



Zoning of Boron contamination under influence of hot spring in the northwest of Lake Urmia, Iran

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Article Info	Abstract
<p>Article type: Research Article</p> <p>Article history: Received: <i>August 2022</i> Accepted: <i>December 2022</i></p> <p>Corresponding author: b.hessari@urmia.ac.ir</p> <p>Keywords: Boron Groundwater Water quality Geostatistical approach Lake Urmia</p>	<p>Groundwater is one of the main sources of drinking and agricultural water in the Salmas Plain in northwest of the Lake Urmia basin. Recently, boron contamination was reported in the down-plain. Boron (B) is an essential micronutrient for human health and plant growth, however high concentration (more than 1.5 mg/l) of boron is very detrimental to agriculture and human health. The present study examined the major water bodies which possibly contribute to boron contamination by identifying the origin of boron contents in the study area. A total of 42 groundwater and surface water samples were collected. The spatial distribution of boron contents showed that contamination occurred mainly in the south where thermal and mineral springs are dominant. An anomalous concentration of boron (more than 400 mg/l) was found at Abgarm thermal springs which discharge directly into the surface waters. The contamination spread over the central and east areas. This is because contamination moves through the faults. The high concentration of boron in this region may be attributed to the rock-water interaction.</p>

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Introduction

Boron (B) is an essential micronutrient for human health and plants growths (Gupta et al., 1985; Yau and Ryan, 2008). Boron and its compounds have many uses including ceramics, glasses, medicine, cosmetics, insulation and textiles fibers, flame retardants, detergents and soaps, agricultural fertilizers and pesticides (Paliewicz et al., 2015). The world's leading producers of boron minerals are Turkey (approximately 61% of the world's boron reserves) and the US and to a

lesser extent Argentina, Bolivia, Chile, China, and Peru (Crangle, 2016).

Boron is rarely found in natural waters in concentrations greater than 1 mg/l, but even this low concentration can have deleterious effects on certain crops and at high concentrations, boron can be detrimental to sustainable agriculture (Bañuelos et al., 1993; Cakmak, Kurz and Marschner, 1995; Ballance, 1996; Nable, Bañuelos and Paull, 1997). According to World Health Organization the limit value for boron in drinking water is 0.5 mg/l

(WHO, 2009) and a value of 1 mg/l is given by EU drinking water directive (Council of the European Union, 2015) and a health reference level of 1.4 mg/l is given by the USEPA (USEPA, 2008). Short-term and long-term effects of exposure to boron on human health and animals have been reported (Coughlin, 1998; Institute of Medicine (IOM), 2001; USEPA, 2008; WHO, 2009). Boron is released naturally into the atmosphere from seawater, volcanoes, and geothermal ducts (Sprague, 1972). Natural boron in groundwaters is found in areas where the water comes in contact with igneous rocks (Kadam et al., 2020) or as a result of seawater intrusion in coastal areas. Major sources of anthropogenic boron are industrial waste, municipal effluents as well as irrigation with wastewater (Ballance, 1996; Paliewicz et al., 2015).

Boron concentration in groundwater across the world range widely from below 0.3 to over 100 mg/l (WHO, 2009). Schofield (1960) examined groundwater analyses to find out the origin of boron contents of Waikato groundwaters and thermal springs of New Zealand. Schofield found that only warm groundwaters are significantly enriched in boron (21.5-112.0 mg/l) and the heat acquired from the magma is probably the dominant factor in mobilizing boron.

Arnórsson and Andresdottir (1995) analyzed samples from wells, springs and rivers in Iceland. The high concentration of boron was found in geothermal waters. Similarly, 27 Icelandic geothermal fluids from both high- and low-temperature systems were measured by Aggarwal et al. (2000). Samples from representative wells discharging water in southwestern Germany and northern Switzerland were collected during 1984-1986 and 1995 and the result showed that natural temporal variations in the total boron contents of thermal and mineral waters are a common feature (Barth, 2000). The concentration of boron was determined in surface freshwaters (lake and river) of northern Italy by Tartari and Camusso (1988). They reported that boron concentrations were under detection limits (0.06 mg/l) in bulk deposition, and below

