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Arsenic in the rock-soil-plant system and related health risk in a magmatic-metamorphic belt, West of Iran

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Abstract

Following earlier reports of water contamination and arsenic (As) toxicity symptoms in residents of Kurdistan Province, As was determined in rock, soil and plant samples to investigate its fate from rock to crops and its potential effects on human health. Total As content ranged from 4.9 to 10044 mg/kg, 7.7 to 429.5 mg/kg and <0.05 to 25079 µg/kg (dry weight) in rock, soil and plant samples, respectively. The Qorveh-Bijar region data indicated that magmatic differentiation has enriched late magmatic fluids in As. High rare earth elements concentration, dissociation coefficient, and positive Eu anomaly in volcanic rocks, indicated the prevalence of intermediate to felsic composition. The highest As concentration was measured in travertine. In soil, As average level in Qorveh and Bijar was 48.50 and 106.60 mg/kg, respectively. Higher pollution index (PI) and geoaccumulation index (I_{geo}) were also calculated for Bijar County. The As concentration in crop samples was greater than the recommended maximum permissible concentration for foodstuff. Mann-Whitney U test revealed significant differences between As concentration in different plant species and no difference between plants in Bijar and Qorveh. Also, alfalfa displayed the highest biological accumulation coefficient among the investigated plants. The calculated chronic daily intake of As in Bijar County was higher than the recommended levels for wheat and barley grains. Moreover, the hazard quotient (HQ) and incremental lifetime cancer risk assessments revealed high non-cancer ($HQ > 1$ for both adults and children) and cancer (particularly for barley in Bijar) risks for inhabitants via consumption of As contaminated crops cultivated in the study area.

Keywords: Arsenic; Rock; Soil; Plant; Bijar; Qorveh

1. Introduction

Rocks enriched in arsenic (As) can release As, and this metalloid may enter a more active biogeochemical cycle, posing risk to ecosystems (Dradrach et al. 2020). The As average concentration in Earth's crust, igneous rocks and sedimentary rocks range from 0.5-2.5, 0.5-2.5 and 1-13 mg/kg, respectively, which may be associated with several minerals, including arsenite minerals, arsenopyrite, orpiment, realgar, and some other polymorphous types of minerals. The geochemical behavior of As (V) is similar to that of phosphates because of their similar ionic radii (Kabata-Pendias and Mukherjee 2007). Over time, rock weathering can release As and other elements, maintaining a steady supply of macro- and micro- nutrients, and some toxic elements, to soil (Myrvang et al. 2016). The predominant forms of arsenic in soil solution are mainly anionic including AsO_4^{3-} , HAsO_4^{2-} and $\text{H}_2\text{AsO}_3^{2-}$ (Kabata-Pendias and Sadurski 2004), largely mediated by soil characteristics, in particular Eh-pH influences. As forms, in turn, affect its sorption-desorption in soils (Bissen and Frimmel 2003), influencing its uptake by plants. In food crops, As uptake is highly variable, commonly ranging from 10–60 $\mu\text{g kg}^{-1}$, depending upon its natural soil concentration, soil properties and plant species, and appears to increase in green vegetables and plants grown in contaminated soils (Kabata-Pendias and Mukherjee 2007).

Epidemiological evidence so far has revealed the relationship between long-term chronic As exposure and increased risks of various cancers, diabetes mellitus, cardio-vascular disease, ocular disease and neuropathies (States et al. 2008; Kundu et al. 2011; Rana et al. 2012; Keshavarzi et al. 2015a). Most reported studies in literature have focused on anthropogenic sources of As contamination in water and soil, including mining and smelting, application of arsenic-containing pesticides, herbicides and fertilizers, wood preservatives, arsenic additives in livestock feeds, electronic industries, pharmaceutical works, galvanizing and ammunition factories, and coal or petroleum combustion (Ongley et al. 2007; Lee et al. 2008; Liu et al. 2010). Also, As contamination of groundwater by geogenic sources is reported from various regions around the world (Ahmed et al. 2001; Bhattacharya et al. 2007; Kumar et al. 2016; Sharifi et al. 2017).

Naturally high levels of As in groundwater cause various diseases in human and constitutes a high-priority water quality problem, particularly in Asian countries, including India, Bangladesh, Pakistan and Iran (Kumar et al. 2018; Nickson et al. 2005; Rahman et al. 2011; Keshavarzi et al. 2011). On the other hand, it is generally accepted that soil–plant transfer of As is a principal pathway of human exposure to As, particularly in regions where drinking/ground water As levels do not exceed the WHO drinking water standard of 10 $\mu\text{g As/L}$. Arsenic inputs in soils either through the use of As-containing water for irrigation purposes or weathering of As-rich rocks could accumulate in the soil and consequently be leached into ground and/or surface waters. Soil arsenic may also be metabolized and possibly volatilized by microorganisms and be taken up by crops from the soil–water system (Martin et al. 2014). The role of As-contaminated groundwater or springs which are used for cropland irrigation, elevating soil As, and consequently resulting in crops contamination, is widely acknowledged (e.g. Rahman et al. 2013; Chen et al. 2014; Farooq et al. 2019).

The plant availability of soil arsenic is determined by soil properties, notably mineral composition, organic matter content, pH and redox potential (Tu and Ma 2003; Warren et al. 2003). However, soil total arsenic content remains a key factor affecting its uptake by food crops. Most studies have focused on the biogeochemistry of arsenic in soils with anthropogenically elevated arsenic concentrations (e.g. Smith et al. 2009; Otones et al. 2011; Adamo et al. 2014; Mathee et al. 2018).

Some soils naturally can have high levels of arsenic due to the mineralogy of their parent materials (Wang et al. 2015), which may pose risk to human health via uptake by food crops. It is therefore important to understand the behavior of arsenic in the rock-soil-plant system to better assess its entry in the food-chain and the risk it may pose to human health.

