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An Integrated Statistical-Graphical Approach for the Appraisal of the Natural
Background Levels of Major Ions and Some Potentially Toxic Elements in the
Groundwater of Urmia Aquifer, Iran

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Abstract

In this study, we attempted to calculate the Natural Background Level (NBL) for 19 selected chemical compounds in the Urmia aquifer, northwestern Iran. In this study, combined methods including pre-selection and statistical methods for determining NBL have been used. In the pre-selection method, the concentration of nitrate ($\text{NO}_3 \geq 19.97$ ppm) and chloride ($\text{Cl} \geq 200$ ppm) were used as the main criteria to identify and eliminate samples affected by human activities. The selected concentration of nitrate is determined using the comparison of the results of various statistical and graphical evaluations including Quantile-Quantile plot (Q-Q plot), Box & Whisker plot (BW), Box & Whisker plot Iterative (BWI), Grubbs test, Mean and standard deviation ($\text{mean} \pm 2\sigma$) (MSD), and median absolute deviation (MAD). After identifying the final data set, the NBL of the selected chemical compounds was calculated by two techniques including the Iterative 2σ technique (2σ) and calculated distribution function (CDF). Due to higher concentration relative to the reference values (REF), this study has focused on the calculation of NBL of SO_4 , F, As, Fe and Mn. Results showed that the upper limit of NBL calculated for these variables is about 125 ppm, 1 ppm, 8.5 ppb, 570 ppb, 80 ppb, respectively. Given that no study has been conducted to determine the NBL of chemical compounds in groundwater in Iran, the results of this study can be a roadmap for decision-makers and researchers to better manage this aquifer and other water resources in this country with limited freshwater resources.

Keywords: Natural Background Level, Groundwater Pollution, Human Effects, Iterative 2σ Technique, Calculated Distribution Function, Ambient Background Level

Introduction

Groundwater is one of the most important sources of water needs for various uses, especially drinking so that about one-third of freshwater is extracted annually from groundwater sources (Wang et al. 2018; Gao et al. 2020; Wang et al. 2020). In recent decades, the development of cities and the increase of industrial activities have caused serious groundwater pollution, in addition to overexploitation of groundwater resources (Li et al. 2016, 2017; Wu et al. 2017). Various pollutants enter the water and soil environment, which is threatening human health and ecological security (Falkenmark, 2005; Amiri et al., 2020b; Sohrabi et al. 2020; Li et al. 2021). Today, access to adequate and safe water has become one of the concerns of various

governments. Therefore, quantitative and qualitative management of groundwater resources is one of the most important and necessary measures to be taken to ensure the health of the consumer community (Sohrabi et al. 2013; Amiri et al. 2021b; Amiri and Berndtsson 2020).

In such circumstances, accurate assessment of the natural background level (NBL) of various chemical compounds and the determination of anthropogenic anomalies and effects are essential for the optimal management of groundwater quality (Gao et al. 2019, 2020). Determination of natural/geochemical background values was first proposed by Hawkes and Webb (1962) as the natural concentration of chemical elements and compounds in geological materials without the effect of anthropogenic agents. In 1993, the term geochemical baseline was introduced and many researchers considered it synonymous with NBL and used it to study natural changes in the concentration of chemical compounds in soil and water environments (e.g. Hernandez-Garcia and Custodio 2004; Bech et al. 2005).

In groundwater science, the natural background (baseline) level is the range of natural change of an element, species, or chemical compound in an aqueous solution of biological, geogenic, or atmospheric origin (Edmunds et al. 2003). However, some researchers believe that NBLs no longer exist today due to increased human activity; in other words, most water resources have varying degrees of anthropogenic effects (Li et al. 2014; Nakic et al. 2007; Sellerino et al. 2019; Gao et al. 2020). On the other hand, the calculated NBL for each chemical compound is determined by a threshold value (TV) (European Community 2006). Using these values, the quality of groundwater can be assessed more accurately.

