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Investigation of the Effects of Phosphate Fertilizer Application on the Heavy Metal Content in Agricultural Soils with Different Cultivation Patterns

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Abstract The use of phosphate fertilizers is essential in agriculture, because they supply farmland with nutrients for growing plants. However, heavy metals might be included as impurities in natural materials and minerals, so heavy metals can also be present in phosphate fertilizers or other chemical fertilizers. The aim of this work was to assess the heavy metal content and contamination status of agricultural soils in the Hamadan province of Iran used for the cultivation of different crops, including cucumber, potatoes, and sugar beet. Surface soil samples were collected and analyzed to determine the total concentration of specific elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), before the pollution index was calculated for each element. Soils used for the cultivation of the three types of crop were not contaminated with As, Cr, Cu, Pb, or Zn. However, the pollution indices for Cd were 1.1, 4.4, and 3.8 in cucumber, potato, and sugar beet fields, respectively, which indicated moderate, high, and high levels of contamination, respectively. Soils from potato and sugar beet fields were heavily contaminated with Cd, which may have resulted from long-term overuse of phosphate fertilizers.

Keywords Phosphate fertilizer · Heavy metal · Pollution index · Soil

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Introduction

Soil is a long-term sink for the potentially toxic elements usually referred to as heavy metals. The harmful effects of heavy metal pollution on the soil environment and human health, and their control, are currently a hot topic in the environmental research field [9, 12, 22, 24, 25]. Heavy metals are characterized by long residual periods, low visibility, low transfer, high toxicity, and the complexity of their chemical behaviors and eco-reactions [4]. They are also capable of entering the food chain [33]. Heavy metals are absorbed by crops, and they find their way into water and air by means of transfer, which poses a threat to the health of humans and animals [26, 29].

Fertilizers enhance the natural fertility of soil and replace the chemical elements taken from the soil by harvesting, grazing, leaching, or erosion [32]. Phosphorus is taken up by plants in a water-soluble form as $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. Phosphate fertilizers are essential for agriculture because they supply farmland with nutrients for growing plants. Phosphates are also important constituents of animal feed stocks, as well as being used by the food industry and other chemical industries [7, 10]. The world phosphate rock consumption approaches 150 million tons annually, and about 95% is consumed by the fertilizer industry [2]. The majority of the world's phosphate resources are accessed via sulfuric or nitric acid attack of phosphate rocks [31]. Phosphate rocks are natural mineral deposits that bear phosphorus and calcium, which belong to the apatite family. These ores contain levels of trace metal contaminants that vary over a wide range, depending on their geological origin and geographical location [1]. World phosphate resources are distributed approximately as follows, according to their type: 75% from sedimentary marine deposits; 15–

20% from igneous, metamorphic, and weathered deposits; and 2–3% from biogenic sources, i.e., bird and bat guano accumulations [15, 30]. Metal concentrations found in rock phosphate are variable, depending on their source of origin. Igneous rocks contain lower concentrations, whereas sedimentary rocks contain higher concentrations [27]. Heavy metals might occur as impurities in natural materials and minerals, so heavy metals can be present in phosphorus fertilizers or other chemical fertilizers. Rock phosphate and phosphorus fertilizers were found to contain the following levels: cadmium (Cd) 9.5–96.4 mg kg^{-1}, arsenic (As) 19.4–273.0 mg kg^{-1}, lead (Pb) 5.6–17.2 mg kg^{-1}, and mercury (Hg) 0.01–0.42 mg kg^{-1} [20], Levels of As were found to be 50–60 mg kg^{-1} in ammonium nitrate, ammonium phosphate, and compound fertilizers [19]. A previous survey [18] also provided a clear picture of trace metal concentrations in various rock phosphate deposits (Table 1).

Little information is available on the effects of long-term overuse of chemical fertilizers, especially phosphate fertilizers, and the subsequent accumulation of heavy metals from them in agricultural soils. This study focused on analyzing the heavy metal content and contamination status of agricultural soils in the Hamadan province of Iran used for the cultivation of different crops, including cucumber, potatoes, and sugar beet. The results will provide a scientific basis for improving environmental quality in agricultural soils.