Various arsenic toxicity health effects are widely documented from Kurdistan Province in west of Iran located in the so-called northern Sanandaj–Sirjan magmatic-metamorphic belt. Mosaferi et al. (2008) studied the prevalence of skin lesions among residents in Kurdistan province in Iran with emphasis on intake of arsenic from drinking water. They found a significant relationship between total lifetime intake of arsenic from drinking water and hyperkeratosis and hyperpigmentation. Barati et al. (2010) measured 42 to 1500 $\mu\text{g/L}$ arsenic in drinking water in Western Iran. The results of their study revealed that there was a significant correlation between exposure to arsenic and arsenic poisoning in inhabitants, and Mee's line was the dominant disorder in the study area. Keshavarzi et al. (2015a) reported anemia and liver damage in sheep population exposed to As via drinking water and fodder in Kurdistan Province. Karimi et al. (2019) suggested that weathering and degradation of the ultramafic rocks in the West of Iran will increase the concentration of heavy metals including Ni, Cr, Co, Pb and V in soil, and subsequently can pose environmental hazards. Sharifi et al. (2017) investigated the relationship between soil As and its accumulation in vegetables in some villages of Kurdistan Province, and reported high hazard quotients particularly for consumption of root and tuber crops. Wheat (mainly Triticale, Bahar, Saionz, Falat, Chamran, Pishtaz, Sepahan, Pishgam, and Tous varieties) and barley (Bahman, Makooei, Reyhan, Nosrat, Fajer and Kavir varieties) bread, have a large share in the diet of people in Iran (Pourreza et al. 2012; Ghezeljeh et al. 2011). The majority of the studies in this region has shown that the main source of As is geogenic, particularly igneous rocks and travertine deposits (Nasrabadi and Bidabad, 2013; Sharifi et al. 2017; Karimi et al. 2019). However, it is not entirely clear whether the source of elevated As accumulation in food crops in this region is its natural occurrence in the soils or the use of groundwater that in this region contains high levels of As (Mosaferi et al. 2008; Barati et al. 2010; Keshavarzi et al. 2011). The main objectives of this study were: a) to investigate the relationship between arsenic in rock, soil and plants, b) to determine the degree to which selected soils and crops are contaminated with naturally occurring As, and c) to assess the risk of local residents' exposure to As through consumption of local food crops.

2. Materials and Methods

2.1. Geological setting of the study area

Kurdistan Province with an area of 29,137 km^2 is located in the West of Iran between 34° 45' - 36° 28' N and 45° 34' - 48° 14' E. The local climate is characterized with an average annual precipitation and humidity of 480 mm and 47%, respectively. The average annual temperature is 6.13 °C, peaking in July (32°C) and the minimum temperature in January (-3°C). The focus of this study is on a part of the so-called Northern Sanandaj–Sirjan magmatic-metamorphic belt, east of Kurdistan Province, and includes Qorveh and Bijar counties covering 4900 km^2 and with populations of 260,961 and 93,714, respectively. The exposed geological units in this sector are mostly sedimentary rocks with andesitic, basaltic and travertine outcrops (Fig 1). Widespread travertine deposits cover the volcanic rocks and represent the waning stages of Tertiary–Quaternary volcanic activity (Boni et al. 2007). Travertine springs in the study area are related to the basic volcanoes that extend from North West to South East. The spring's pathway is probably

fractures connected to deep active hydrothermal systems. The travertine deposits are intensely fractured and contain numerous springs probably related to hydrothermal fluid circulation (Keshavarzi et al. 2011).

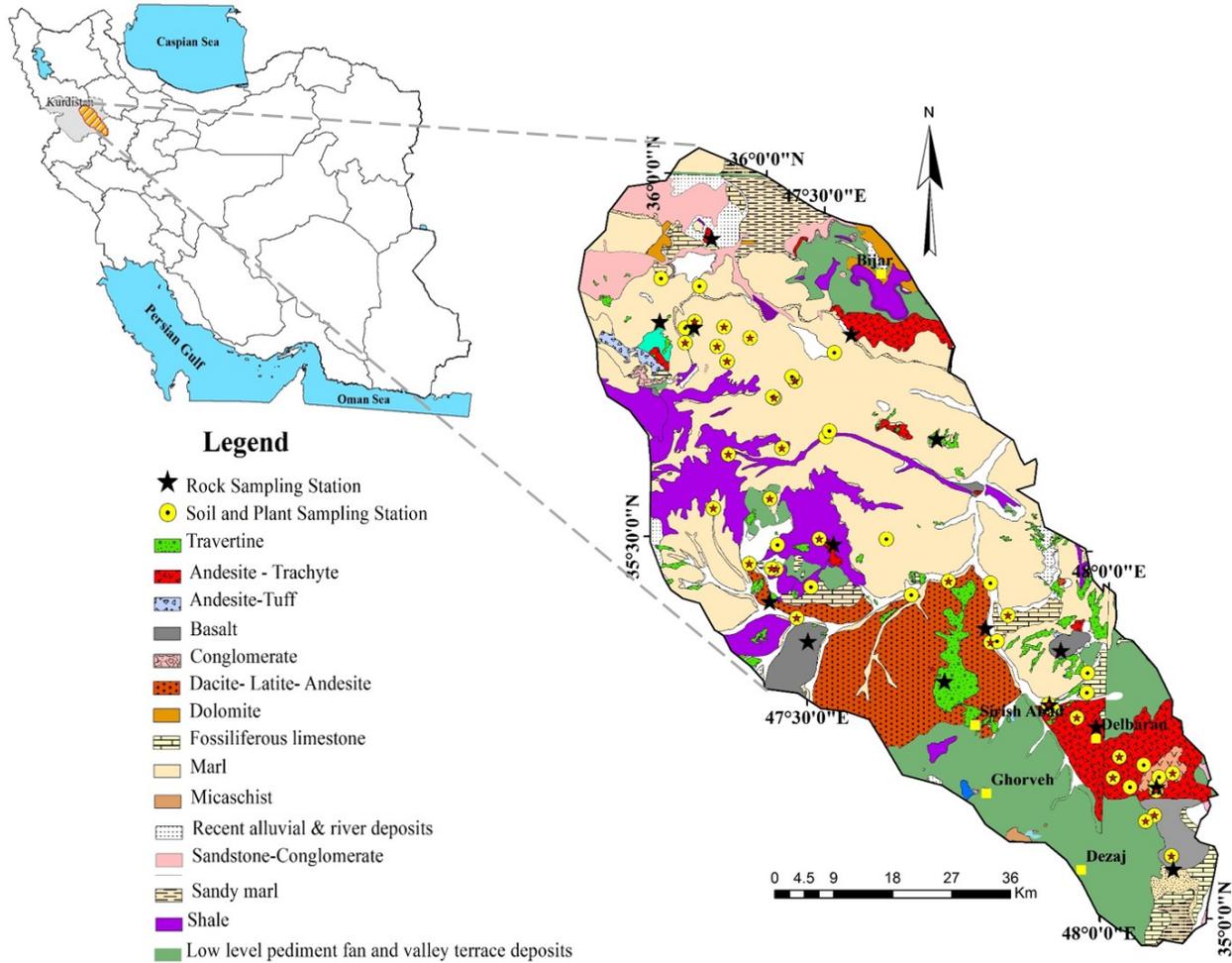


Figure 1. Geological map of the study area, showing sampling stations.