0.09 mg/l in lake waters. In southeast Spain, the maximum boron concentration was 8 mg/l, while at some points within the coastal zone boron content was 1.5 mg/L (Sanchez Martos, Bosch and Calaforra, 1999; Sanchez-Martos and Pulido-Bosch, 1999). Molina et al. (2003) reported that boron content of water varies between 0.15 mg/l and 13.8 mg/l with a mean concentration of 1.93 mg/l in southeastern Spain. Boron contamination of Mediterranean groundwater resources was comprehensively examined by the BOREMED project (Kloppmann et al., 2005). About 23% of the samples recorded boron concentrations above 0.5 mg/l and 14% above 1 mg/l. The highest values of boron contaminations were observed in Italy, northern Greece, central region of Cyprus, as well as east of the Gaza strip. There are many geothermal fields and thermal springs in western Turkey, and groundwaters in this region are generally rich in boron (Gemici and Tarcan, 2002a&b; Omwene et al., 2019, Mott et al., 2022). Ozgur (2001) analyzed the boron contents of 77 samples of groundwaters, thermal waters, rain water, and river waters of western Anatolia in southwestern Turkey. The maximum concentration of boron in river water, where the wastewater of Kızıldere geothermal power plant flows into the river, was 32 mg/l. What is generally evident in Europe is that concentrations of boron were greatest in southern part, particularly in Spain and Italy, and least in northern part (WHO, 2009).

In the US, concentrations of boron vary in different regions. For example, in northwestern Indiana it was reported between 0.03 and 24.4 mg/l (Buszka et al., 2007), while well water samples of Staten Island in New York have boron concentration ranging from 0.01 to 2.58 mg/l (Hogan and Blum, 2003). Ravenscroft and McArthur (2004) compared the mechanism of regional enrichment of groundwater by boron in Bangladesh, where concentration of boron reach 2.1 mg/l, and Michigan in the US, where concentrations reach 6.1 mg/l. It was also reported that the high values of

concentrations are widespread in the northeast of the US (Ravenscroft and McArthur, 2004) and in southeastern Pennsylvania (up to 5.24 mg/l) (Senior and Sloto, 2006). According to the USEPA analyses on both groundwater sources and surface water sources in the US, boron contamination occurs less frequently and at lower concentrations in surface water (highest value was 0.345 mg/l) than in ground water (highest value was 3.3 mg/l) (USEPA, 2008).

Unusual high concentrations of boron have been reported in different regions. Furst (1981) reported a large amount of boron (500-700 mg/l) in marine siliceous sponge spicules from temperate, high-productivity regions which is also confirmed by other researchers (e.g. de Leon et al. (2009)). In western Turkey near a borate mine, 391 mg/l boron concentration was measured by Gemici et al. (2008). Anomalous concentrations of boron (243 mg/l) was found in gold mine tailings, Canada (Paliewicz et al., 2015). The potentially lethal boron (861 mg/l) was observed in northern Chile, where hydrothermal springs discharge at the headwaters of Colpitas River (Ramila et al., 2015).

Iran's most known boron mines are located in the northwestern of the country, particularly in Zanjan Province, with estimated production of 1,000 tons in 2014 (Crangle, 2016; USGS, 2016). Qara Goul mine is the only active borax mine in Iran. However, taking into account the conditions favorable for the formation of economic boron bodies, one can expect discovery of more such deposits in various parts of the country (Qorbani and Kani, 2005). Despite the proven and possible boron reserves and thermal springs scattered across the country (SUNA, 1998), lack of comprehensive study on concentrations of boron in the country is evident. Recently, high concentration of boron were reported in groundwaters of southeastern regions of Iran (Hosseinfard and Aminiyan, 2015; Shakeri, Ghoreyshinia and Mehrabi, 2015). In recent years, boron

concentration of groundwater resources in northwestern Lake Urmia basin exceeded the limit value of national standard (ISIRI, 2010) as well as WHO drinking water standard (> 0.5 mg/l). Considering the role of region's groundwater resources in domestic and agricultural water supply, there is a need to identify boron concentration and its origin of high concentrations in this region.

Geostatistical approaches have been applied successfully in studies of groundwater contamination to identify the origin of contamination (Cooper and Istok, 1988; D'Agostino et al., 1998; Zhu, Charlet and Poffijn, 2001; Sarangi et al., 2005; Lado et al., 2008; Chung et al., 2016). The use of spatial interpolation enables the delineation of patterns and distribution of pollution across the study region. The objective of this study is to identify the origin of boron contamination in groundwater resources of the down-plain at the Agh Ziarat village.