Determining the role of natural and anthropogenic factors in controlling the chemical composition of surface/groundwater resources and different sediments and soils has been pursued by various researchers (Ren et al. 2021). Naturally, different methods are used for each of these studies, and each of them has advantages and disadvantages. Therefore, by analyzing these studies, the optimal method can be identified and used for the study area. Rotiroti et al. (2015) used a new component separation-based (CS) tool called COMPSEC to calculate background concentrations of heavy elements in different hydrogeological environments. The results showed that the CS method can be a suitable and reliable method for estimating the background value, but in some cases, the superimposition of a log-normal distribution for the natural component may not be sufficient. Kim et al. (2015) used a heuristic procedure to statistically determine the natural background and anthropogenic polluted levels of nitrate in

groundwater. They showed that compared to classical methods, this method can use a finite normal-mixture model to distinguish polluted samples from samples with natural concentrations more accurately. Yan et al. (2019) evaluated the pollution and determined the background value of heavy elements in the sediments using the methods of enrichment factor, geoaccumulation index, contamination factor, principal component analysis, and cluster analysis. Sun (2019) compared statistical and spatial analysis methods to determine background concentrations of lead in groundwater. This study, using box plots and spatial autocorrelation analyzes, showed that the appropriate method for determining background values should be selected based on the distribution of elements or contaminants in aquatic environments. Duan et al. (2019) used a three-step method including single index recognition, limiting factors, and a synthetic index to distinguish the background values of some chemical parameters in surface waters.

In many studies, the NBL assigned to each chemical component is presented as a unique value, which is incorrect given the nature of the change in groundwater chemical composition (Nakic et al. 2007; Gao et al. 2020; Su et al. 2020; Ji et al. 2020). As mentioned before, change in the chemical composition of groundwater triggers from the place and time of recharging and after reacting with solid materials in the path of movement, it can be elevated by processes such as surface water infiltration, biological activities, evapotranspiration, water abstraction, deep saline water intrusion, agricultural return water infiltration and effluent of residential areas or industrial units (Nakhaei et al. 2015; Ren et al. 2021; Sohrabi et al. 2017; De Caro et al., 2017; Vázquez-Suñé et al., 2004; Amiri et al. 2021 a, b). Therefore, since the chemical composition of groundwater is controlled by natural and anthropogenic factors, and the effect of these factors changes in different places and times, the NBL should normally be considered as a range and not a unique value (Nakic et al., 2007).

Statistical methods such as parametric and non-parametric approaches can determine the NBL for the desired chemical compounds (De Caro et al. 2017). The role of natural and human factors in controlling changes in chemical compounds in groundwater can be identified by distribution functions and their normality (Wendland et al. 2005; Molinari et al. 2012). Unlike nonparametric methods, most parametric methods can determine the NBL by assuming that the data distribution follows a normal or log-normal distribution (such as 4σ outlier test, 2σ or calculated distribution function (CDF)). These methods are based on determining and removing anomalies from data sets and creating a normal distribution (Gałuszka, 2006; Nakic et al., 2007).

Matschullat et al. (2000) by examining various methods such as 4σ -outlier, 2σ , and CDF revealed that in the first method, a small number of samples are removed from the data set, in other words, the computational NBL is estimated to be higher than the actual value. Therefore, if the number of available data for each chemical compound is more than 30, two other methods (i.e. 2σ and CDF) can provide more accurate results (Gao et al. 2020).

So far, various studies have examined the background values of various elements and compounds in soil and water environments. As a highly practical method, Nakic et al. (2007) showed that removing outliers from the data set of some compounds in an iterative process can lead to their normal distribution and NBL determination. Kelly and Panno (2008), Rodrigues et al. (2013), Urresti-Estala et al. (2013), Preziosi et al. (2014), Salomão et al. (2018), Salomão et al. (2019), Bulut et al. (2020), Gao et al. (2020) and Duan et al. (2020) used Iterative 2σ and CDF methods to determine the NBL.