2.2. Sampling and analyses

A total of 16 rock samples (travertine, basalt and intermediate volcanic rocks), 51 crop field topsoil (0-10 cm) samples and 58 crop samples (28 samples of wheat grain, 16 samples of barley grain and 14 samples of alfalfa stem and leaves) were collected at harvest time. It should be noted that alfalfa fields are irrigated but wheat and barley are cultivated by dry farming. Small chips of rock were broken off from different outcrops in the study area. The rock sampling stations were determined in such a way that all major outcrops as well as all parts of the study area are covered. The rock chips free of veining and alteration, were collected in sealable plastic bags, labeled and transferred to the laboratory. In the laboratory the rock samples were crushed to powder using a

grinder (Tema Machinery Ltd. UK, model T 750), analyzed for arsenic and rare earth elements by Inductively Coupled- Mass Spectrometry (Perkin Elmer Sciex Elan 6100 ICP-MS System), following microwave-assisted digestion (CEM, model Mars 6) (T =180 °C) in Aqua Regia, following sample preparation and quality assurance protocols.

The soil sampling locations were chosen based on their cultivated crops and proximity to the sampled rock outcrops, including travertine, basalt, andesite and latite. To obtain representative samples from each agricultural soil sampling site, composite soil samples were taken. For this purpose, each sampled field was divided into 10 similar size portions, and 10-15 randomly selected soil samples were collected from each portion (at 0-20 cm in depth) using an auger and a plastic scoop and placed in a bucket. The samples were mixed thoroughly, quartering was achieved by splitting the thoroughly mixed sample into four equal parts, two opposite quarters were discarded, and the remaining quarters were remixed, and the process repeated until the desired sample size (1 kg) was obtained. The collected samples were kept in polyethylene bags and transported to the laboratory for preparation and analysis. The soil samples were air dried at room temperature and sieved through a 63 µm sieve for the analyses. Total As concentrations were measured using ICP-MS following microwave-assisted digestion with aqua regia. Crop samples were collected freshly from the same fields where the soil samples were collected (Sharma et al. 2020). Six sub-samples of wheat, barley and alfalfa were collected at each sampling site, and then, aggregated into one sample for further treatment (Bhattacharya et al. 2010). The samples were transported to the laboratory, cleaned with deionized water, and air dried. Crop samples were then ground in a pre-cleaned stainless steel grinder and passed through a 250 µm sieve. The finely ground crop plant/grain powder was then stored in polythene zipped bags. The powdered plant samples were digested in a microwave digester (with a mixture of hydrochloric acid, nitric acid and hydrogen peroxide, the solution was cooled by 25 mL double distilled water, filtered through No. 1 Whatman filter (Sharma et al.2020), and then analyzed by ICP-MS. All the rock, soil and plant samples analyses were performed in the Labwest Analytical Laboratories, Perth, Western Australia.

For quality assurance and quality control purposes, standard reference materials, sample replicates and method blanks were used. The successive dilution of reference standard solutions (STD OREAS45EA and STD CDV-1) was applied to prepare the calibration curve in 2% (v/v) 1N nitric acid. During the analysis, the appropriate conditions were maintained based on Kumar et al. (2020). Results showed that the recovery percentages ranged from 89-106%, relative standard deviation was less than 7% for each element, and the blanks were below the detection limit (50 µg/kg).

2.3. Data analysis

2.3.1. Pollution Index (PI)

Soil arsenic pollution was evaluated using the pollution index (PI_i), calculated as the ratio between the As concentration (C_i) in a soil sample and its reference value (S_i) (Hu et al. 2013):

$$PI_i = \frac{C_i}{S_i} \quad (1)$$

In this study, soil quality guideline of 12 mg As/kg (CCME 2007) was used as the reference value (S_i) to calculate the pollution index.

2.3.2. Index of geoaccumulation (I_{geo})

Another approach for assessing the contamination level of soil is the geoaccumulation (I_{geo}) index according to Equation 2 (Zhang et al. 2016):

$$I_{geo} = \log_2 (C_n/1.5 \times B_n) \quad (2)$$

The main difference between this index and PI is that the effect of lithology is limited by a correction factor. In Equation 2, C_n is the measured total concentration of As in the soil sample, B_n is reference value, and 1.5 is the factor compensating for background data (correction factor) related to lithogenic effects. In this study, mean As concentration in world soils (6 mg/kg) was used as reference (Adriano et al. 2001). $I_{geo} < 0$ indicates practically unpolluted, 0.01-1 is unpolluted to moderately polluted, 1.01-2 is moderately polluted, 2.01- 3 is moderately to strongly polluted, 3.01-4 is strongly polluted, 4.01-5 is strongly to extremely polluted and $I_{geo} > 5$ shows extremely polluted soil (Qing et al. 2015; Amjadian et al. 2018).

2.3.3. Biological absorption coefficient (BAC)

Biological absorption coefficient was used to examine the transfer of As from soil to plant. It was calculated as proposed by Edwards et al. (1998) as follows:

$$BAC = \frac{C_p}{C_s} \quad (3)$$

Where C_p is the arsenic concentration in the plant and C_s is its concentration in the soil.

2.3.4. Health risk assessment

The United States Environmental Protection Agency developed a model to assess human health risk. In this study, the model was used to evaluate the risks posed by As via consumption of cultivated food crops. Hazard Quotient (HQ) expressing potential non-cancer risk for As was calculated as follows (USEPA 1989):

$$HQ = \frac{CDI}{RfDo} \quad (4)$$

$$CDI = \frac{CM \times IR \times EF \times ED}{BW \times AT} \quad (5)$$

where chronic daily intake (CDI) and oral reference dose (RfDo) have the same unit ($\text{mg kg}^{-1} \text{ day}^{-1}$); CM is the average values of total As concentrations in crop plants (mg kg^{-1}); IR is the crop ingestion rate ($\text{kg person}^{-1} \text{ day}^{-1}$); exposure frequency (EF) is $350 \text{ days year}^{-1}$; exposure duration (ED) was taken 70 years for adults and 6 years for children; BW is body weight, 70 kg for adults and 20 kg for children; AT is the average exposure time ($ED \times 365 \text{ days year}^{-1}$); and the RfDo value for As is $3 \times 10^{-4} \text{ mg kg}^{-1} \text{ day}^{-1}$ (USEPA 1998). The exposed population is assumed to face no potential risk when HQ is below unity (USEPA 2000; Huang et al. 2008; Keshavarzi et al. 2015b).