Material and methods

Study area

Geography and climate

The Salmas plain lies in the northwest of Lake Urmia (Figure 1a&b). The lake, with salinity ranging from 217 to more than 300 g/l, has shrunk during the past few years (AghaKouchak et al., 2015). Rivers in the plain run eastward into the lake from the mountains farther west. The valley is hemmed in by the surrounding mountains; the meeting point of the two mountain ranges: the Alborz Mountains, which is stretching from northeast to northwest, and the Zagros Mountains, which begin at the bottom of the Persian Gulf, form the boundary to the Iranian plateau, and ending in northwestern Iran.

The study region extends between 38°-38°12' N, and 44°5'-45° E, and the elevation ranges from 1,135 to 2,500 masl (Figure. 1c). The climate is characterized as semi-arid based on de Martonne aridity index ($15 \leq I \leq 24$) (de Martonne, 1926), and classified as 'Dsa', a cold snow climate with dry summers and wet winters,

according to Köppen-Geiger climate classification (Rubel and Kottek, 2010). Mean annual temperature is 9.5°C (in

February $\leq -3.5^{\circ}\text{C}$ and in July $\approx 22.5^{\circ}\text{C}$) and average annual precipitation is 297 mm.

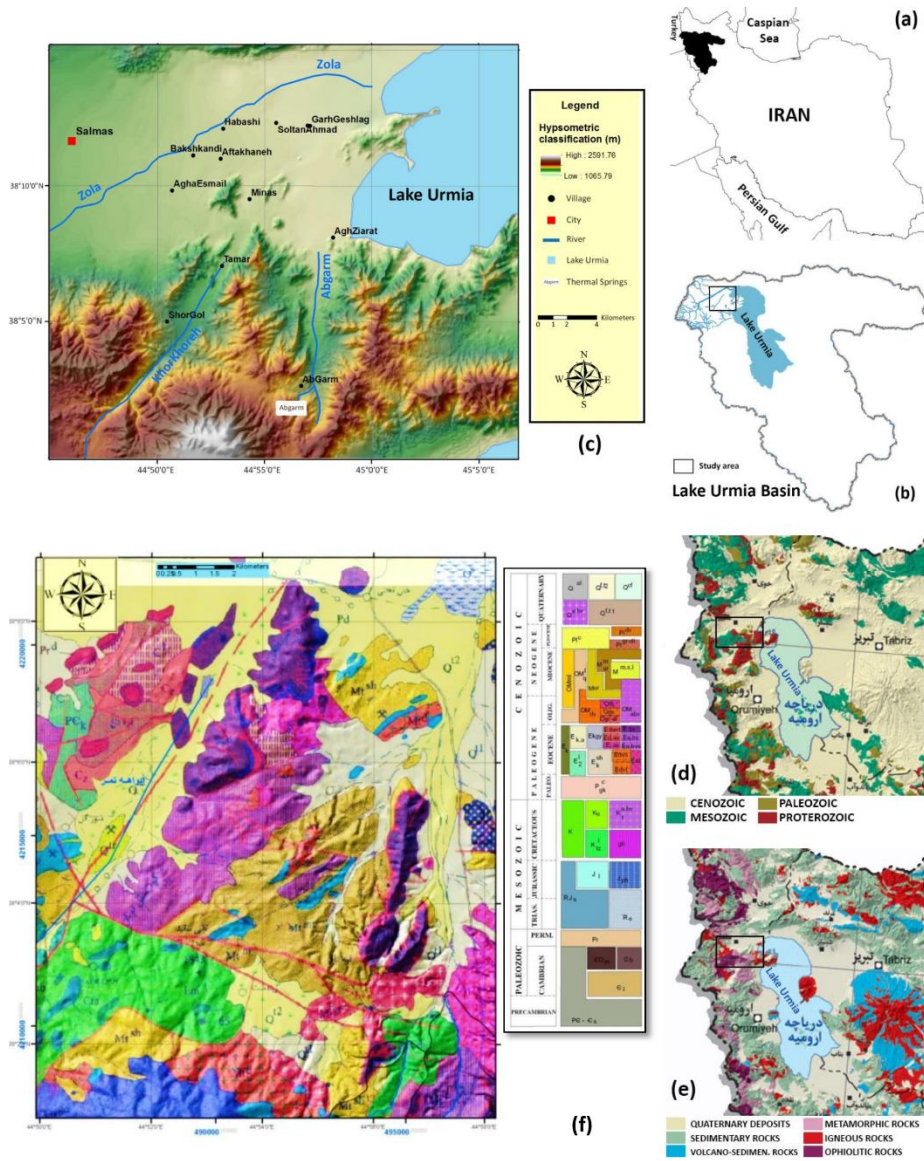


Figure 1. Study Area: a&b. location of study area; c. topography map; d, e&f. geology map adopted from (GSI, 2013).