Materials and Methods

Soil Sampling and Analysis

Soil samples were collected from the surface (0–20 cm) in the Hamadan province of western Iran. The selected areas were used for the cultivation of three types of crop, i.e., cucumbers, potatoes, and sugar beet, the last of which consumed more phosphate fertilizer than the others. Each sampling area was greater than 2,000 m^2, 8 ha, and 4 ha for cucumbers, potato, and sugar beet, respectively, and a total of 60, 180, and 30 soil samples were collected from the respective field types. Soil samples were air-dried and ground before being passed through a 2-mm sieve prior to analysis. One sample from each treatment received three replicate analyses. Soil characteristics are shown in Table 2.

The electrical conductivity (EC) and pH of soils were measured in a 1:5 (*w*/*v*) soil/water mixture. Soil samples were digested using aqua regia (HCl/HNO_3, 3:1 solution)–$HClO_4$ [21], and the concentrations of total As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined by ICP-AES.

Fertilizer application rates were averaged. Annual phosphate fertilizer application rates were considered to be the total amount of the phosphate fertilizer applied for the first and second crops each year.

Pollution Index

The pollution index was calculated using the following formula [35]:

$$P_i = C_i / S_i \qquad (1)$$

where P_i represents the pollution index of the pollutant i in the soil, C_i is the concentration of the pollutant *I* in the soil, and S_i denotes the assessment standard of the pollutant i (*n.b.*, these values were 15, 0.2, 90, 35, 35, and 100 mg kg^{-1} of air-dried soil, respectively, for As, Cd, Cr, Cu, Pb, and Zn). $P_i \leq 0.7$ indicates that a soil is not contaminated with heavy metals. $1 < P_i \leq 2$ indicates low pollution, $2 < P_i \leq 3$ indicates moderate pollution, while $P_i > 3$ indicates heavy

Table 1 Average micrometal concentrations in PR deposits [18]

Phosphate rock deposits	Trace metal concentrations (mg kg^{-1})						
	Cu	Cd	Ni	Zn	Co	Pb	Mn
Russia							
Kola	30	0.1	2	19	2	3	250
USA							
Florida	25	8	40	90	–	14	220
West. region	80	100	85	870	–	12	75
South Africa	130	0.15	35	6	1.5	35	145
Morocco							
Bou Craa	15	35	19	120	0.7	5	35
Youssofia	16	40	–	490	1	22	20
Khourigba	34	18	32	240	1	6	15
Middle East							
Jordan	15	6	17	250	1	4	8

Table 2 Contents of heavy metals (milligrams per kilogram) in soils under different types of cultivation

Cultivation pattern		Number	Mean	Standard deviation	Minimum	Maximum
Soils from the cucumber field	As	60	3.73	1.53	1.40	7.44
	Cd	60	0.22	0.08	0.08	0.31
	Cr	60	16.49	1.74	7.69	19.63
	Cu	60	9.30	5.52	0.84	16.74
	Fe	60	4,253	2,700	101.42	6,720
	Mn	60	116.34	77.57	0.95	276.6
	Ni	60	12.66	8.19	0.36	21.85
	Pb	60	4.92	4.43	0.09	14.36
	Zn	60	19.02	15.16	0.02	78.91
Soils from the potato field	As	180	3.91	1.55	0.47	12.31
	Cd	180	0.88	0.94	0.09	4.47
	Cr	180	15.85	2.99	6.90	28.62
	Cu	180	10.75	4.04	0.59	20.05
	Fe	180	5,024	1,760	63.62	7,229
	Mn	180	122.82	50.62	0.43	276.90
	Ni	180	13.35	5.36	0.14	29.65
	Pb	180	4.19	2.42	0.21	13.37
	Zn	180	21.93	6.47	0.26	55.80
Soils from the sugar beet field	As	30	7.33	14.19	2.67	38.95
	Cd	30	0.76	4.53	0.43	1.43
	Cr	30	54.60	25.01	26.32	78.17
	Cu	30	19.50	15.05	8.12	34.08
	Fe	30	5,480	1,364	1,557	7,964
	Mn	30	198.96	94.13	6.65	324.03
	Ni	30	16.16	15.08	0.14	32.43
	Pb	30	9.96	3.46	1.40	23.87
	Zn	30	22.10	14.51	0.35	98.24

pollution (Environmental Quality Standard for Soils, GB15618-1995).