In addition, in order to determine the cancer hazard, incremental life-time cancer risk (ILTCR) was calculated using the following equation (USEPA 1998; Halder et al. 2014):

$$ILTCR = \frac{C_{TAs} \times IR \times CF \times EF \times ED}{BW \times AT} \times CSF \quad (6)$$

where C_{TAs} is the upper limit of the 95% confidence interval for the mean (95% UCL) in crop plants, CF is conversion factor (0.085 mg kg^{-1}) and CSF is the cancer slope factor ($1.5 \text{ mg kg}^{-1} \text{ day}^{-1}$ and $4.5 \text{ mg kg}^{-1} \text{ day}^{-1}$ for adults and children, respectively) (Sharifi et al. 2017). The acceptable risk range for carcinogens is set as 10^{-6} to 10^{-4} by the USEPA (USEPA 2001). Additional action is required to reduce the exposure and resulting risk for ILTCR above 10^{-4} (USEPA 2008).

In this study, the chronic daily intake and hazard quotient (HQ) were calculated to evaluate the potential human health risks in the study area. Alfalfa was not considered in this evaluation as only wheat and barley grains are consumed by human in the region. However, we acknowledge that elevated As concentrations in alfalfa present indirect risk to human health via the plant-animal-human food-chain. Since bread forms a large part of the diet in Iran, per capita ingestion rate of wheat and barley in the study area were estimated as 500 and 200 g/day for adults and children, respectively (Sharifi et al. 2017).

2.3.5. Statistical analysis

Statistical analyses were carried out using SPSS 19 software package. The normality of As concentration was assessed using the Kolmogorov-Smirnov normality test ($p > 0.01$). The data were found not normally distributed, therefore, the effects of the sampling site (Qorveh and Bijar Counties) and plant species on As concentration in plant samples were evaluated by the Mann-Whitney U test which is considered as nonparametric alternative to the independent t-test. Also, As concentration in soil samples collected from fields in close proximity of the four main rock types in the study area was compared using Kruskal-Wallis H test.

3. Results and discussion

3.1. Source of arsenic in rock samples

The concentration of As and REEs in different rock samples are presented in Table 1.

Table 1. Arsenic and REEs concentrations in the analyzed rock samples (mg/kg) \pm SD.

Sample ID	Rock type	As	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Limit of detection		0.5	0.05	0.05	0.02	0.02	0.02	0.02	0.02	0.02
R1	Andesite	45.6 \pm 0.6	64.4 \pm 0.1	113 \pm 0.07	12.5 \pm 0.02	44 \pm 0.1	6.64 \pm 0.03	1.7 \pm 0.01	5.04 \pm 0.04	0.72 \pm 0.03
R2	Andesite	46.8 \pm 0.7	62.6 \pm 0.05	114 \pm 0.1	13 \pm 0.03	46 \pm 0.02	7.16 \pm 0.02	1.76 \pm 0.02	5.79 \pm 0.04	0.84 \pm 0.03
R3	Nepheline trachyte	82.7 \pm 0.5	108 \pm 0.03	176 \pm 0.2	19.1 \pm 0.02	66.6 \pm 0.04	10 \pm 0.05	2.5 \pm 0.03	7.59 \pm 0.02	1.03 \pm 0.04
R4	Andesite	57.4 \pm 0.6	67 \pm 0.06	114 \pm 0.2	12.8 \pm 0.03	44.3 \pm 0.01	6.64 \pm 0.03	1.74 \pm 0.06	5.39 \pm 0.02	0.81 \pm 0.02
R5	Andesite	49.3 \pm 0.7	40 \pm 0.1	70 \pm 0.05	8.34 \pm 0.02	29.6 \pm 0.03	4.85 \pm 0.02	1.27 \pm 0.02	3.85 \pm 0.02	0.55 \pm 0.02
R6	Andesite	44.1 \pm 0.5	65.6 \pm 0.05	115 \pm 0.1	12.5 \pm 0.04	44 \pm 0.02	6.83 \pm 0.03	1.65 \pm 0.02	5.27 \pm 0.03	0.76 \pm 0.03
R7	Trachyte	4.9 \pm 0.5	49.5 \pm 0.05	89.1 \pm 0.1	10.2 \pm 0.04	36.9 \pm 0.02	6.19 \pm 0.03	1.62 \pm 0.02	5.19 \pm 0.03	0.78 \pm 0.04
R8	Latite	5140 \pm 2	60 \pm 0.05	120 \pm 0.2	15.7 \pm 0.1	63.9 \pm 0.05	10.8 \pm 0.04	2.46 \pm 0.04	7.48 \pm 0.02	0.93 \pm 0.03
R9	Nepheline latite	62.3 \pm 0.7	37.3 \pm 0.02	62.4 \pm 0.06	7.4 \pm 0.03	26 \pm 0.03	4.14 \pm 0.02	1.13 \pm 0.03	3.21 \pm 0.02	0.44 \pm 0.02
R10	Basalt	6.5 \pm 0.5	103 \pm 0.5	181 \pm 0.1	20.3 \pm 0.01	75.1 \pm 0.05	10.8 \pm 0.03	2.98 \pm 0.03	8.39 \pm 0.05	1.1 \pm 0.05
R11	Basalt	8.1 \pm 0.5	134 \pm 0.3	249 \pm 0.1	28.7 \pm 0.1	110 \pm 0.01	15.3 \pm 0.04	4.03 \pm 0.05	10.6 \pm 0.03	1.22 \pm 0.03
R12	Travertine	>10000	1.38 \pm 0.01	2.6 \pm 0.05	0.29 \pm 0.02	1.13 \pm 0.02	0.02 \pm 0.001	0.06 \pm 0.01	0.21 \pm 0.02	0.03 \pm 0.001
R13	Travertine	562 \pm 1	0.09 \pm 0.01	0.65 \pm 0.05	0.04 \pm 0.01	0.06 \pm 0.01	0.2 \pm 0.01	0.02 \pm 0.001	0.05 \pm 0.001	0.02 \pm 0.001
R14	Travertine	>10000	1.22 \pm 0.02	2.05 \pm 0.06	0.26 \pm 0.01	1.02 \pm 0.02	0.1 \pm 0.001	0.04 \pm 0.001	0.1 \pm 0.001	0.02 \pm 0.001
R15	Travertine	>10000	0.84 \pm 0.02	1.28 \pm 0.05	0.16 \pm 0.01	0.61 \pm 0.02	0.17 \pm 0.001	0.02 \pm 0.001	0.06 \pm 0.001	0.02 \pm 0.001
R16	Travertine	>10000	1.13 \pm 0.01	1.89 \pm 0.07	0.25 \pm 0.01	0.94 \pm 0.02	0.2 \pm 0.001	0.02 \pm 0.001	0.1 \pm 0.001	0.02 \pm 0.001
Sample ID	Rock type	Dy	Ho	Er	Tm	Yb	Lu	Σ REE	(La/Lu) _N	(Eu)/(Eu*)
Limit of detection		0.02	0.02	0.02	0.02	0.02	0.02	-	-	-
R1	Andesite	3.43 \pm 0.02	0.65 \pm 0.02	1.67 \pm 0.04	0.28 \pm 0.02	1.54 \pm 0.05	0.38 \pm 0.02	255.95	16.9	0.9
R2	Andesite	4.25 \pm 0.04	0.81 \pm 0.02	2.11 \pm 0.06	0.36 \pm 0.02	2.03 \pm 0.05	0.36 \pm 0.02	261.07	17.4	0.84
R3	Nepheline trachyte	4.74 \pm 0.05	0.85 \pm 0.03	2.24 \pm 0.04	0.38 \pm 0.02	2.23 \pm 0.04	0.36 \pm 0.03	401.62	30	0.88
R4	Andesite	3.94 \pm 0.04	0.79 \pm 0.03	2.03 \pm 0.04	0.32 \pm 0.03	1.83 \pm 0.02	0.29 \pm 0.03	261.88	23.1	0.89
R5	Andesite	2.91 \pm 0.03	0.55 \pm 0.03	1.49 \pm 0.02	0.27 \pm 0.03	1.48 \pm 0.02	0.25 \pm 0.02	166.81	16.24	0.9
R6	Andesite	3.71 \pm 0.03	0.74 \pm 0.02	1.94 \pm 0.02	0.32 \pm 0.02	1.83 \pm 0.02	0.29 \pm 0.03	260.44	22.6	0.84
R7	Trachyte	3.93 \pm 0.02	0.79 \pm 0.02	2 \pm 0.03	0.33 \pm 0.03	1.94 \pm 0.03	0.31 \pm 0.03	208.78	15.7	0.88
R8	Latite	4.26 \pm 0.04	0.74 \pm 0.02	1.77 \pm 0.02	0.29 \pm 0.02	1.48 \pm 0.02	0.24 \pm 0.02	290.05	25	0.84
R9	Nepheline latite	2.04 \pm 0.04	0.38 \pm 0.02	0.92 \pm 0.03	0.14 \pm 0.002	0.76 \pm 0.02	0.11 \pm 0.002	146.37	33.9	0.95
R10	Basalt	5.06 \pm 0.02	0.92 \pm 0.03	2.21 \pm 0.03	0.33 \pm 0.002	1.83 \pm 0.02	0.26 \pm 0.001	413.28	39.6	0.96
R11	Basalt	5.07 \pm 0.03	0.86 \pm 0.02	2.05 \pm 0.02	0.3 \pm 0.002	1.5 \pm 0.03	0.22 \pm 0.001	562.85	60.9	0.97
R12	Travertine	0.16 \pm 0.02	0.04 \pm 0.001	0.11 \pm 0.02	0.04 \pm 0.001	0.09 \pm 0.003	0.02 \pm 0.001	6.31	6.9	0.91
R13	Travertine	0.02 \pm 0.001	0.02 \pm 0.001	0.04 \pm 0.001	0.04 \pm 0.001	0.04 \pm 0.001	0.02 \pm 0.001	0.26	0.45	1.95
R14	Travertine	0.12 \pm 0.02	0.03 \pm 0.001	0.11 \pm 0.02	0.04 \pm 0.001	0.08 \pm 0.001	0.03 \pm 0.001	5.26	4.06	0.88
R15	Travertine	0.06 \pm 0.001	0.02 \pm 0.001	0.04 \pm 0.001	0.04 \pm 0.001	0.04 \pm 0.001	0.02 \pm 0.001	3.15	4.2	0.8
R16	Travertine	0.1 \pm 0.001	0.03 \pm 0.001	0.08 \pm 0.001	0.04 \pm 0.001	0.07 \pm 0.001	0.02 \pm 0.001	4.8	5.6	0.47