Geology

There is no general agreement on the structural divisions of northwestern Iran-Azerbaijan. Using mostly the National Iranian Oil Company database, Stöcklin (1968) published the map of structural zones of Iran and the Sanandaj-Sirjan zone was first recognized as a separate linear structural element by Stöcklin (IBP, 2015). A striking feature of this zone is the presence of immense volumes of magmatic and metamorphic rocks of Paleozoic and

Mesozoic eras (Ghorbani, 2013). According to Stöcklin (1968), NW Iran is a part of Sanandaj-Sirjan zone and ophiolites of NW Iran have many similarities with ophiolites surrounding the central Iran micro-continent (Moazzen, 2014). However, Nabavi (1976) suggested that most of Azerbaijan lies in a zone called Azerbaijan-Alborz. In recent years, new geological maps of Iran were published based on the new observations and findings (Nogole-Sadat, 1993; Aghanabati, 2004; Nezafati,

2006). The geology map of the study area is illustrated in Figure. 1d, e&f.

Isi Su borax mineral indication was reported at the region (Ghorbani, 2013; NGDIR, 2016) which is famous with its thermal spring (*Abgarm village*). At the study area, there are a number of thermal springs which flow into the surface water resources increasing their boron concentration. Likewise, due to high mineral content of groundwater resources, thermal springs represent point source of natural pollution. As groundwater moves along faults its mineral concentrations tend to increase.

Groundwater sampling and analysis

The major water bodies in the study area which potentially contribute to boron contamination were identified. Therefore, 42 samples were collected from the groundwater and surface water resources. The analyses were completed in the microbiology laboratory of Rural Water and Sewage Company of West Azerbaijan province.

Geo-statistical approach

Before producing the final surface, we should know how well the model predicts the values at unknown locations. Cross validation and validation approaches provide the best predictions, the approach removes one or more data locations and predict their associated data using the data at the rest of the locations. In this way, one can compare the predicted value to the observed value (ESRI, 2014). The Inverse Distance Weighted (IDW) assumes that variable values at the predicted points are similar to those of nearby sampling points. It estimates the predicted values by weighted averaging of the nearby sampled values, in which the weights are computed as a function of the distance between the two points (Li et al., 2011). The IDW is a mapping technique which is an exact, convex interpolation method that fits only to the continuous model of spatial variation (Hengl, 2009). The IDW technique in ArcGIS Spatial Analyst contains barriers

option which is used to specify the location of linear features known to interrupt the surface continuity (ESRI, 2014). This is useful for our study region which contains faults. The IDW is expressed mathematically in the equation given below (Hengl, 2009):

$$\lambda_i = \frac{d_i^{-\alpha}}{\sum_{i=1}^n d_i^{-\alpha}} \quad (1)$$

where λ_i is the weight for neighbor i , d is the distance from the sampled point to a known point, α is a coefficient to adjust the weights (i.e. to emphasize spatial similarity) and n is the total number of points. Further detailed and public formulas of the geostatistical methods are mentioned in text books and ESRI (2014).

Results and discussion

The water samples were split into three major groups: samples from Abgram region, the Khor Khoreh valley and the Salmas plain. Concentration of boron, EC and TDS of water samples present in varied concentrations at various sampling locations were spatially interpolated using several geostatistical method to identify the origin and distribution pattern of contamination over the study region (Figure. 2). Table 2 shows RMSE of cross validation of different geo-statistical methods. Figure3 shows the result of zoning boron in the region.

Abgarm

The Abgarm River originates from the mountains in southern region with an average annual flow rate of 0.086 cubic meters and total annual discharge of about 2.7 million cubic meters. The river flows to the downstream in the east, recharges groundwaters and ultimately opens into a pasture land. At the Abgarm River basin, thermal and mineral springs are dominant and the springs discharge directly into the river. Therefore, possible high mineral contents of springs could potentially affect the quality of downstream groundwaters.