This study aimed to identify the factors that control the natural changes in the chemical composition of groundwater resources as well as the possible role of anthropogenic factors. Therefore, we have tried to use the Iterative 2σ and CDF methods to calculate the NBL of the main ions and some metallic and non-metallic elements in the coastal part of the Urmia aquifer, northwestern Iran. So far, various hydrochemical, geochemical, isotopic, hydrogeological, and geophysical studies have been performed by the authors in this aquifer (Amiri et al. 2016a, b, c, 2017, 2020, 2021). In most of these studies, several possible sources have been proposed for occasionally high concentrations of major and potentially toxic elements. Therefore, NBL determination of such elements can be very effective in improving the management of groundwater resources and preventing adverse consequences for the health of residents through water consumption. This study is the first attempt to determine the NBL of elements in groundwater in Iran and can be considered by many researchers in this country.

Materials and Methods

Geology, climate, and hydrogeology of the study area

Since the hydrogeological conditions and groundwater flow system can change the groundwater chemistry, this section introduces the study area in terms of geology and hydrogeology. Urmia aquifer (UA) with an area of nearly 750 km² is located in northwestern Iran and west of Lake Urmia as one of the salt lakes in the world with a salinity changing about 300-350 gr/L (Amiri

and Berndtsson 2020). This aquifer is mostly unconfined, but in some areas, it has a convertible structure. It is surrounded by various rock formations. The oldest rocks in this area belong to the Precambrian. This area includes a collection of metamorphic rocks such as gneiss, amphibole, metadiorite, volcanic structures, and carbonate rocks (Sohrabi et al. 2017 and 2018).

According to the global bioclimatic classification system, this area is located in the east of the Zagros Mountains and the east of the Mediterranean climate range (Amiri et al. 2016a). Moisture originating from the Mediterranean Sea is transferred to the region by cyclonic currents. The average annual temperature in this region over the last 35 years is about 12 °C. Also, the average maximum and minimum temperature in the same time is about 31 and -6 °C, respectively. Compared to the average rainfall of Iran (about 280 mm), the average annual rainfall in this area in the long period is about 346 mm. The wet season in Urmia begins in late October and early November and ends in June. The maximum rainfall is in March and April (Amiri et al. 2021c).

Rainfall is the most important recharging factor of this aquifer. Besides, currents from perennial rivers (including Nazluchai, Baranduz Chai, Shahr Chai, and Rouzeh Chai) and some temporary rivers are other factors that recharge the aquifer. The connection of karst water resources as well as hard rock formations through dissolution systems and fractures is also one of the most probable factors in recharging groundwater resources (Amiri et al. 2016c). This aquifer is drained by several thousand wells. Despite the high rate of rainfall in the aquifer, the uncontrolled abstraction of groundwater due to the activity of more than 25,000 unlicensed wells and 17,000 authorized wells has caused that in 34 years, the average drop in water level is equal to 15 cm annually and in 34 years is equal to 536 cm (IWRM 2017).

Geophysical studies show that the maximum thickness of the alluvial part of UA in its northern half is about 160 meters, which is observed in the central and eastern regions (near Urmia Lake (UL)). Also, its southern half has a maximum thickness of about 120 to 130 meters and these changes are observed along the shore of UL and often in the central regions (Amiri et al. 2016b).

This lake deepens from south to north. Therefore, it is expected that UA and UL have a common bedrock. Due to the reduction of topographic slope from west to east, it is expected that the groundwater level in this aquifer in the western regions is at a greater depth than the eastern regions. Accordingly, by recharging the aquifer and reducing groundwater abstraction, in many

coastal areas, the groundwater level is at a very shallow depth and close to the ground, even when the water level of UL is lower than the groundwater level. Based on hydrogeochemical, isotopic, and geophysical studies performed in this part of UA, there is little evidence of the direct hydraulic relationship between fresh groundwater and UL, and this is due to the presence of thick, very hard and impermeable salt layers at the border of these two water bodies (Amiri et al. 2017).

Data collection & analysis

In this study, 175 groundwater samples were collected from the eastern part of the Urmia Aquifer. These samples were collected with the financial support of the Geological Survey and Mineral Exploration of Iran in 2014 and 2015 and by the first author of this article. The initial monitoring network consisted of 84 sampling locations and 91 duplicate samples were collected from the network twice (Fig. 1). The depth of selected wells was between 10 and 120 meters (with an average of 47 meters). All sampling, storage, laboratory transfer, and physicochemical analysis processes are performed according to international standards (APHA 1985; ISO 1993).