The highest As concentration was measured in travertine samples, probably due to the presence of Aragonite in their mineralogy. This mineral is a calcium carbonate polymorph, and arsenic can

reside in Ca layers perpendicular to the C axis. Substitution of calcium by arsenic generally occurs only in aragonite crystal structure (Pentecost 2005). Travertines rich in As (and also Sb) are commonly known as hydrothermal travertines (Bernasconi et al. 1980). The mean As concentrations of the intermediate rocks, basic rocks, and travertines were 614, 7.3 and 7994 mg/kg, respectively, indicating the greater role of felsic rocks in hydrothermal formation of travertines in the study area. The highest As concentration (5140 mg/kg) of the volcanic rock samples was observed in a latite, sampled around Babagorgor Spring (Table 1).

Geochemistry of REEs is a powerful tool for assessing magmatic processes, partial melting or magma mixing and crystal fractionation (Jones et al. 1995). The results of this study showed relatively high Σ REEs concentration (146-401 mg/kg), REEs' dissociation coefficient [(La/Lu)_N] of 15.7-33.9, and positive anomaly of Eu (0.84-0.95) for volcanic rocks, except basalt samples, indicating intermediate to felsic rock composition (Henderson 2013). The Eu anomaly in felsic-intermediate magmas is controlled by feldspars. Contrary to other rare earth elements (with trivalent oxidation state), Eu could also have a divalent oxidation state and commonly enters the plagioclase and K-feldspar structures as a compatible element. Therefore, the occurrence of primary feldspars, or their formation in the late stages of differentiation have resulted in a positive anomaly of Eu in volcanic rocks of the area, a feature characteristic of continental margins and their related magmatism (Henderson 2013). The mean Σ REEs concentration, REEs' dissociation coefficient and Eu anomaly in basic volcanic rock samples were 488.06 mg/kg 50.2, and 0.96, respectively (Table 1). Based on Henderson (1989), Σ REEs and Eu anomaly of basic rocks range from 25-150 mg/kg and 0.01-0.05, respectively. The higher values observed in basic rocks of this study may reflect the mixing of these rocks with felsic magma. This magma may have lost its As due to rapid oxidation.