The Abgarm River is divided into four tributaries (Figure 2).

Boron concentration of stream #1 in upstream is 0.68 mg/l (sample #14). In downstream (sample #13) however, 3.48 mg/l boron was measured. This concentration of boron was taken during low flow of about 1 l/s and the concentration was likely to be diluted during high flow conditions. Stream #2 (sample #8) showed a relatively higher concentration of boron (265 mg/l). Stream #3 is a small stream (flow rate \approx 3.0 l/s). This stream was enriched in boron mainly because thermal and cold mineral springs discharge into it. Anomalous concentrations of boron were observed in thermal springs (sample #1-7) ranging from 435 to 451 mg/l

and EC values reached 16000 μ S/cm. By not letting the thermal spring discharges into this stream could improve the water quality of the other tributaries (e.g. stream #2) and downstream groundwaters. Sample #11 which was taken from stream #4 shows a low concentration of boron (0.48 mg/l) and people in the Abgarm village use the stream for drinking and agricultural needs. TDS and EC were measured at 291 mg/l and 450 μ S/cm in this stream, respectively. Approximately one kilometer downstream of the Abgarm valley, the upstream surface water and groundwater are controlled by bedrock outcrop. Therefore, the upstream surface water and groundwater flow discharge into a stream.

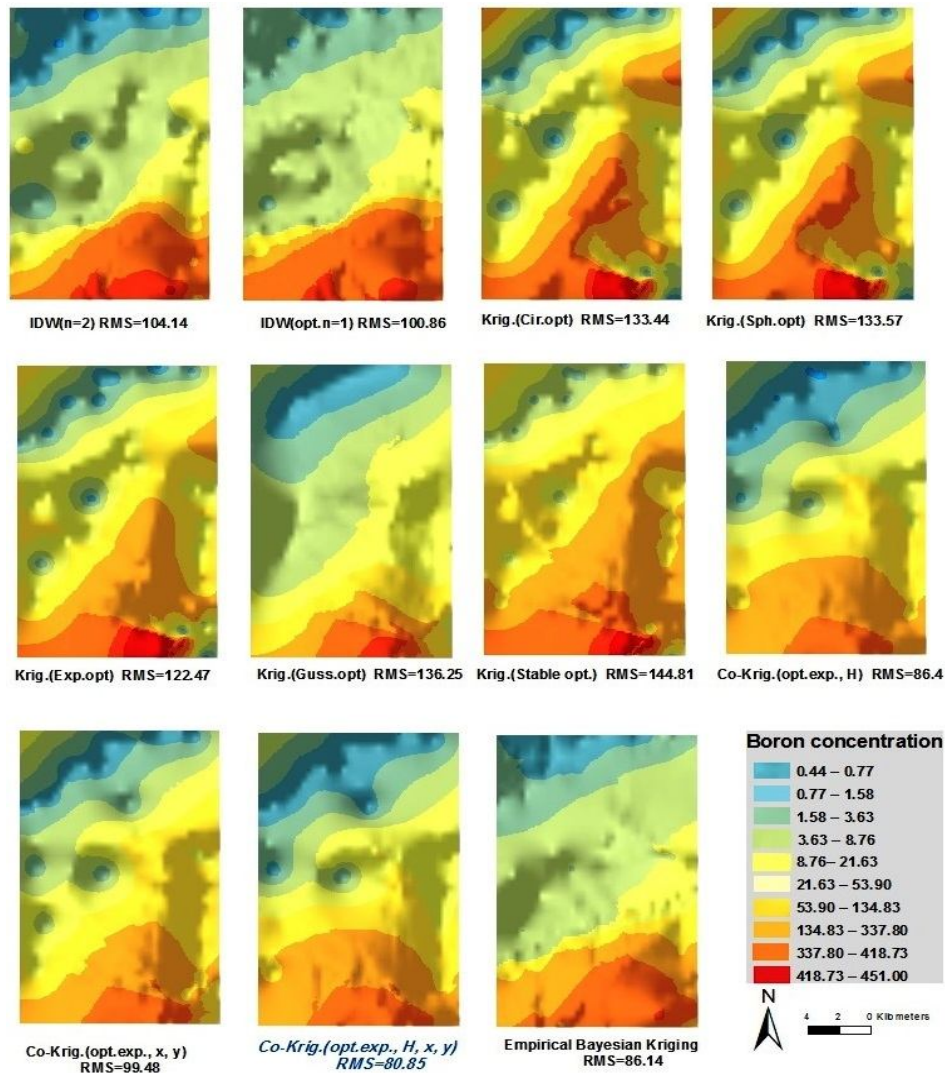


Figure 2. Boron spatial variation in different Geostatistical methods with root mean square error.