At each sampling position, the collected water was stored in two 250 ml PET bottles. To extract freshwater without high retention time in the well, sampling was done from the pumping wells and if the pump was off, the pumping was done for several minutes and then the water sample was stored in a bottle. Before storing water, the bottles were washed several times with the desired water. One bottle was used for the analysis of anions without any manipulation and the other bottle, whose acidity was reduced by 65% v/v nitric acid ($\text{pH} \approx 2$), was used to analyze cations and other elements. Before analysis, these samples were stored at standard temperature (4°C). Some physical parameters including electrical conductivity (EC), total dissolved solids (TDS), pH, Eh, and temperature were measured on-site using a HACH Multimeter device. Besides, the concentrations of chemical parameters include SO_4 , F, Cl, NO_3 , $\text{HCO}_3 + \text{CO}_3$, Ca, K, Mg, Na, B, Br, Al, As, Ba, Cd, Fe, Li, Mn, Mo, Ni, P, Rb, Se, Si, Sr, U, and Zn were also measured in the laboratory.

Fig. 1 Geographical location of the study area. Green circles: included water samples, red circles: excluded water samples

Based on geological, hydrogeological, hydrogeochemical studies and the authors' experience in the study area, we have tried to calculate the NBLs of 19 chemical compounds in the groundwater. According to studies, the selected compounds have both natural (geochemical) and human (due to agricultural, industrial, and mining activities).

Methods of calculating NBLs

In this study, Iterative 2σ and CDF methods were used to determine the NBL of various chemical compounds in groundwater.

In the Iterative 2σ method, after calculating the mean and standard deviation of the data set, the mean $\pm 2\sigma$ calculation is repeated until the data follow the normal distribution (Matschullat et al. 2000). Thus, all outliers are removed from the mean $\pm 2\sigma$ range and they are considered as data affected by anthropogenic factors. The process of calculating and plotting the distribution of data is repeated until all the data fall in the desired range (i.e. mean $\pm 2\sigma$). The data in the calculated range is known as the NBL and the upper limit of this range is considered as the background value (Rodrigues et al., 2013). The Lilliefors test is used to check the frequency distribution and normality of the data. Besides, the t -test is used to calculate the t -statistic and the value obtained is compared with the t -critical value (t -crit.). In these calculations, α and confidence level are 0.05 and 95%, respectively. If the t -statistic is lower than the t -crit., the data distribution is normal and this method is suitable for determining the NBL of the desired chemical compounds (Urresti-Estala et al., 2013). In this method, the upper mean $\pm 2\sigma$ can be considered as TV (Nakic et al. 2007).

The CDF method works on the basis that human factors can increase the concentration of chemical compounds in groundwater. Similar to the Iterative 2σ technique, this method tries to fit a normal curve on the data sets. In this method, samples with a concentration higher than the median are excluded from the data set, and in contrast, it is assumed that the samples in which the concentration of the studied parameter is between min. and median, are unaffected by anthropogenic effects (Matschullat et al. 2000). In this way, the remaining values can be considered as NBL (Urresti-Estala et al. 2013). In both the Iterative 2σ and CDF method, determining acceptable NBLs for different compounds is depends on the frequency distribution of the data set as well as their nature (Bulut et al. 2020).

In this study, a Visual Basic macro entitled BACKGROUND, developed by Nakić et al. (2007), has been used to calculate the NBLs based on Iterative 2σ and CDF methods. One of the essential information for calculating Iterative 2σ and CDF is to determine the interval or bin value for each of the desired physicochemical compounds. In this study, Strurge's Rule, which is a function of the number of samples (n) and the min. and max. of a chemical variable in the data set, was used to calculate the bin value (Salomão et al. 2019; Eq.1):

$$\text{Bin value} = \frac{1 + 3.222 \times (\log_{10}^n)}{\text{Max.} - \text{Min.}} \quad (1)$$

In cases where the concentration of a chemical variable is less than the detection limit of the measuring device, dividing the min. value by the square root of 2 has been used as an alternative (Amiri et al. 2017; Succop et al. 2004).