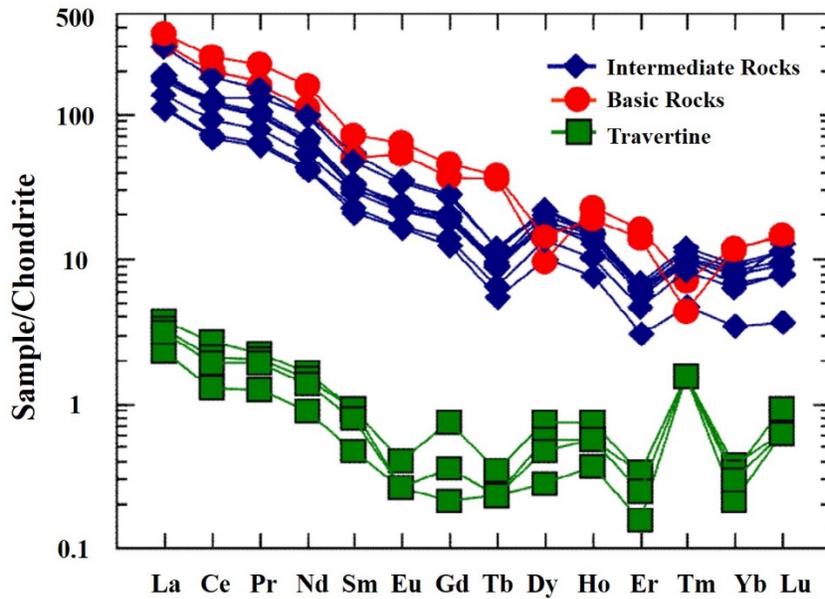


Figure 2. REEs pattern in the volcanic rocks of the study area, normalized by composite chondrite (Wakita et al. 1971).

Hydrothermal travertines in the study area showed a relatively similar REEs pattern with the intermediate volcanoes (Fig 2). However, Σ REEs concentrations in travertines in this study, with an average of 3.9 mg/kg are significantly ($p < 0.05$) lower than those for volcanic rock samples, while Eu anomaly increases and the ratio of dissociation degree (average = 4.2) decreases significantly. Lower Σ REEs concentrations in travertines is related to the post-depositional mobilization of these elements. Figure 2 shows that heavy rare earth elements (HREEs) including Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu were more depleted during travertine deposition. REEs differentiation in carbonate rocks depends highly on physicochemical conditions of the initial environment, diagenesis and metamorphism, composition of secondary hydrothermal fluids, and mineralogy (Bao et al. 2004). During rock-fluids inter-reactions, light rare earth elements (LREEs) including La, Ce, Pr, Nd and Sm will be leached more readily. This is a specific feature of carbonate rocks coming into contact with hydrothermal fluids (Lottermoser 1992). On the other hand, differences in the ionic radius of Mg^{2+} , Ca^{2+} , Fe^{2+} and $REEs^{3+}$ may also be responsible for the exclusion of LREEs from calcite and dolomite crystallographic structures (Fernández-Nieto et al. 2003).

3.2. Soil and plants pollution

Total soil As concentrations are presented in Table 2 with concentrations ranging from 7.7 to 429.5 mg/kg. Mean concentration of As in the study area soils (66.76 mg/kg) was much higher than the maximum acceptable limit for agricultural soil recommended by the European Community (20 mg/kg) (Rahman et al. 2007). Also, there is a large difference between soil mean As concentration in Qorveh and Bijar being 48.5 and 106.6 mg/kg, respectively (Table 2). This difference probably reflects different geogenic and hydrothermal processes, since in this belt, magmatic differentiation and ratio of acidic/intermediate rocks increases from Qorveh towards Bijar. In many parts of the world, release of geogenic As is associated with Tertiary volcanic activity and the resulting formation of volcanic ashes, hydrothermal springs and other related geothermal features (Bundschuh et al. 2007).

Table 2. Summary statistics of arsenic concentration (\pm SD) in soils and crops.

Arsenic	Soil (mg/kg)			Wheat (μ g/kg)	Barley (μ g/kg)	Alfalfa (μ g/kg)
	Whole area	Qorveh	Bijar			
Limit of detection		0.5			50	
Mean	66.73 \pm 0.6	48.5 \pm 0.5	106.62 \pm 0.8	107.95 \pm 0.6	348.67 \pm 1	3911.81 \pm 2
Median	45 \pm 0.6	38 \pm 0.5	60.2 \pm 0.5	62 \pm 0.5	176 \pm 1	1281 \pm 1
Std. Deviation	81.58	37.55	128.49	94.21	418.47	6437.16
Skewness	3.01	1.79	1.7	1.72	2.21	3.12
Min	7.7 \pm 0.15	7.7 \pm 0.15	11 \pm 0.2	<50	<50	71
Max	429.5 \pm 0.9	187.2 \pm 0.5	429.5 \pm 0.9	429 \pm 0.9	1633 \pm 3	25079 \pm 2
Maximum acceptable concentration		20 ^a			1000 ^b	

^a Rahman et al. (2007), ^b Australian National Food Authority (1993)

In order to investigate the relationship between the major rock outcrops of the study area and adjacent soils, mean As concentrations in the four rock types (basalt, andesite, latite and travertine) and 18 surrounded fields where the rock and soil samples are in close proximity were considered (Fig 3). As shown in the diagram, the soil samples adjacent to travertine outcrops have the highest As concentration, which corresponds to the high concentration of this element in travertine compared to other rock types. Also, the results of Kruskal-Wallis H test (Table 3) showed a significant difference ($p < 0.05$) in As concentration of soils around travertine outcrops (with highest mean rank) and other rock types. On the other hand, lower soil As concentration around Dashakasan Gold Mine (maximum of 187 mg/kg) in Southeast of the study area, relative to areas with no gold mineralization (such as Aliabad with 429.5 mg As/kg) in North of the study area reveals that in comparison with gold mineralization and mining activities, hydrothermal processes play a more important role in soil arsenic enrichment. As discussed earlier, hydrothermal travertines are rich in arsenic, and its weathering could in turn produce As-rich soils. It should be noted that most of the agricultural fields in the area are associated with travertine outcrops. In Qorveh-Bijar region, deep groundwater circulation is responsible for high As pollution of water resources, and As concentrations ranging from 0.4 to 688.9, and 212 to 842.3 $\mu\text{g/L}$ were reported in groundwater and travertine springs, respectively. These high concentrations coincide to areas with the highest arsenic concentrations in the soil samples (Keshavarzi et al. 2011). Therefore, using groundwater and travertine springs for irrigation purposes particularly for vegetable crops (Sharifi et al. 2017) and alfalfa (one field in this study) will subsequently cause further arsenic enrichment in agricultural soils, and the use of such waters for irrigation could be considered as an important As source in croplands.

