Journal of Geochemical Exploration 185 (2018) 74–80

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Role of irrigation water, inorganic and organic fertilizers in soil and crop contamination by potentially hazardous elements in intensive farming systems: Case study from Moghan agro-industry, Iran

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ARTICLE INFO

Keywords:
Agricultural soils
Potentially hazardous elements
Fertilizers
Alfalfa (*Medicago scutellata*)
Transfer factor
Moghan's plain

ABSTRACT

There is interconnection between soil quality, water quality, and food safety that is necessary to evaluate pollution levels in these components. Soil contamination by potentially hazardous elements may pose direct and indirect threats as negative impacts on the plant growth and yield, entering the human food chain with potentially negative effects on human health. Intensive agriculture (industrial agriculture) in agro-industry could have resulted in an enrichment of potentially hazardous elements in soils and accumulation in crops because of excess use of fertilizers and amendments. Unfortunately, despite these conditions, there were few or no investigations of potentially hazardous elements in farming areas of agro-industry sectors. This research was undertaken in agricultural lands of Moghan agro-industry complex located in the Moghan's plain (as one of the main poles of agriculture) in the north of Ardebil province and west of the Caspian Sea. The present study was designed to investigate the concentrations of Cd and Pb in agricultural soils, irrigation water, Alfalfa and commonly used fertilizers in the agricultural lands of Moghan agro-industry. The results showed that the average concentrations of the Cd and Pb in agricultural soils of Moghan agro-industry complex were 0.55 and 163.60 $mg{\cdot}kg^{-1}$, respectively. Moreover, the mean concentrations of Cd and Pb were 0.61, and 0.07 $\mu g{\cdot}l^{-1}$ in irrigation water samples, respectively, 0.45, and 0.009 $mg{\cdot}kg^{-1}$ in Alfalfa samples, 0.62 and 51.87 $mg{\cdot}kg^{-1}$ in superphosphate fertilizer samples, 0.67 and 51.87 $mg{\cdot}kg^{-1}$ in animal manure samples and 0.001 and 3.66 $mg{\cdot}kg^{-1}$ in urea fertilizer samples. Superphosphate fertilizer showed higher content of Cd and Pb than urea fertilizer, indicating the importance of phosphate fertilizer on the accumulation of potentially hazardous elements in soils. Based on the results of this research and values of Transfer Factor (TF), it was found that the Alfalfa (*Medicago scutellata*) had high ability to accumulate cadmium from contaminated soils, but the accumulation rate of Pb was much lower than Cd. Phosphate fertilizer and/or animal manure may be the main sources of contribution by Cd and Pb in the agricultural soils of the study area, but irrigation water had no significant effect on the potentially hazardous elements accumulation in soil.

1. Introduction

Nowadays, one of the most important environmental pollutants is heavy metals. Although heavy metals are naturally found throughout the earth's crust, more environmental pollution and human exposure arise through anthropogenic activities such as smelting, mining, electroplating, energy and fuel production, power transmission, sludge dumping, melting operations and intensive agriculture (Chehregani et al., 2009). The heavy applications of micronutrient fertilizer, sewage sludge, animal manure, and composts in agricultural systems increase the amount of metals in agricultural soils. In agricultural soil heavy metals analyzing is important due to transfer of heavy metals from soils to crops, animals, and humans (Karanlık et al., 2011). Increasing ecotoxicological risks and chemical pollutants impacts on water and soil, because of intensification of crop production, have been reported during the past century and conservation practices have been undertaken by nations around the world (Casentini et al., 2011; Nunes et al., 2007; Stoate et al., 2009; Ongley, 1996). In addition, arable intensification has led to the incorporation of pollutants to soils such as heavy metals, due to excess use of agrochemicals and amendments. Therefore, the analysis of metal concentrations in agricultural lands, particularly intensive agriculture is necessary for policy making and

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https://doi.org/10.1016/j.gexplo.2017.11.008
Received 29 July 2016; Received in revised form 14 September 2017; Accepted 10 November 2017

