	535.7	0.058	0.92	0.69	
5		8.2	2.05	0.07	87	284.7	0.024	0.56	12.56	Clay loam
6		8.3	1.96	0.12	97.6	479.9	0.044	0.74	4.99	
7		8.2	2.28	0.08	70.6	294	0.014	0.46	2.69	Sandy clay loam
8		8.1	5.72	0.06	42.9	396.2	0.136	0.72	7.92	Clay loam
9		8.2	1.52	0.08	68.4	275.4	0.022	1.9	17.77	Sandy clay loam
10	Southern Jordan Valley/cultivated	8.7	27.3	0.1	84.9	684.4	0.028	0.4	16.24	Sandy clay loam
	Southern Jordan Valley/uncultivated	8.5	32.8	0.02	4.9	331.1	0.01	0.64	0.85	Sandy loam
11	Al-Yadoda	7.9	1.13	0.14	81.4	572.9	0.216	0.84	2.46	Clay
12		8.3	0.65	0.09	33.1	377.6	0.11	0.9	1.08	
13	Jarash	8.0	1.95	0.08	17.9	563.6	0.024	0.52	0.75	Clay

lower values of available P(4.9 ppm), K(331.1 ppm), total N(0.02%) and extractable Cd (0.01 ppm), Pb (0.64 ppm) and As (0.85 ppm) than those of most of the cultivated soils of the same farm and other farms. The source of the heavy metals in this virgin soil is mainly from natural resources like soil parent material [36]. However, fertilizer addition is the most probable reason for the high contents of the nutrients in the agricultural soils [37], whereas, the potential source for the heavy metals might be, primarily, from long-term using of pesticides [18,23,36,38,39]. Addition of P fertilizers might, also, contribute to the heavy metals contents of these soils [11,18,23,39-42]. This can be inferred from the poorly positive correlations between the soil available P and soil DTPA-extractable Cd and Pb, and $NaHCO_3$-extractable As (r=0.109, 0.111 and 0.249, respectively) as depicted in Figure 1. However, the cultivated soil in the Farm no. 10 can be considered as contaminated soil, especially, with respect to Cd (0.03 ppm) and As (16.24 ppm), as compared with the virgin uncultivated soil of the same farm. This is because the levels of these heavy metals exceeded those in the unfertilized soil more than 2-3 times [11]. On the other hand, the relatively high salinity level for the uncultivated soil might be due to the inadequate rainfall to leach downward the natural accumulated soluble salts from surface where evaporation exceeds precipitation [43]. Also, the high content of the available K in this soil was attributed to the presence of high amounts of soluble salts, whereas long-term additions of fertilizers might, also, be responsible for the high K contents in the other agricultural soils [44].

Chemical analysis for fertilizers

As shown in Table 2, the maximum levels of Cd, Pb and As in the ten most commonly forms of P fertilizers used by farmers in the selected farms were 7.9 ppm (DAP), 8.2 ppm (NPK, 16:8:24) and 43.0 ppm (MAP), respectively. Generally, these levels are considered below the critical limits of Cd (20 ppm), Pb (500 ppm) and As (75 ppm) in fertilizers according to the Canadian Standards [45]. However, the investigated P fertilizers can be regarded as one of the potential sources of these heavy metals in the agricultural soils and crops in Jordan under long-term, heavy, and continuous application [11,42,46,47].

Chemical analysis for the irrigation water

Results of the chemical analysis of the irrigation water samples collected from the selected farms showed that the pH values ranged from 7.1 to 8.4, while, the water salinity (EC) varied from 0.7 to 3.4 dS/m. On the other hand, the levels of Cd, Pb and As were below the instrumental detection limits, as shown in Table 3.

Chemical analysis for lettuce plant

The results suggested that lettuce plants collected from the three farms were within allowable levels of Cd and Pb of 0.2 and 0.3 mg kg^{-1} of fresh weight for leafy vegetables, respectively [48], as shown in Table 4. The high pH values of the investigated soils may be responsible for the lower levels of the positively charged heavy metals of Cd and Pb [49]. This could be related to immobilization of the heavy metals which limits their bioavailability to the plant [49,50]. The formation and precipitation of metal hydroxides are enhanced under such environments. This means that the concentration of the heavy metals in the immobile fraction, consecutively, increases [51]. The plant lettuce samples, also, were safe with respect to As as their contents of this heavy metal were much less than the established permissible concentration of 1 mg kg^{-1}fresh weight [38]. The nutrients content (N, P and K) of the plant samples are also presented in the table. It was ranged from 2.56-3.50% for N, 0.61-0.65% for P and 7.59-12.09% for K. According to the previously established nutrient leaf sufficiency ranges [52]; the N and P