Results

pH and EC of the Soils

Mean EC values of the treated soil samples ranged from 0.152 to 0.437, 0.262 to 0.815, and 0.341 to 0.718 dS m^{-1}, respectively, for the soils used in the cultivation of cucumber, potatoes, and sugar beet. The mean pH values of the treated soil samples ranged from 7.1 to 8.12, 7.6 to 8.56, and 7.3 to 7.87, respectively, for soils used for cucumber, potatoes, and sugar beet.

Heavy Metal Content of Soils

Recent trends toward agricultural intensification have resulted in a dramatic increase in fertilizer usage. Our results show significantly higher total soil contents for the following: As, Cr, Cu, Mn, Ni, and Pb in soils from sugar beet fields; Cd, Pb, Cr, As, and Cd for soils from potato fields; and Fe and Zn for soils from both potato and sugar beet fields (Table 2).

We also tested whether ion concentrations were correlated with each other (Table 3). There was a positive correlation between heavy metals. Regressions between Ni vs. Cu, Fe vs. Mn, and Mn vs. Cu and Fe, were significant (r^2>0.90) in cucumber and potato fields. There was also a strong correlation between Mn vs. Fe (r^2>0.90) in sugar beet fields.

There was no significant correlation for As vs. any ions in potato and sugar beet fields, whereas the remaining elements showed only weak relationships with others. This suggested that the As content of soils came from a source other than fertilizer.

Pollution resulting from single heavy metals is found in nature, whereas synchronous pollution with several heavy metals is defined as combined heavy metal pollution. The high correlation between several heavy metals indicated multiple (combined heavy metal) pollution due to intensive agriculture.

Table 3 Pearson correlation between the heavy metal contents in soils under different types of cultivation

Cultivation pattern		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Ni
Soils from the cucumber field	As	1								
	Cd	0.781[a]	1							
	Cr	0.432[a]	0.301[b]	1						
	Cu	0.879[a]	0.953[a]	0.374[a]	1					
	Fe	0.788[a]	0.992[a]	0.283[b]	0.965[a]	1				
	Mn	0.748[a]	0.956[a]	0.286[b]	0.918[a]	0.966[a]	1			
	Ni	0.790[a]	0.981[a]	0.312[b]	0.948[a]	0.986[a]	0.977[a]	1		
	Pb	0.906[a]	0.729[a]	0.346[a]	0.872[a]	0.748[a]	0.655[a]	0.714[a]	1	
	Zn	0.761[a]	0.802[a]	0.316[b]	0.842[a]	0.802[a]	0.753[a]	0.784[a]	0.746[a]	1
Soils from the potato field	As	1								
	Cd	0.173	1							
	Cr	−0.102	0.400[b]	1						
	Cu	0.336	0.399[a]	0.341[a]	1					
	Fe	0.384	0.331[a]	0.281[a]	0.899[a]	1				
	Mn	0.238	0.326[a]	0.406[a]	0.912[a]	0.922[a]	1			
	Ni	0.030	0.513[a]	0.455[b]	0.962[b]	0.901[a]	0.937[a]	1		
	Pb	−0.049	−0.052	0.171[b]	0.767[a]	0.[a]	0.692[a]	0.651[a]	1	
	Zn	0.084	0.315[a]	0.426[b]	0.527[a]	0.319[a]	0.474[a]	0.528[a]	0.456[a]	1
Soils from the sugar beet field	As	1								
	Cd	0.279	1							
	Cr	−0.191	0.617[a]	1						
	Cu	0.288	0.518[a]	0.828[a]	1					
	Fe	0.152	0.650[a]	0.963[a]	0.720[a]	1				
	Mn	0.190	0.543[a]	0.904[a]	0.820[a]	0.900[a]	1			
	Ni	0.169	0.555[a]	0.939[b]	0.765[a]	0.921[a]	0.866[a]	1		
	Pb	0.092	0.282	0.415[b]	0.299	0.457[b]	0.499[a]	0.321	1	
	Zn	0.253	0.548[a]	0.924[a]	0.951[a]	0.853[a]	0.923[a]	0.864[a]	0.361	1