will assist in developing strategies for reducing heavy metal inputs to agricultural land (Micó et al., 2006). Agro-industry is a clear example of intensive agriculture that is one of industrial branches that process agricultural products as raw materials in its production process (Abdul Quddus, 2009). This is developed based on the intensive agriculture. Agro-industry enlarges agricultural products by applying huge amounts of chemical fertilizers and pesticides, herbicides and insecticides that result in soil pollution by heavy metal toxicity such as Cd, Cu, Zn, Ni, Cr, Pb, and As. Whereas less information is available about the effect of agriculture on soil-plant environment deterioration due to agro industry processes. Soil contamination by metals will lead to crop losses of agricultural plants and adverse health effects as they enter into the food chain (Schickler and Caspi, 1999). High levels of metals in soil can negatively affect crop growth or growth can be inhibited by heavy metal absorption. However, some plant or crop species can accumulate relatively high concentrations of heavy metals without showing symptoms of stress, which represents a potential serious risk to human or animal health (Oliver, 1997). Crops may have a range of both essential and toxic heavy metals over a wide range of concentrations (Jan et al., 2010). Contamination of soils and crops by heavy metal may be because of irrigation with contaminated water, excessive use of fertilizers (organic and inorganic) and metal-based pesticides (Maleki and Zarasvand, 2008). In environmental studies, there are some computational indices for determination of degree and severity of pollution in soil and sediment. These indices are used to comparison, evaluation, monitoring, and management the effects of contaminated elements. Pollution indices are powerful tools, but simple for analyzing, processing, and conveying raw environmental information to managers, decision makers, technicians, and the public (Qingjie et al., 2008). The evaluation of soil pollution was done bossed on the calculation of the factors such as contamination factor (CF), ecological risk factor (Er), potential ecological risk index (RI), and index of geo-accumulation (Igeo) (Mugoša et al., 2016).

This research was capable to make a basic cognition of the extent of contamination of metals and produce baseline information on the level of heavy metals from Moghan agro-industry on soil, irrigation water, Alfalfa, and inorganic (manure) and organic fertilizers. The main objectives of the present study were: (1) to determine Cd and Pb concentrations in agricultural soils, irrigation water, crop, and used fertilizers in Moghan agro-industry (Iran); (2) to evaluate the role of irrigation water and different types of fertilizers in soil and crops contamination by toxic metals; (3) to estimate the soil-to-plant transfer factors (TF) for Pb and Cd; (4) to evaluate the possible association among the concentrations of the Cd and Pb in soils, irrigation water and crops; (5) to use of pollution indices for the assessment of soil pollution in the study area.

2. Materials and methods

2.1. Study area and sampling

Moghan agro-industry complex (MAIC) is located in the Moghan's plain as one of the main poles of agriculture in the north of Ardebil province (Iran) and west of the Caspian Sea (Ziyae et al., 2015). Moghan agro-industry complex (MAIC) was established in 1975 and is one of the largest and most important agro-industries of the country in agriculture, animal husbandry, horticulture, crop and fruit production, dairy fanning, meat production and other agriculturally based industries. The Moghan district usually has fertile soil and suitable climate that is ideal for agriculture. The Aras River is the most important water resource for Moghan's plain.

According to the research objectives, the study contained sampling such as: soil of the agriculture; Alfalfa as selective crop, irrigation water, chemical fertilizers, and animal manure (Fig. 1). The number of 10 composite soil samples was collected from a depth interval of 0 to 8 in. using a stainless-steel spade and preserved in a plastic bag for next analysis. Each sample was composed of multiple sub-samples. The subsamples are mixed together to create the composite soil sample. In the laboratory, after drying at room temperature, the soil sample was then grounded and passed through both < 2 and < 0.15 mm sieve. Alfalfa (*Medicago scutellata*) samples ($n = 10$) were collected from the same locations where the soil samples were gathered. The Alfalfa samples were placed in plastic bags, and transported to the laboratory for further analysis. For removing foreign materials and contaminations, all plant samples were washed with deionized water (2–3 times). Then samples were air dried for a few days. The dried samples were ground and passed through a 0.5 mm diameter sieve. Water samples were collected at ten stations of the Aras River as an irrigation source. Plastic bottles cleaned by soaking it in 10% nitric before use and rinsed with deionized water. At the sampling site, the bottles were washed twice with the water being sampled, prior to the filling. The samples were acidified in the field with HNO_3.

Two types of fertilizers (urea and superphosphate) that are commonly used were selected for this research. These fertilizers were prepared from a store of MAIC. Seven fertilizer samples (urea = 3, superphosphate = 4) were randomly obtained from among the many bags. Four animal manure samples were collected from depot places of manure of MAIC. The manure samples were air dried, crushed, and sieved to < 0.25 mm using a Nylon sieve to ensure the powder particle sizes are homogeneous (Irshad et al., 2013).

2.2. Chemical analysis

A 0.5 g sample of air-dried and homogenized soil was weighed and digested with 2.5 ml HNO_3, 7.5 ml HCL, and 2.5 ml $HClO_4$ (Liu et al., 2008). The residue was diluted to 25 ml with deionized water and analyzed for Cd and Pb by Atomic absorption spectroscopy (AAS). In order to digestion of Alfalfa samples, 0.5 g of each sample was mixed with 12 ml perchloric acid ($HClO_4$) and nitric acid (HNO_3) solution in the ratio of 1:2 (Ryan et al., 2001). The mixture was heated on a water bath at 90 °C for 4–6 h. After digestion, the samples were filtered with filter paper No 42 and diluted to 25 ml volume with de-ionized water. One gram of the fertilizer sample was accurately weighed and digested with 10 ml of HNO_3 and 5 ml of $HClO_4$ on a water bath (Hseu, 2004). After extraction, the cooled residues were diluted with deionized water to 25 ml and analyzed for metals by AAS. The concentrations of considered heavy metals of the present study (Cd and Pb) in the agricultural soils, Alfalfa, water, fertilizer and manure extracts were analyzed by AAS. Depending on the concentration range of the metals, flame and furnace spectroscopy was used for the analysis of metals. For quality control triplicate analysis of each sample was done together with blank digested without the samples. Also the precision of the analysis was evaluated by the values of percentage relative standard deviations (% RSD) and $< 7\%$.