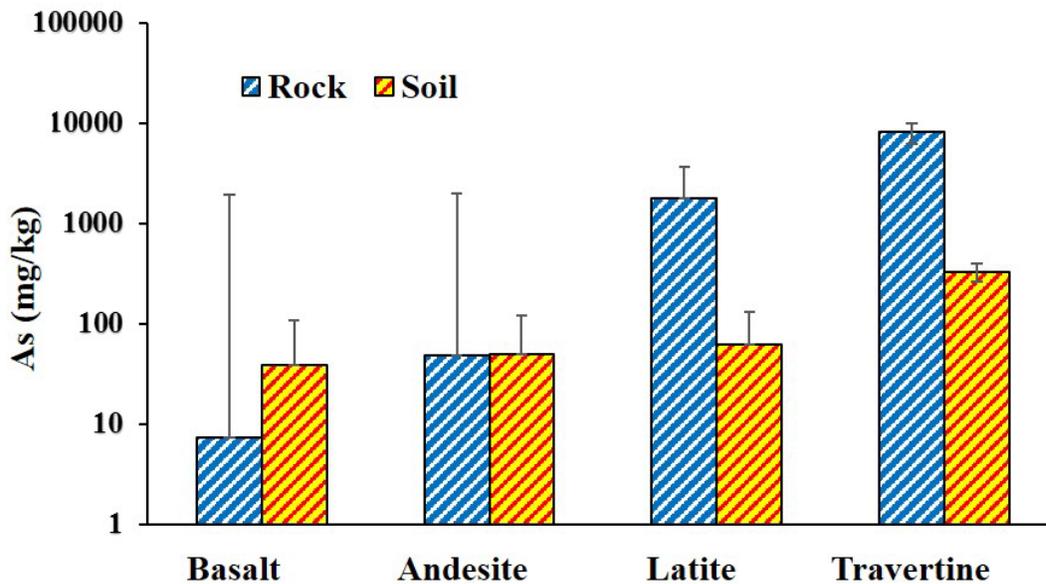


Figure 3. Comparison of mean As concentration (\pm standard error) in the soil and rock study samples.

Pollution index (PI) and index of geoaccumulation (I_{geo}) are two useful means of evaluating the degree of soil pollution (Fig 4). Results showed that calculated PI ranges from 0.64 to 35.79 with

the highest values occurring in Aliabad village soil in Bijar County. According to pollution index classification (Yang et al. 2011), 50% and 34% of the soil samples must be categorized as highly polluted (PI>5) in Bijar and Qorveh, respectively. Also, minimum, maximum and mean value of I_{geo} in this study are -1.22 (two samples in Qorveh), 4.57 (Aliabad village in Bijar) and 1.24, respectively. Only 17.64% of the soil samples were classified as unpolluted, and the highest proportion (i.e. 35.30% of the samples) was classified as “moderately polluted”. Moreover, 25.49%, 13.72%, 1.97% and 5.88% of the soil samples were categorized as unpolluted to moderately polluted, moderately to strongly polluted, strongly polluted, and strongly to extremely polluted, respectively (Fig 4).

Table 3. Kruskal-Wallis H test for As in soils around different rock types.

Group	Basalt	Andesite	Latite	Travertine	Chi-Square	df	Asymp. Sig.
Mean Rank	7.67	7.6	13.5	19	10.31	3	0.016

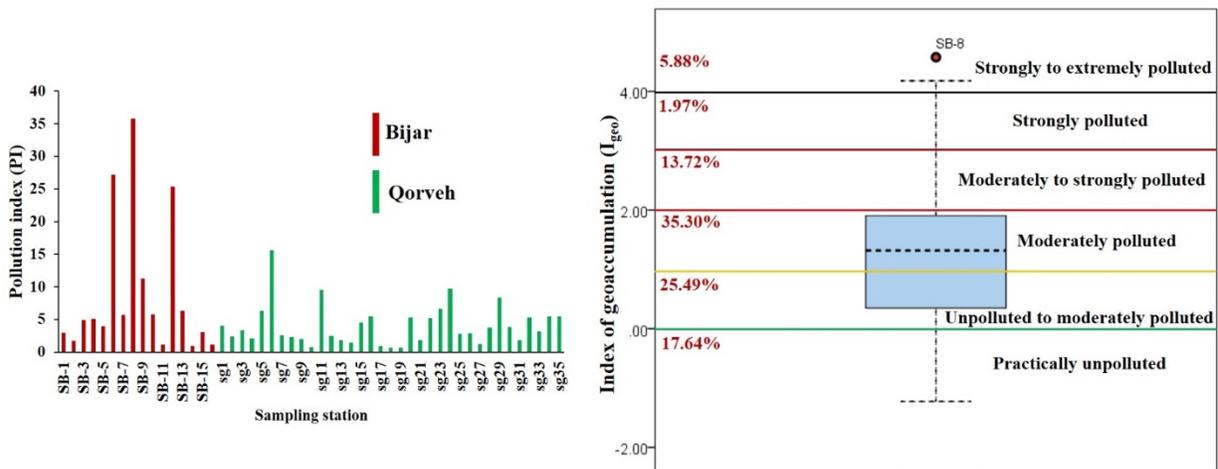


Figure 4. PI bar graph and I_{geo} boxplot for arsenic in soil samples.

Arsenic concentrations in wheat, barley and alfalfa ranged from <50 to 429 $\mu\text{g}/\text{kg}$ dw (mean; 107.95 $\mu\text{g}/\text{kg}$ dw), <50 to 1633 $\mu\text{g}/\text{kg}$ dw (mean; 348.67 $\mu\text{g}/\text{kg}$ dw), and 71 to 25079 $\mu\text{g}/\text{kg}$ dw (mean; 3911.81 $\mu\text{g}/\text{kg}$ dw), respectively. The highest concentrations in the three analyzed crop plants were found in Gilaklou, Ebrahimabad and Babagorgor villages, for wheat, barley and alfalfa, respectively. The farm from which alfalfa samples were collected at Babagorgor village is the only arable land directly irrigated with travertine spring in which, 80% of the arsenic was available in trivalent state (Keshavarzi 2011), resulting in high As content in alfalfa. Compared

with maximum permissible concentration (MPC) for foodstuffs, average As content in the plant samples were higher with concentrations above MPC being measured in one barley and 11 alfalfa samples. Mann-Whitney U test was used to examine the statistical significance of the differences in As content among three sampled crop species, and the two counties (Table 4). The results revealed significant differences between As concentration in different plant species ($p < 0.001$ to 0.021), reflecting the following trend for As concentration: alfalfa stem and leaves > barley grains > wheat grains. Irrigation of alfalfa fields by As contaminated groundwater may be an important factor, elevating concentrations of arsenic in alfalfa compared to rainfed wheat and barley. However, no significant difference was found between Bijar and Qorveh Counties in regard to As in plants ($p = 0.100$).

Table 4. Mann–Whitney U test for As between the plant species, and studied counties.