[a] Significant at 1% level of significance

[b] Significant at 5% level of significance

Pollution Index

The pollution indices of soil As, Cr, Cu, Pb, and Zn, which were based on the Environmental Quality Standard for Soils, were lower than the critical value (0.7) for cucumber, potato, and sugar beet fields (Table 4), which indicates that soils from the three forms of cultivation were not contaminated with As, Cr, Cu, Pb, and Zn. However, the pollution indices for Cd were 1.1, 4.4, and 3.8 for cucumber, potato, and sugar beet fields, respectively, which indicates moderate, high, and high levels of contamination, respectively.

Discussion

Heavy metals can enter the environment by natural and anthropogenic means. The most significant natural sources are the weathering of minerals, erosion, and volcanic activity. Anthropogenic sources include the extraction and processing of minerals, especially phosphate rock, industrial processes, waste, and the application of phosphate fertilizers to soil [14]. Phosphate fertilizers contain heavy metals, where the amount present depends upon the source of the fertilizer, with some containing significant amounts of metal impurities, particularly Cd [34]. The persistent

Table 4 Pollution index for heavy metals in soils under different types of cultivation

Cultivation pattern	As	Cd	Cr	Cu	Pb	Zn
Soils from the cucumber field	0.25	1.1	0.18	0.27	0.14	0.19
Soils from the potato field	0.26	4.4	0.18	0.31	0.12	0.22
Soils from the sugar beet field	0.49	3.8	0.61	0.56	0.28	0.22

application of phosphate fertilizers has led to metal accumulation in soils. Our results are supported by those of Biasioli et al. [6], who found that Pb, Zn, and Cu were well correlated in urban soils from Turin in Italy, thereby confirming their mainly anthropogenic origin. Huang and Jin found combined heavy metal pollution in agricultural soils under different patterns of land use, which substantiates the correlation coefficients obtained for the seven heavy metals we analyzed [13]. It is also known that Cu, Zn, Pb, and Cd are common anthropogenic elements in agricultural soils [3, 11, 28].

The pollution indices of the studied soils suggested serious pollution in potato and sugar beet fields. The Cd input in soils is mainly derived from deposition, phosphate fertilizers, sewage sludge, and farmyard manure [5, 16, 23]. Previous studies also demonstrated the accumulation of Cd in soils mainly from long-term overuse of phosphate fertilizers and organic manures [25, 35]. Ju et al. reported that the increase in soil Cd concentrations in Huimin county, Shandong province, China, was mainly attributable to high levels of phosphate fertilizer and manure application [17]. Carnelo et al. reported that the application of conventional inorganic phosphorus fertilizers in Argentina led to soil contamination with Cd, Cr, Cu, Zn, Ni, and Pb [11]. Nicholson et al. (2003) pointed out that phosphate fertilizers are an important source of heavy metals entering agricultural soils in England and Wales, particularly Zn, Cu, and Cd [25]. Thus, the long-term overuse of phosphorus fertilizers, or other chemical fertilizers, with a relatively high content of Cd and other heavy metals may lead to the inadvertent addition of heavy metals to soils, which could potentially result in heavy metal pollution of soils.

Conclusion

Cd, Cu, Zn, and other heavy metals are found in some phosphorus fertilizers and other chemical fertilizers. The long-term overuse of chemical fertilizers can lead to the accumulation of Cd, Cu, Zn, and other heavy metals in agricultural soils. This study found that soils sampled from potato and sugar beet fields had high levels of Cd contamination. Pollution indices for Cd were 1.1, 4.4, and 3.8 in cucumber, potato, and sugar beet fields, respectively. This indicates moderate, high, and high levels of contamination, respectively. Cd has strong chemical activity in soils, and it is easily absorbed by plants, thereby entering the food chain [8, 33]. More attention should be paid to reducing the accumulation of heavy metals in soils by more rational use of phosphate fertilizers, particularly in the potato and sugar beet fields located in our test area.

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