2.3. Data analysis

Transfer factor (TF) has been used for transition of metals from soil to plant tissues. TF is described as an obtained concentration of metal in plant tissues divided by metal concentration in soil. High Transfer factors ($TF > 1$) show that plant species might be a good metal phytoextractor and can be used in phytoremediation of polluted soil. Contrariwise, lower values of this factor indicate low uptake of heavy metals by plants at high metal levels and this plant act as excluders that can be applied for human consumption (Rangnekar et al., 2013). The transfer factor from soil in plant was calculated by the formula:

$$TF = \frac{C_{plant}}{C_{soil}}$$

where, TF = transfer factor, C_{plant} = metal concentration in plant ($mg \cdot kg^{-1}$), C_{soil} = metal concentration in soil ($mg \cdot kg^{-1}$).

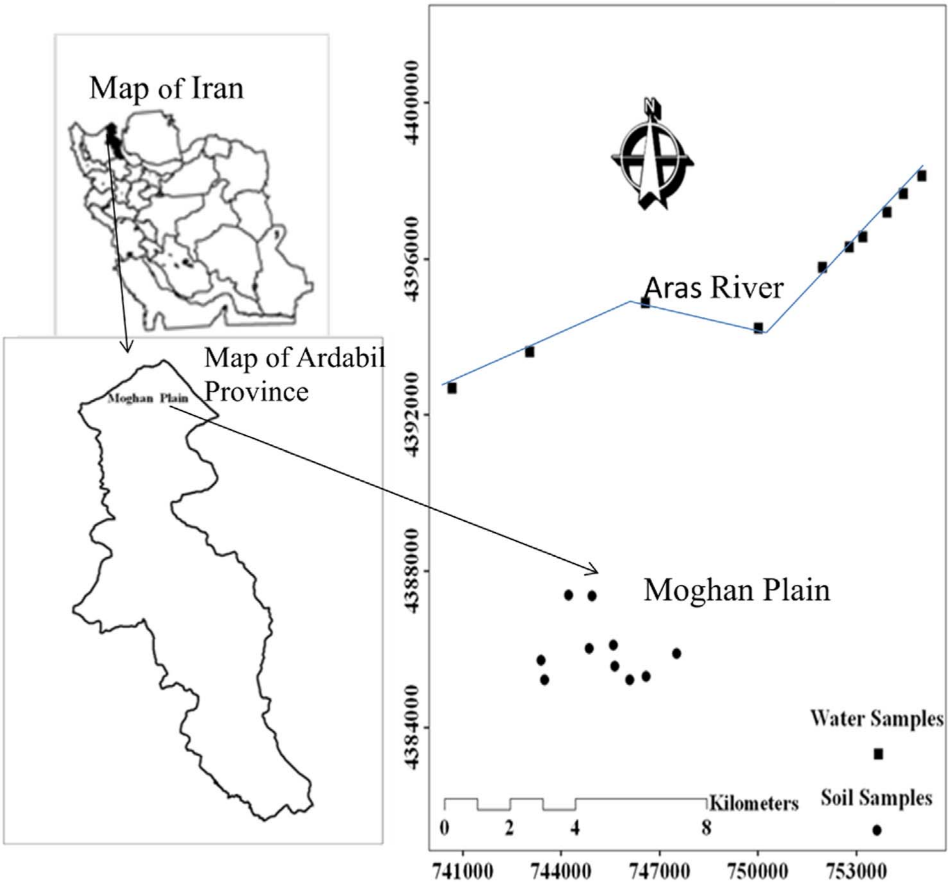

Fig. 1. Schematic map of the study site and location of the sampling points.