At the lower end of the valley, the bedrock is covered by river alluvium and the surface water seeps into the groundwater. Groundwater flow follows the topography and moves north wise. The Salmas plain groundwater flow directs groundwater originated from Abgram down-plain, where Agh Ziarat village is located. High concentration of boron was found in groundwater samples located in the Abgram valley (sample #15-20) and in Agh Ziarat village (sample #24-26) ranging from 6.65 to 16.88 mg/l. The Average TDS in groundwaters of the village is about 700 mg/l and the average EC is 800 μ S/cm. High boron concentration was also detected in drinking water of the village (sample #27). It appears to be the thermal springs at Abgarm that contribute to boron contamination of groundwater in the Agh Ziarat village.

Khor Khoreh valley

The Khor Khoreh valley is rich in both surface water and groundwater resources.

The Khor Khoreh River originates from mountains in the south. The river flows into the northeast pasture adjacent to the Lake Urmia (Figure. 1c). The average annual flow of Khor Khoreh River is 0.24 cubic meters (at Tamar station). Sample #31 was taken from one of the Khor Khoreh River tributaries at upstream of the Shorgol village. High concentration of boron (12.56 mg/l) was observed in this stream at 0.5 cubic meters flow rate. Due to the permeability of the rocks in this basin, groundwater resources in this valley are recharged by surface water throughout the year. Boron content of groundwater samples in this region (sample #28-30 at Tamar) suggest that boron is transferred from Abgarm through faults as far as 16 kilometers away to the Tamar fault in the northwest. Boron contamination was also observed in drinking water sample from Tamar village (sample #32). The average TDS and EC in this region are 617 mg/l and 950 μ S/cm, respectively.

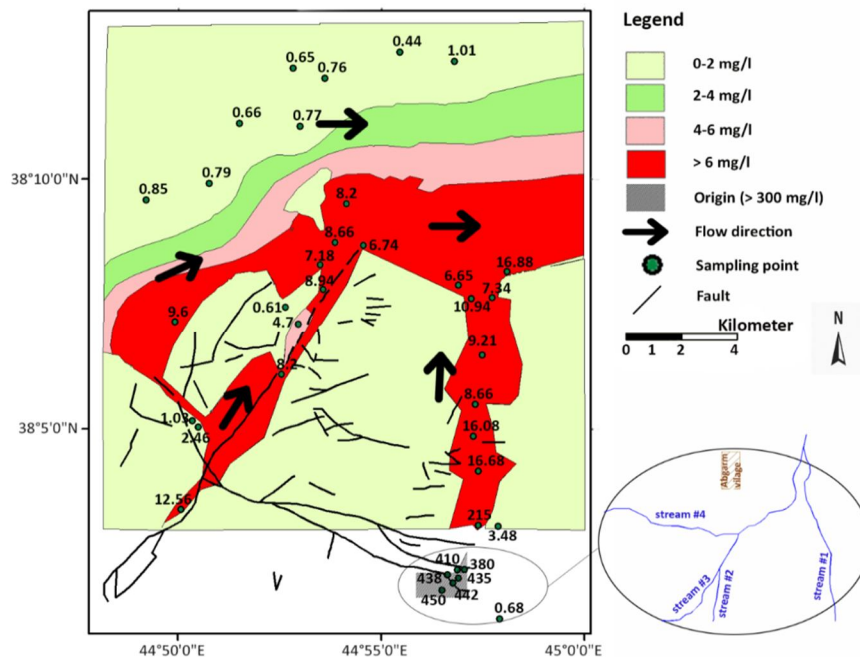


Figure 3. Spatial distribution map for the concentration of boron in water samples

The Salmas plain

The general slope of the Salmas plain is to east and surface waters and groundwaters

discharge into the Lake Urmia. The Zola River which is the main river of the plain is flowing eastward and has a continuous flow

all year round. The Zola River and its tributaries have been used for irrigation of fruit farms in the west and north of the plain. The apple tree farms are the main fruit farms in the region and such trees are very sensitive to boron concentration above 0.5 mg/l. Farm investigations suggested no boron toxicity in the apple tree farms which are irrigated using surface waters.