Results and Discussion

One of the challenges in determining the NBL of various chemical compounds in groundwater is how to identify and determine samples affected by anthropogenic factors (Biddau et al., 2017; Cruz and Andrade, 2015). Nitrate is one of the most common human contaminants that can be easily measured (Almasri 2007; Masetti et al. 2008; Mencio et al. 2016; Li et al. 2019). Therefore, in several studies, it has been used as a criterion for identifying groundwater pollution by human activities and for the pre-selection of data sets. In some studies, samples with a nitrate content of more than 10 ppm were considered contaminated and removed from the data set (Muller et al. 2006). However, in areas with intensive agricultural activities, the concentration of nitrate in groundwater increases more than usual, and therefore, considering the 10 ppm limit for the pre-selection process leads to the elimination of a large number of samples and unacceptable reductions in the size of data set (Preziosi et al. 2010).

Given in the importance of the number of samples remaining in a data set, it is important to select the appropriate concentration of nitrate as a criterion for the pre-selection step. As a first suggestion, Muller et al. (2006) used $\text{NO}_3 \geq 10 \text{ mg/L}$ for the pre-selection of the data set. Some studies have suggested that 75% of the standard drinking water (WHO 2011) equal to 37.5 mg/L can be used. Nevertheless, Parrone et al. (2019) showed that selecting a local value or limit appropriate to the study area can help to better understand the chemical behavior of groundwater resources and select a more optimal data set. Accordingly, this calculated value should not exceed 37.5 mg/L. This criterion of separation of affected and non-affected samples by nitrate concentration has not been studied comprehensively. According to the definition of Reimann and Garrett (2005), these limits are considered as Ambient Background Level (ABL).

In this study, the local ABL of nitrate was determined using the following methods:

- *Quantile-Quantile plot (Q-Q plot)*: The concentration of nitrate is displayed using this distribution method, and after identifying inflection points, values outside the main trends are recognized as outliers and removed from the data set.
- *Box & Whisker plot (BW)*: In this method, the distribution of nitrate in the study area is shown using the BW method, and outliers are removed from the original data set.
- *Box & Whisker Iterative (BWI)*: By repeating the remaining data from the BW method, any remaining outliers are identified and removed. This method continues until all outliers are removed from the data set.
- *Mean and standard deviation (MSD)*: In this method, the mean value and standard deviation (σ) of the data set are calculated and considering the mean $\pm 2\sigma$, at each step a part of the samples with nitrate content outside this range is excluded. In this method, the calculations using the remaining data must be repeated until the desired result is obtained.
- *Grubbs test*: This parametric method is a suitable tool for identifying outliers using Z-values calculation (Li et al., 2018b). Based on this, samples with Z-values above a threshold can be removed from the data set. In this method, the upper 1% significance level ($\alpha = 0.01$) was considered as a criterion for identifying outliers. The general equation in this method is as follows (Rahman et al. 2020):

$$G_t = \frac{(x_s - \mu)}{\sigma} \quad (2)$$

Where μ is the mean of the data set, σ is the standard deviation, x_s is the suspected value, and G_t is the Grubbs test.

- *Mean absolute deviation (MAD)*: In this method, we have tried to calculate the MAD value of the data set and remove samples with values above the threshold of 4.5 from the data set (Parrone et al. 2019).

Fig. 2 shows the processes performed on nitrate data using the Q-Q plot, Box & Whisker plot, and Grubbs test methods.

Fig. 2 Identifying the outliers in nitrate data set by Q-Q plot, BW, and Grubbs test.