In this survey, the index of geoaccumulation (Igeo) has been used to determine the anthropogenic contamination in soils as proposed by Muller (1969). This index (Igeo) is computed by computing the following mathematical relation:

$$\mathrm{Igeo} = \log_2 (C_n/1.\ 5B_n) \tag{1}$$

where: C_n = measured concentration of metal n in the soils; B_n = geochemical background for the metal and n 1.5 is a correction factor to minimize the effect of possible variations in the background concentrations due to lithological variations. The Igeo classes based on Muller (1969) were adopted for this research; Igeo $<$ 0 = practically uncontaminated; 0 $<$ Igeo $<$ 1 = uncontaminated to moderately contaminated; 1 $<$ Igeo $<$ 2 = moderately contaminated, 2 $<$ Igeo $<$ 3 = moderately to strongly contaminated; 3 $<$ Igeo $<$ 4 = strongly contaminated; 4 $<$ Igeo $<$ 5 = strongly to extremely contaminated; and Igeo $>$ 5 = extremely contaminated.

The Potential Ecological Risk (RI) primarily proposed by Häkanson (1980) was applied to assess the ecological risk of heavy metals in surface soil. This index is composed of three modules: 1) the contamination factor (C_f); 2) toxic-response factor (TR) and 3) potential ecological risk factor (ER). Based on this method, E_i^r: the potential ecological risk index of a single metal and RI: comprehensive potential ecological risk index (Jiang et al., 2014) was calculated via the following formula:

$$C_f^i = C_s^i / C_b^i \tag{2}$$

$$E_r^i = T_r^i \times C_f^i \tag{3}$$

$$RI = \sum_{i=1}^{m} E_r^i \tag{4}$$

where C_f^i is the contamination factor of heavy metal; C_s^i: Concentration of heavy metal in soil; C_b^i: background concentration of heavy metal in the study area; E_r^i: Ecological risk potential of heavy metal; T_r^i: Toxicity response factor of heavy metal; RI: potential ecological risk index of the multielement. The values of toxicity response (Tr) for Pb and Cd is 5 and 30, respectively (Häkanson, 1980). Based on Häkanson, the following classification is offered for the Er and RI amounts: (1) Er $<$ 40 indicates a low ecological risk; 40 $<$ Er $\leq$ 80 shows moderate ecological risk; 80 $<$ Er $\leq$ 160 indicates considerable ecological risk; 160 $<$ Er $\leq$ 320 indicating high ecological risk; and $>$ 320 indicates disastrous ecological risk; (2) RI $<$ 150, low ecological risk; 150 $<$ RI $<$ 300, moderate ecological risk; 300 $<$ RI $<$ 600, high ecological risk; and RI $\geq$ 600, very high ecological risk.

All statistical analyses were done through SPSS (PASW Statistics 18). Parameter distribution normality for variables was checked using the Shapiro-Wilk test. ANOVA was used to test the significance of differences in metal concentrations in different fertilizer and mean values was grouped by Dunnett T3 test for comparison ($P < 0.05$).

3. Results and discussion

The EC, pH and metal concentrations of water from the ten stations from the Aras River as an irrigation water source are given in Tables 1 and 2. As it is demonstrated, the values of water pH ranged between

Table 1
The pH and Electrical conductivity (EC) of the investigated samples.

		Min	Max	Mean	Standard deviation
Water	pH	7.57	8.71	8.22	0.42
	EC (dS/m)	0.681	1.99	1.25	381.69
Soil	pH	7.25	7.74	7.47	0.13985
	EC (dS/m)	0.08	0.72	0.20	0.18709

Table 2
Concentrations of cadmium and lead in the soil, irrigated water, and Alfalfa.

	Metals	N	Minimum	Maximum	Mean	Std. deviation
Soil	Cd (mg·kg^{-1})	10	0.40	0.63	0.55	0.08
	Pb (mg·kg^{-1})	10	111.50	205	163.60	26.88
Water	Cd (μg·l^{-1})	10	0.01	2.90	0.61	0.92
	Pb (μg·l^{-1})	10	0.04	0.10	0.07	0.02
Alfalfa	Cd (mg·kg^{-1})	10	0.20	0.79	0.45	0.16
	Pb (mg·kg^{-1})	10	0.00	0.02	0.009	0.005

Table 3
Cadmium and lead concentrations (mg·kg^{-1}) in agricultural soil from various areas around the world.

Location	Pb	Cd	Reference
Argolida basin (Greece)	19.74	0.54	Kelepertzis (2014)
Thiva (Greece)	24	–	Antibachi et al. (2012)
Huizhou (China)	16.74	0.1	Cai et al. (2012)
Zagreb (Croatia)	25.9	0.66	Romic and Romic (2003)
Piemonte (Italy)	16.1	–	Facchinelli et al. (2001)
Shunyi (China)	20.4	0.136	Lu et al. (2012)
Iran (Isfahan)	4.6	0.43	Esmaeili et al., 2014
Turkey (Amik Plain)	5.56	0.19	Karanlık et al., 2011
Moghan	163.6	0.55	This study