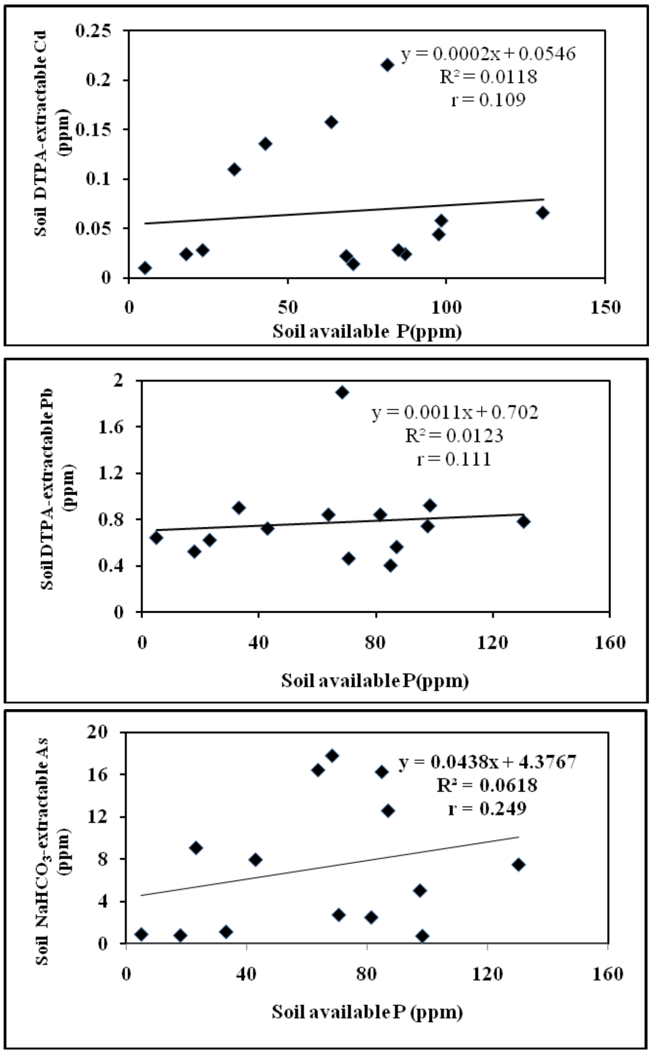

Figure 1: The correlations between soil available P and soil DTPA extractable Cd and Pb, and $NaHCO_3$-extractable As in the selected farms.

Table 2: Average values of some nutrients and heavy metals contents for some selected chemical fertilizers usually used by farmers in Jordan.

Fertilizer		Nutrients			Heavy metals*		
		N	P_2O_5	K_2O	Cd	Pb	As
		%			(ppm)		
1.	Urea Phosphate	17.4	46.7	0	2.76	0.4	13.74
2.	DAP	18.2	44.0	0	7.9	2.1	2.8
3.	MAP	12.3	61.1	0	0.5	1.8	43.0
4.	SSP	0	17.4	0	6.1	2.2	5.5
5.	NPK	13	40	13	1.02	5.8	0.26
6.	NPK	15	15	30	0.7	6	3.77
7.	NPK	30	10	10	0.42	3.4	7.85
8.	NPK	20	5	10	0.6	5	1.85
9.	NPK	19	19	19	0.86	5.6	16.36
10.	NPK	16	8	24	0.8	8.2	0.70

*The critical limits of Cd, Pb and AS in chemical fertilizers are 20, 500, and 75 ppm, respectively, according to the Canadian Standards (Heckman 2006).

Table 3: Results of chemical analysis for the irrigation water samples from the selected farms.

Farm number	Location	pH	EC	Cd	Pb	As
			dS/m	(ppm)		(ppb)
1	Middle Jordan Valley	7.1	2.2	<0.002	<0.01	< 0.2
2		7.3	1.4	<0.002	<0.01	< 0.2
3		7.2	3.4	<0.002	<0.01	< 0.2
4		8.3	2.3	<0.002	<0.01	< 0.2
5		8.4	1.7	<0.002	<0.01	< 0.2
6		8.4	1.7	<0.002	<0.01	< 0.2
7		8.3	1.7	<0.002	<0.01	< 0.2
8		8.4	1.7	<0.002	<0.01	< 0.2
9		8.3	1.8	<0.002	<0.01	< 0.2
10	Southern Jordan Valley	8.4	1.8	<0.002	<0.01	< 0.2
11	Al-Yadoda	7.6	0.9	<0.002	<0.01	< 0.2
12		7.7	0.7	<0.002	<0.01	< 0.2
13	Jarash	7.7	0.8	<0.002	<0.01	< 0.2

Table 4: Average values of the heavy metals (Cd, Pb), metalloid (As) and nutrients (N, P and K) contents of lettuce plant (iceberg type) from three investigated farms in the conducted survey during spring-summer period of the year 2010.

Farm no.	Cd	Pb	As	N	P	K
	(ppm)		(ppb)	%		
	Fresh weight basis				Dry weight basis	
11	0.05	0.2	10.76	3.5	0.65	12.09
12	0.04	0.25	12.76	3.31	0.62	11.5
13	0.03	0.12	12.78	2.56	0.61	7.59

contents were generally in close agreement, meanwhile the K content was higher. Hartz et al. [52] suggested that the leaf optimum ranges for lettuce (iceberg and romaine types) were 3.3-4.8% for N, 0.35-0.75% for P and 2.9-7.8% for K.

Conclusions

Lettuce which was considered as an indicator plant for potential heavy metals contamination of vegetables was within the allowable levels of Cd and Pb of 0.2 and 0.3 mg kg^{-1} of fresh weight for leafy vegetables, respectively. The plant was, also, safe with respect to As as the level of this metalloid was much less than the established acceptable concentration of 1 mg kg^{-1} fresh weight. Long term applications of P fertilizers and pesticides are likely sources of heavy metals in agricultural soils and crops in Jordan. This, essentially, may constitute a threat to the human health and surrounding environment.

Recommendations

A national strategy should be developed and adopted in Jordan to monitor and minimize the concentration of the heavy metals and inputs into agricultural soils and their transfer to the plant crops. This could help protect the environment from pollution and, thus, jeopardy to the human health could be reduced.

Acknowledgements

The author would like to thank farmers of the investigated farms for their collaboration during samples collection of plant, water, soil and fertilizers. Special gratitude and appreciation for the team work of The National Center for Agricultural Research and Extension (NCARE) Laboratories (Soil, Water and Fertilizer Section) for their assist in samples preparation and analysis. Technical assistance and support of NCARE during the survey are, also, highly valued.

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