Then, by comparing the results, examining the distribution curves, and their normality, the final value obtained was determined by each method. In each method, if after statistical calculations and a graphical representation, the distribution of the remaining data set after removing the outliers was normal, the maximum value was considered as the final number. The Shapiro-Wilk test was used to determine the normality of the remaining data sets (Shapiro and Wilk 1965). Otherwise, the 95th percentile of the remaining data was considered as ABL of nitrate. After determining the local ABL of nitrate, samples containing greater values were considered as affected by human activities and removed from the original data set. In addition to nitrate, a recommended amount of chloride ($\text{Cl} \geq 200$ ppm) was used to increase the accuracy of selecting samples unaffected by human activities (Ducci et al. 2016). Finally, these pre-selected data were used to calculate the NBL of the chemical compounds using Iterative 2σ and CDF methods.

The results of ABL nitrate calculation using different methods are presented in Table 1. Accordingly, the three methods, including Q-Q plot, BW, and BWI, offer the same values of 16.23 ppm. The similarity of the values obtained by these methods has already been reported by Parrone et al. (2019). On the other hand, the computational ABL by the Grubbs test method is equal to 19.97 ppm. As expected, the MSD method provides less value. Due to the intensive agricultural activities in the Urmia plain (see Fig. 1) and the average nitrate concentration in these samples (about 8.5 ppm), it seems that a more conservative amount of nitrate should be considered. On the other hand, considering low ABL values leads to deleting a large number of samples and decreasing the data set. So we decided to consider 19.97 ppm as the final ABL.

Table 1 Results of the pre-selection process

Methods for calculation of ABL of NO ₃ (values are in ppm and equal to 95 percentile of remaining data sets)	Q-Q plot ^a	16.23
	BW ^b	16.23
	BWI ^c	16.23
	Grubbs test	19.97
	MSD ^d	1.89
	MAD ^e	12.63
Final ABL of NO ₃ (ppm)		19.97
Cl (ppm)	Min.	34
	Mean	501.93
	Max.	2061.4
NO ₃ (ppm)	Min.	0.5
	Mean	23.20
	Max.	97
Exclusion criteria (# of samples)	Cl excess (≥ 200 ppm)	28
	ABL of NO ₃ (≥ 19.97 ppm)	15
	Both (Cl ≥ 200 ppm, NO ₃ ≥ 19.97 ppm)	8
	All	35
Excluded samples	Northern part	19
	Southern part	16
	All	140
Included samples	Northern part	68
	Southern part	72

^a Quantile-Quantile plot, ^b Box & Whisker plot, ^c Box & Whisker plot Iterative, ^d Mean and standard deviation (mean ± 2σ), ^e Median absolute deviation

In addition to nitrate, according to the hydrogeological conditions and the location of the study area near the Urmia Salt Lake, another criterion (Cl ≥ 200 ppm) was used for the pre-selection step. Based on these two criteria, 35 samples affected by human activities were removed from the data set. Thus, the number of samples was reduced from 175 to 140.

Subsequently, NBL of different chemical compounds were determined using these 140 samples. Table 2 provides statistical information related to the original and final data set selected by the pre-selection process.