7.57 and 8.71, and electrical conductivity (EC) between 0.68 and 1.99 dS/m (Table 1). The EC values are within the allowable range recommended (0–3 dS/m) for irrigation waters and pH values slightly higher than the limit value of 6.5–8.4 (Ayers and Westcot, 1985). More or less similar findings of pH values were found in the irrigation water of Western Cape Province of South Africa by Malan et al. (2015) and in surface water used for irrigation of the Turag River in Bangladesh by Arefin et al. (2016). Also Ali et al. (2016) measured the mean of 7.89 for pH in water of Karnaphuli River, Bangladesh. The concentrations of the metals in irrigation water were in the ranges of (0.01–2.9), and (0.04–0.1) μg·l^{-1} for Cd and Pb, respectively (Table 2). In general, irrigation waters have low concentrations of these metals. Threshold values of heavy metals in waters intended for irrigation (Pescod, 1992) that leading to crop damage are 5000 μg·l^{-1} and 10 μg·l^{-1} for Pb and Cd respectively. Based on obtaining data in Table 2 the levels of Cd and Pb in all irrigation water stations were below the permissible concentration limit for irrigation waters (Ayers and Westcot, 1985). Also, when these given data compared with toxicity reference values (TRV) proposed by USEPA (1999), metal concentrations were below the TRV (3 and 2 μg·l^{-1} for Pb and Cd respectively) showed that water from this river is not safe for drinking. It could be concluded that the concentrations of Cd and Pb in irrigation water are appropriate for irrigation purposes. Results of a research (Bichi and Bello, 2013) showed that the high concentration of Cd (13.7 mg l^{-1}) and Pb (1.3 mg l^{-1}) in surface waters of River Tatsawarki in the Kano (Nigeria) used for irrigation. In a recent study, Ali et al. (2016) assessed the concentrations of some heavy metals such as Cd and Pb in water and sediment of Karnaphuli River, Bangladesh. The data revealed that the ranges of these metals in water were 2.54–18.34 and 5.29–27.45 g l^{-1} for Cd and Pb respectively. The presence of heavy metals in the natural surface water is primarily the result of natural processes and then via human activities. Natural sources include chemical geological weathering and decomposition of biotic detritus (Greenfield et al., 2012). Heavy metals in the Aras River originate from human activities such as industrial and agricultural activities within the Aras River basin in Iran, Armenia, and Azerbaijan (Nasehi et al., 2013). The presence of low levels of these heavy metals in irrigation waters may decrease their concentrations in soils, and subsequently in crops.

Our results indicated that agricultural soil of Moghan plain at present influenced by the MAIC activities. The pH and EC (electrical conductivity) were less influenced so that the values of soil pH ranged between 7.25 and 7.74 (Table 1). Among soil properties, soil pH plays an important role in the metal uptake by plants. An increase in soil pH, i.e. the soil environment becomes more alkaline, lead to decrease in the metals availability for crops. However, under more alkaline soil conditions, the metals are more firmly connected to soil particles, resulting in the accumulation of heavy metals in agricultural soils during the time (Malan et al., 2015). Also, according to the Food and Agriculture Organization (FAO), the soil is saline when the pH is < 8.2 and more often near neutrality (FAO, 1983). Al-Rashdia and Sulaiman (2013) reported similar results for pH in Alfalfa Farm Soils in Oman. EC values were between 0.68 and 1.99 dS/m (Table 1). Based on the USDA salinity classes (EC: 0–2 dS/m), salinity effects on crop plants is negligible.

Concentration of Cd and Pb ranged between 0.40 and 0.63 (mean = 0.55) and 111.50–205 (mean = 163.6) mg·kg^{-1} dry soil, respectively (Table 2). The Pb mean concentration in soil samples exceeded the threshold value (60 mg·kg^{-1}) set by MEF (2007) but the mean concentration of Cd was less than the threshold of 1 mg·kg^{-1} set by MEF. Also worthy to mention that the content of Pb in the soils was exceeded the maximum permissible limits of 100 mg·kg^{-1} and 70 mg·kg^{-1} set by European Union Standard (EU) (2009) and Canadian Environmental Quality Guideline (CCME) (1999), respectively. The comparison of the concentration of Cd in the soils with these maximum permissible limits (EU and CCME) indicated that its concentration were below the CCME and EU standards of 1.4 and 1 mg·kg^{-1}, respectively. A comparison of metal levels in soils from MAIC with those from other studies is shown in Table 3. The concentrations of Pb in the soils in our research were much higher than the concentrations obtained in soils from other studies (Table 3). In the case of the Cd, it was higher than the other regions exception of Zagreb (Croatia). Compared to the background concentrations of metals in agricultural soils from different countries (Table 4), Cd and Pb in the study area showed very high concentrations. To better distinguish the soil metal pollution, the geo-accumulation index (Igeo) values for Cd and Pb in the study area were computed and the findings are shown in Fig. 2. Cd displayed positive geo-accumulation index changes from 0.41 to 1.07 and belongs to the class uncontaminated to moderately contaminated. For Pb, geo-accumulation index falls into the class moderately to strongly contaminated. This index proposes that concentrations of metals in the soil samples are greater than their normal concentration in soil. Also, this suggests that Pb and Cd input in the agricultural soils relate to agricultural practices. Also in this research, we further estimated the potential ecological risk index (RI) of surface soils from the MAIC (Table 5). The findings indicate that the E_r^i for Cd in all the soil samples was < 40 that this element shows a low potential ecological risk. The E_r^i for Pb in all of the soil samples was between $40 < Er \le 80$ shows moderate ecological risk. The RI ranged from 45.97 to 83.51with a mean value of 66.752, which showed a low ecological risk for the studied heavy metals in this area. Consistent with our result, Amuno (2013) found that potential ecological risk index (RI) of heavy metal of showing low ecological risks. Study of Mazurek et al. (2016) in surface layers of Roztocze