Groundwater is the main source of

domestic water supply in the region. Due to the droughts in the last decade, ground waters were also used for the irrigation. In order to identify boron concentration of drinking water in northern areas of the plain, samples taken from drinking waters of the villages were analyzed (samples #33-40&42). Except for the Minas village (sample #33), concentrations of boron in the rest of the samples were below 1 mg/l.

Table 1. Boron concentration of surface water and groundwater samples in NW Lake Urmia basin.

Sample	Type of water resource	Boron (mg/l)	EC (μ S/cm)	TDS (mg/l)	Sample	Type of water resource	Boron (mg/l)	EC (μ S/cm)	TDS (mg/l)
1	Thermal spring	442	16860	10960	24	Deep well	6.65	875	569
2	Thermal spring	450	16750	10890	25	Deep well	7.34	670	670
3	Thermal spring	435	16770	9900	26	Deep well	10.94	857	857
4	Thermal spring	438	16870	9900	27	Drinking Water	16.88	885	885
5	Thermal spring	440	16850	10950	28	Spring	1.03	815	530
6	Cold spring	446	15730	10220	29	Drinking Water	2.46	1453	945
7	Stream (#3;Thermal spring)	451	17450	11280	30	Spring	0.61	948	616
8	Stream (downstream #2)	265	6710	4360	31	Stream	12.56	580	377
9	Thermal spring	410	15750	10240	32	Drinking Water	4.70		
10	Junction (stream #2)	380	11400	7410	33	Drinking Water	8.20		
11	Stream #4	0.48	450	291	34	Drinking Water	1.01		
12	Junction (stream #1)	21.5	5450	3540	35	Drinking Water	0.44		
13	Stream	3.48	777	505	36	Drinking Water	0.76		
14	Stream #1	0.68	680	442	37	Drinking Water	0.65		
15	Deep well	16.08	887	577	38	Drinking Water	0.77		
16	Deep well	16.68	964	627	39	Drinking Water	0.66		
17	Deep well	8.66	660	429	40	Drinking Water	0.79		
18	Deep well	9.21	657	427	41	Drinking Water	9.6		
19	Deep well	6.74	1050	683	42	Drinking Water	0.85		
20	Deep well	8.66	1183	769					
21	Deep well	7.18	1245	809					
22	Deep well	8.94	1255	816					
23	Deep well	8.2	981	638					

Table 2. The RMSE of cross validation of different geo-statistical methods

Empirical Bayesian Kriging	Co-kriging with selected Semi-Variogram model			Kriging					IDW optimized(n=1)	IDW(n=2)
	Exponential(H,x,y)	Exponential(x,y)	Exponential(H)	Semi-Variogram model						
				Stable	Gussian	Exponential	Spherical	optCircular_		
86.1	80.9	99.5	86.4	144.8	136.3	122.5	133.6	133.4	100.9	104.1

Table 3. The groundwater Boron contamination expansion in the region

Degree of contamination	Contamination range (mg / l)	Area (ha)
Very High	>6	7270
High	4-6	2120
Average	2-4	2320

Geostatistical approach

The highest concentration of boron was observed in the thermal springs at Abgarm village which is identified as a source of contamination. Initially, the contamination was distributed in two directions through the faults from south to north (through the Abgarm valley), and to northwest (from Abgarm thermal springs to the Khor Khoreh valley). The spatial distribution map (Figure. 3) reveals that boron contamination could not reach the northern areas due to the prevailing easterly slope of the Salmas plain and groundwaters and surface waters flow easterly into the Lake Urmia. Table 3 shows polluted areas in the region.

Conclusion

An anomalous concentration of boron was found in the northwest of Lake Urmia basin with concentration above 400 mg/l. The

findings of this research are in accordance with the findings of Assadpour et al. (2017) and Mosaferi et al. (2020). Boron pollution is the result of natural geogenic and rock-water interaction and brought to the surface water by thermal springs located at the Abgarm village. To prevent the spread of boron contamination to the down-plain, building an underground dam could be a sustainable solution. Moreover, the Salmas plain is relatively rich in surface water resources and it could be used as an alternative for drinking and irrigation purposes, and also collecting polluted water and industrial extraction of boron is highly recommended as a justified economic activity.

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