	Wheat-Barley	Wheat-Alfalfa	Barley-Alfalfa	Bijar-Qorveh
Mann-Whitney U	123	14	26	272
Wilcoxon W	529	420	162	1052
Z	-2.514	-4.913	-3.577	-1.646
Asymp. Sig. (2-tailed)	0.012	0.000	0.000	0.100

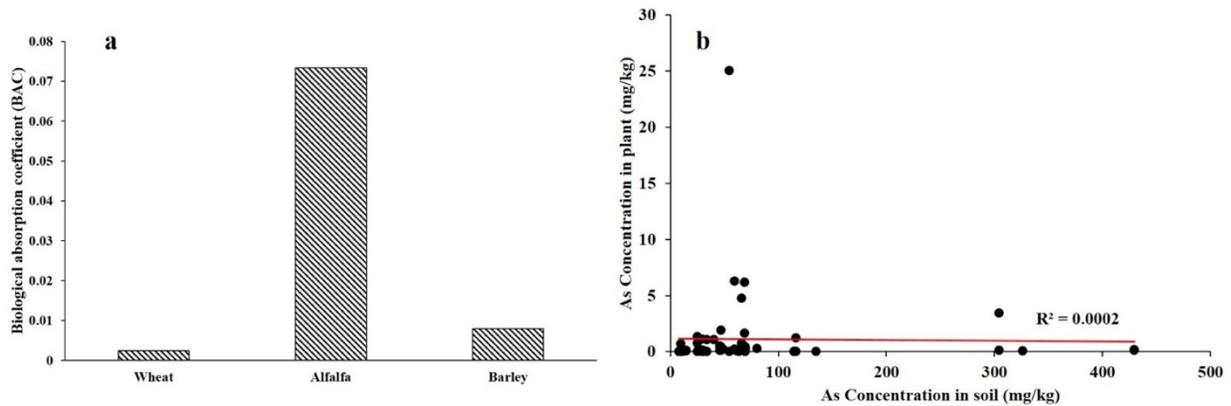


Figure 5. (a) Mean Biological absorption coefficient and (b) relationship between As contents of the study soil and crop plants.

Biological absorption coefficient (BAC) was calculated to examine the transfer of As from soil to plant (Fig 5a). The BAC values differed across the three crop plants, indicating the importance of plant species on arsenic accumulation in the crop’s edible parts. Alfalfa showed the highest BAC among the studied plants, which is in accordance with other reported data that leafy plants/vegetables accumulate higher arsenic than cereal grains (Alam et al. 2003; Samal 2005;

Sharifi et al. 2017). As mentioned earlier, irrigation of alfalfa fields by groundwater is a likely contributor to greater uptake of As by this crop. The relationship between soil and crop plants (Fig 5b) indicates that there is no significant correlation between the concentration of As in soil and crops. This is hardly surprising as total soil arsenic concentration is not the sole factor controlling its bioavailability. As reported in other works, soil properties including soil organic matter (SOM), sulphate (SO₄²⁻), soil texture, phosphate (PO₄³⁻), silica, nitrate (NO₃⁻), As speciation etc., may also affect arsenic bioavailability for plants (Huang et al. 2006; Zhao et al. 2009; Keshavarzi et al. 2015b; Yu et al. 2016; Sharma et al. 2020).

3.3. Health risk assessment

Table 5. The calculated values of CDI, HQ and ILTCR for wheat and barley.

County	Species	CDI		HQ		ILTCR	
		Adults	Children	Adults	Children	Adults	Children
Qorveh	Wheat	7.05E-04	2.47E-03	2.35	8.23	1.30E-04	1.37E-03
	Barley	7.53E-04	2.64E-03	2.51	8.79	1.61E-04	1.69E-03
Bijar	Wheat	9.25E-04	3.24E-03	3.08	10.79	1.69E-04	1.77E-03
	Barley	1.42E-03	4.96E-03	4.72	16.53	4.58E-04	4.80E-03

The results of chronic daily intake (CDI), hazard quotient (HQ) and incremental lifetime cancer risk (ILTCR) are summarized in Table 5, showing relatively high CDI values for both children and adults particularly in Bijar. Compared with tolerable intake level of 3 µg As/kg body weight per day (WHO 2011), As in Bijar County displayed higher CDI values. On the other hand, the HQ exceeds unity for both adults and children, indicating that potential non-cancer effects from the cereal consumption should be considered a concern, particularly for barley. Also, due to their smaller bodyweight and consequently higher values of the indices, children are at higher risk in comparison with adults. Moreover, the calculated ILTCR values were 1.3×10^{-4} to 4.58×10^{-4} , and 1.37×10^{-3} to 4.80×10^{-3} for adults and children, respectively. The higher ILTCR values for children suggest that they are at greater risk of cancer than adults. Due to higher As concentration, barley grain displayed a higher cancer risk compared with wheat grains, and consumption of crops cultivated in Bijar may pose greater cancer risk. The total carcinogenic risk of As was significantly higher than the acceptable limit (10^{-4}) for both adults and children in the study area, so action should be taken to reduce the exposure and cancer risk. The health risk of As from ingestion route (food crops and water) has also been examined in several other studies (Huang et al. 2008; Sharifi et al. 2017; Wen et al. 2019; Kaur et al. 2019). It should be noted that while alfalfa was not considered in human health risk assessment, it could affect both livestock (directly) and human (indirectly) because of its high As content in the study area. Injury to hepatocytes, other liver damages and anemia in sheep are already reported in the study area by Keshavarzi et al. (2015a).

4. Conclusion

The investigation of arsenic distribution in rocks, soils and three crops in affected Qorveh and Bijar counties, as part of Sanandaj-Sirjan magmatic-metamorphic belt demonstrated geogenic origin of arsenic in the area. In view of REEs behavior in rocks and their relationship with As revealed the role of intermediate volcanic rocks especially travertine in increasing As content in the region. Weathering of these high As-bearing rocks, resulted from waning stages of Tertiary–Quaternary volcanic activity, at least partly contributed to As in agricultural soils. This together with irrigating arable lands with groundwater and travertine springs enriched in As seems to have caused severe contamination of the agricultural soils. Therefore, high arsenic content of crop samples in this area seems to have resulted from arsenic mobility and its transfer from rock-soil to plants which may pose high non-cancer and cancer risks for the inhabitants of this region. In recent years, alternative drinking water resources with low As content were supplied to mitigate the potential negative health effects in the population centers of Kurdistan Province, but as the results of this study show, ingestion of cultivated crops in this area also poses a high health risk for consumers. Furthermore, livestock in this area ingest As contaminated forage, along with polluted water, which provide an important indirect pathway for human exposure to arsenic. Reducing the negative health effects of arsenic to near zero, requires an efficient management programme in which all possible exposure pathways are taken into account.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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