Table 4
Soil background concentrations of cadmium and lead in soils from different countries.

Country	Cd (mg·kg^{-1})	Pb (mg·kg^{-1})	References
Spain	0.32	19.7	Tume et al. (2011)
Serbia	–	2.70	Skrbic and Cupic (2004)
Korea	0.15	22.0	KMOE (2013)
Germany	0.17	40.0	Reimann et al. (2003)
China	–	15.5	Su and Yang (2008)
Whole Europe	–	15.0	Salminen et al. (2005)
Albania	0.31	17.6	Gjoka et al. (2008)
Iran	0.12	15.42	Mirzaei et al., 2014
Belgium	0.2	15	Carlon, 2007
Lithuania	0.8	40	Carlon, 2007
China	–	26	Chen et al., 1991

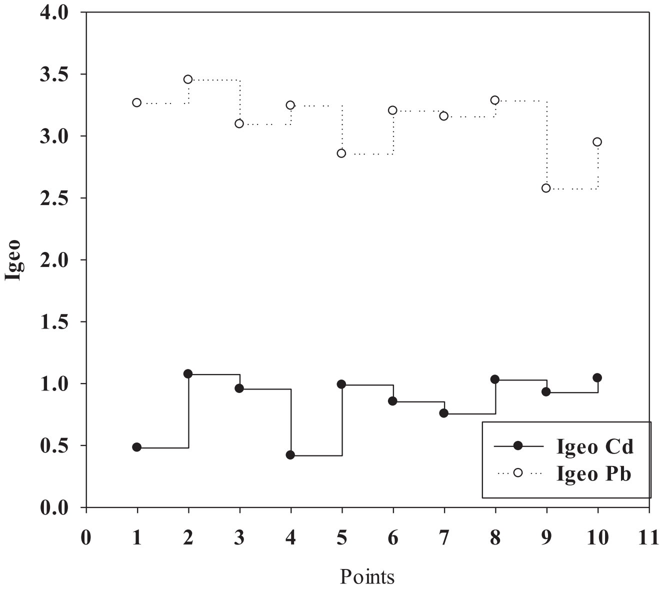

Fig. 2. Geoaccumulation Index (Igeo) of cadmium and lead in agricultural soils.

Table 5
Potential risk of heavy metals pollution in soils from the MAIC.

Point	E_r^i		RI	Risk grade
	Pb	Cd		
1	72	1.00	73.00	Low
2	82	1.51	83.51	Low
3	64	1.39	65.40	Low
4	71	0.96	71.96	Low
5	54.2	1.43	55.62	Low
6	69	1.30	70.30	Low
7	66.8	1.21	68.01	Low
8	73	1.47	74.47	Low
9	44.6	1.37	45.97	Low
10	57.8	1.48	59.28	Low

national park forest soils showed that the study area were characterized low to highly strong ecological risk. Gąsiorek et al. (2017) indicated a low to very strong potential ecological risk for topsoil of the historical urban park in Krakow (Poland). On the whole, the risks of heavy metals in the present research were low to moderate compared to the reported results from other studies. A low ecological risk might be due common anthropogenic sources such as agricultural fertilizers. Also Similarity of ecological risk index values with other studies may be due to the similar soil properties such as clay or TOC content.