Table 2 Statistics of the original data and final selected data

	Original Data						After Pre-selection					
	Min.	Percentile				Max.	Min.	Percentile				Max.
		25th	50th	75th	95th			25th	50th	75th	95th	
EC (µS/cm)	289.0	616.0	918.0	1364.0	3448.0	7180.0	289.0	569.8	762.5	1079.0	1636.5	2200.0
TDS (ppm)	144.5	300	482	690	2132	6462	144.5	282.5	383.8	578.0	991.3	1312.5
Temperature (°C)	13	16	17	18	20	23	13.0	16.0	17.0	18.0	20.0	22.0
pH	6.05	7.18	7.37	7.62	7.94	8.92	6.8	7.2	7.4	7.7	7.9	8.9
Eh (mV)	-88	-35.4	-16.6	5.87	22.982	73.70	-88.0	-42.2	-19.3	2.5	20.3	33.1
SO ₄ (ppm)	0.5	39.0	74.0	155.0	452.0	980.0	0.5	32.3	63.0	124.3	319.0	500.0
F (ppm)	0.1	0.4	0.6	1.2	2.8	5.7	0.1	0.4	0.5	0.9	2.1	5.7
Cl (ppm)	6.1	18.5	38.0	122.5	659.6	2061.4	6.1	14.1	30.0	55.0	144.8	200.0
NO ₃ (ppm)	0.1	1.2	3.9	10.5	29.9	97.0	0.1	1.0	3.0	9.1	15.5	17.3
HCO ₃ +CO ₃ (ppm)	78.5	171.9	323.2	509.8	833.2	1084.8	78.5	161.1	315.6	484.1	726.1	965.8
Ca (ppm)	3.5	52.0	85.0	132.9	209.3	319.9	3.5	48.4	78.0	116.3	192.0	245.3
K (ppm)	0.0	2.5	3.9	8.0	26.0	118.8	0.0	2.2	3.3	5.4	14.9	60.0
Mg (ppm)	5.7	32.4	49.9	83.7	200.9	485.8	5.7	29.6	44.4	68.4	124.4	217.4
Na (ppm)	12.2	31.5	56.1	129.3	500.4	1229.0	12.2	29.4	46.2	78.8	214.4	550.0
B (ppm)	0.0	0.8	1.1	1.8	3.9	64.0	0.0	0.7	1.0	1.5	2.8	6.0
Br (ppm)	0.1	0.3	0.8	1.6	4.8	9.7	0.1	0.3	0.7	1.4	3.2	5.3
Al (ppb)	0.0	30.0	50.0	90.0	462.0	1710.0	0.0	30.0	40.0	90.0	388.5	1710.0
As (ppb)	0.4	2.4	4.7	13.5	109.6	228.4	0.4	2.1	4.4	13.3	107.9	183.7
Ba (ppb)	23.9	72.9	98.9	135.1	192.7	360.5	24.3	75.4	101.7	133.1	174.9	210.1
Cd (ppb)	0.1	0.1	0.5	1.1	2.0	2.8	0.1	0.1	0.6	1.1	2.1	2.8
Fe (ppb)	0.0	0.0	110.0	400.0	1102.0	4070.0	0.0	0.0	120.0	407.5	1018.0	4070.0
Li (ppb)	0.7	5.3	16.1	27.7	93.0	168.3	0.7	4.5	12.4	23.0	50.4	150.0
Mn (ppb)	0.0	0.1	10.0	80.0	290.0	650.0	0.0	0.1	15.0	70.0	228.5	650.0
Mo (ppb)	0.1	0.6	1.4	2.6	5.2	16.6	0.1	0.5	1.4	2.3	5.1	10.0
Ni (ppb)	0.7	0.7	2.8	7.1	16.5	91.5	0.7	0.7	2.8	6.3	15.7	91.5
P (ppb)	0.0	20.0	30.0	80.0	202.0	1810.0	0.0	20.0	30.0	77.5	343.0	1810.0
Rb (ppb)	0.4	5.7	10.6	28.3	121.1	398.0	0.7	5.1	9.8	20.9	101.7	205.6
Se (ppb)	0.1	0.1	0.3	2.9	9.4	41.1	0.1	0.1	0.1	2.0	5.7	10.7
Si (ppm)	0.1	8.1	9.6	11.6	20.4	38.8	0.1	8.0	9.4	11.0	17.6	38.8
Sr (ppb)	0.0	447.9	674.1	1040.0	1908.0	3541.7	0.0	369.6	620.0	875.8	1600.6	2140.0
U (ppb)	0.7	0.7	1.7	3.3	8.7	13.0	0.7	0.7	1.5	2.4	4.7	10.1
Zn (ppb)	0.7	2.2	9.3	16.2	48.8	166.4	0.7	2.0	9.3	16.6	57.7	166.4

Although NO_3 and Cl were used in this study to remove contaminated samples, some other contaminated samples may be present in the data set that cannot be identified by these two criteria. The use of NO_3 can be useful in identifying water sources contaminated by factors such as contaminated wastewater from agriculture, livestock, residential and industrial effluents (Amiri et al. 2021b). Weak correlation of NO_3 and Cl with the main chemical compounds (include SO_4 , F, As, Fe, Mn) indicates that the use of this criterion in the pre-selection step cannot cause a significant change in the calculation of NBLs (Parrone et al. 2019).