The mean concentration of Cd in Alfalfa taken in the sampling sites was 0.45 (mg·kg^{-1}) with a range from 0.20 to 0.79 (mg·kg^{-1}). The Pb concentration in this species varied from 0.00 to 0.02 (mg·kg^{-1}) with a mean value of 0.009 (mg·kg^{-1}) (Table 2). Concentrations of Cd and Pb obtained in this research were lower than range of 0.61–2.74 mg·kg^{-1} and 0.16–081 mg·kg^{-1} reported by Bytyqi and Sherifi (2010). Comparing the findings of this research with the previous study of Taylor and Allinson (1979) on metal concentrations in Alfalfa in Connecticut (New England region of the United States) showed that the levels of Cd in the samples under investigation were higher but values of Pb were lower than. It has been found that the Alfalfa plant has a high potential for uptake and accumulate heavy metals such as cadmium and lead. This species is a heavy metal-tolerant plant that ability to accumulate heavy metals to concentrations much higher than other plants which may be because of many chemicals/functional groups responsible for metal tolerance and accumulation (Bytyqi and Sherifi, 2010). Cadmium content in Alfalfa collected from Moghan plain exceed Maximum allowable limits of 0.02 mg·kg^{-1} (dry weight) of Cd in plants according to WHO (1996). No Alfalfa sample was observed to contain Pb above the allowable concentration of 2 mg·kg^{-1} set by WHO (1996). Alfalfa as "Queen of the Forages" is known to be an important forage crop in many countries around the world that has various benefits including large amounts of proteins, rapid growth rate, tolerant to climate shocks such as drought and soil fertilization with nitrogen fixing bacteria (Hattab et al., 2014). On the other hand, as mentioned Alfalfa could be effectively capable to accumulate of toxic metals (Carrasco-Gil et al., 2012). Accumulation of metals in the aerial parts of Alfalfa could therefore be important that animals feed on contaminated forage; metals are taken into their bodies and finally pose a potential threat to human health.

Metal transfer factor (MTF) or Plant Concentration Factor (PCF) is one of the key parameters of human exposure to heavy metals through the food chain (Cui et al., 2004). In the present research, the Transfer factors of Cd and Pb from soil to Alfalfa are shown in Fig. 3. TF value of 0.1: plant is excluding element accumulation in their green tissues, the values of TF higher than 0.5: chances of plants for metal contamination by anthropogenic activities, values of TF $>$ 1: heavy metals in plants are greater than that in soils (Shammi et al., 2016). Based on data in Fig. 3, Cd and Pb indicated TF values in the range of 0.0001 to 1.36. The trend of TF for metal in Alfalfa samples was in order: Cd $>$ Pb. The TF of Pb was poor despite its high concentrations in soils. TF of Pb in Alfalfa showed relatively low values, indicating an important restriction to soil – Alfalfa transfer of lead. The main source of cadmium pollution

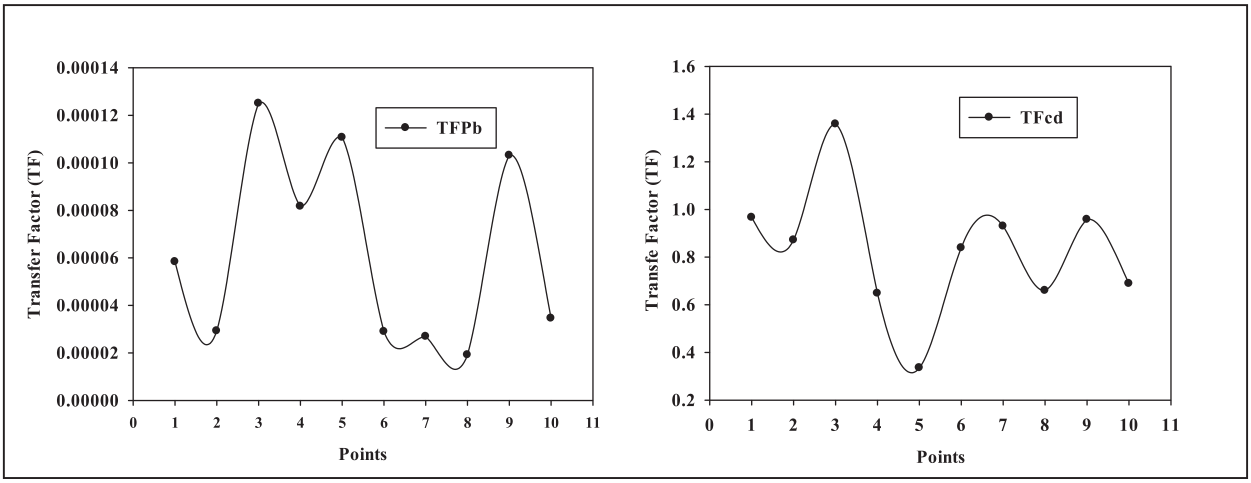

Fig. 3. Transfer factor (TF) values for cadmium and lead in Alfalfa in the study area.

Table 6
Concentrations of cadmium and lead in three used fertilizers.

Metals	Fertilizers	N	Mean	Minimum	Maximum	Std. deviation
Cd	Urea	3	0.001^{b}	0.001	0.002	0.0005
	Phosphate	4	0.62^{a}	0.48	0.85	0.16
	manure	4	0.67^{a}	0.64	0.70	0.03
Pb	Urea	3	3.66^{b}	3	4.25	0.62
	Phosphate	4	51.87^{a}	32.50	62.50	13.6
	manure	4	50.70^{a}	31.60	80	22.48

Note: different letters within columns show significant differences at 5% level.

in soil is phosphate rocks (Qixing et al., 1994) and is transferred into edible plant parts because of its high mobility. Gupta et al. (2010) observed similar results in their research on different plant species from Durgapur of India. They found that all plants have TF > 1 for Cd whereas the TF values for Pb were very low. They explained the high TF of Cd as a result of high mobility of Cd from soil to plant and low TF of Pb due to lower bioavailability. The plants are able to accumulate high concentrations of Cd even with much lower Cd in the soil in comparison to the other heavy metals, therefore Cd is easily absorbed by plants (Wang et al., 2001). Pb is one of the least available and mobile elements to plants (Berg et al., 1995), therefore, despite the higher Pb concentrations in soil, Pb levels in Alfalfa were low.

Fertilizers including organic and inorganic is used to increase the production of the crops. The utilization of fertilizer raises the amount of heavy metals in the soil. Based on this case study in MAIC, annually, large amount of fertilizer used, and most of the fertilizer is used as inorganic fertilizer such as urea and superphosphate which leads to accumulating heavy metal in the surface soil. The levels of heavy metals in three fertilizers (Urea, superphosphate and manure) are abstracted in Table 6. The heavy metal concentrations (Pb and Cd) in superphosphate and manure several fold higher than concentrations in urea. Analysis of variance (ANOVA, $P < 0.05$) indicated that there were significant differences in metals between the superphosphate and urea for Cd and Pb, whereas no significant difference was found between superphosphate and manure. Also there were significant differences between manure and urea for Cd and Pb. The findings of compare means indicated that the highest amount of Cd and Pb was from chemical superphosphate fertilizer and manure that had statistically significant difference with Urea fertilizer (Table 6). Lead concentration in superphosphate fertilizer ranges from 32.50 mg·kg^{-1} up to 62.5 mg·kg^{-1} with an average of 51.87 mg·kg^{-1}, which was higher than concentrations of other worldwide studies such as Modaihsh et al., 2004; El-Taher and Althoyai, 2012; Benson et al., 2014, but Cd concentrations in superphosphate fertilizer ranges from 0.48 mg·kg^{-1} up to 0.85 mg·kg^{-1} with an average of 0.62 mg·kg^{-1} were substantially lower than those reported for superphosphate fertilizer by Modaihsh et al., 2004; El-Taher and Althoyai, 2012; Benson et al., 2014. Cadmium and lead levels in all manure samples of the present study were less than the standards for biosolids (39 mg·kg^{-1} for the Cd and 300 mg·kg^{-1} for Pb) (Walker, 2001). Obtained levels of Cd in the manure of the current study was comparable with studies conducted by Zhao et al. (2014) but Pb concentrations were higher than these data. Phosphorus fertilizers typically contain heavy metals at concentrations above levels observed in other fertilizers (Saltali et al., 2005).

4. Conclusion

This research, designed to evaluate the role of irrigation water and different types of fertilizers in soil and crop contamination by toxic metals. In order to, we sampled soil, irrigation water, fertilizers, and Alfalfa from MAIC. Contamination indices (Igeo and RI) were used to evaluate the degree and extent of soil contamination by heavy metals resulting from Agro-industry activities. The transfer factor (TF) was assessed for Alfalfa capability to accumulate heavy metals from soils. From the findings herein, it is obvious that the irrigation water, agricultural soils, as well as the crops such as Alfalfa in the lands of MAIC contains varying concentrations of Cd and Pb. According to the results of our study, contamination of metals in soil is mostly a consequence of excessive use of chemical fertilizers and organic manures. Generally, the concentrations of metals were higher in superphosphate and manure fertilizers than in urea fertilizer, and as a result application of superphosphate and manure fertilizers in soils could pose health risk to animal and human populations when consuming produced crops and products from these soils. The higher concentrations and TF values of Cd in Alfalfa, indicated Alfalfa, have the ability to accumulate this metal. The concentration levels of heavy metals in irrigation water, agricultural soils, Alfalfa, and fertilizers were below permissible concentrations, except Pb levels in soils, which was higher than the permissible limits. The research recommends that special attention is required to perform proper continuous monitoring and pollution control in order to ensure food safety for the consumers and control the use of fertilizer. The water of the Aras River for agricultural irrigation of MAIC contained little contamination from Cd and Pb. The contradiction in soil metal concentrations with irrigation water concentrations may due to other sources of soil metals such as fertilizers and less relation to irrigation water. So, this research concluded that Agro-industry activities altered the soil properties, especially increased the levels of heavy metals such as Cd and Pb in the soil, and further in agricultural crops as Alfalfa.

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