Calculating the NBLs

NBL of chemical compounds of groundwater were calculated using two Iterative 2σ and CDF methods (Table 3). Examining the efficiency of each of these two methods in creating a normal distribution of the chemical variables shows that out of 19 selected variables, one or both methods can provide a normal distribution for 15 variables. As shown in Table 3, these 15 variables have a t -statistic value less than the t -crit. This means their normal distribution and the efficiency of the methods used to calculate the NBLs. Of course, it should be noted that in some cases, only one method provides a good result. In other words, the efficiency of each of these methods in calculating the NBL is a function of the data frequency distribution.

Based on the results, NBL of Cl, HCO_3+CO_3 , Al, and Mn cannot be calculated using these two methods. For these elements, the t -statistic value is greater than the t -crit. In other words, since the condition for accepting the computational value as NBL is the normal distribution of the data remaining after the calculation, these methods cannot provide acceptable results for NBL of Cl, HCO_3+CO_3 , Al, and Mn. This condition is due to the highly skewed distribution of data. In cases where the distance between the minimum and maximum concentrations of chemical components is very large, these methods do not provide a good result for the NBL calculation because in this case, the data mode is too large and this eliminates a large number of samples to establish a normal distribution. (Bulut et al. 2020).

NBLs calculated by statistical approaches (i.e. Iterative 2σ and CDF) show that in cases that only one method leads to a normal distribution of the remaining data, the upper limit of the calculated background values for the data set can be considered as the NBL of that variable (Table 4). Conversely, if both methods have a lower t -statistic than the t -crit. (i.e. normal distribution), the maximum value of the upper limit of these two methods can be considered as

the final NBL (Parrone et al. 2019). As mentioned earlier, the NBL values of the variables Cl, HCO₃+CO₃, Al, and Mn cannot be calculated using Iterative 2 σ and CDF methods. Therefore, for these elements, the deterministic method (i.e. 95th percentile of remaining data) can be used as NBL (Urresti-Estala et al. 2013; Bulut et al. 2020). It should be noted, however, that when the frequency distribution curve is skewed, or in other words has many outliers, estimating the NBL as a definite percentile may sometimes yield different results compared to other methods (Parrone et al. 2019).

Table 3 General results of using Iterative 2 σ and CDF methods in calculating the NBLs.

Parameter	Iterative 2 σ			CDF		
	TV	<i>t</i> -crit.	<i>t</i> - statistic*	TV	<i>t</i> -crit.	<i>t</i> - statistic
EC (μ S/cm)	1086.1	0.086	0.07	1196.1	0.075	0.06
SO ₄ (ppm)	88.1	0.093	0.061	131.1	0.074	0.063
F (ppm)	0.9	0.086	0.024	1	0.075	0.028
Cl (ppm)	45.1	0.089	0.117	60.7	0.075	0.097
HCO ₃ +CO ₃ (ppm)	592.6	0.080	0.122	619.5	0.075	0.119
Ca (ppm)	126.9	0.084	0.084	145.1	0.076	0.074
K (ppm)	4.3	0.92	0.9	5.9	0.076	0.052
Mg (ppm)	59.5	0.90	0.082	76.4	0.075	0.068
Na (ppm)	61.7	0.092	0.083	84.3	0.075	0.094
B (ppm)	1.8	0.082	0.037	1.9	0.075	0.036
Br (ppm)	0.8	0.098	0.019	1.5	0.073	0.087
Al (ppb)	79.4	0.078	0.172	79.4	0.078	0.172
As (ppb)	6.2	0.097	0.101	9.6	0.074	0.068
Ba (ppb)	157.9	0.081	0.074	169.1	0.075	0.053
Fe (ppb)	611.6	0.104	0.097	558.4	0.099	0.068
Li (ppb)	30.3	0.079	0.067	28.3	0.075	0.072
Mn (ppb)	72.2	0.10	0.238	104.6	0.082	0.186
Si (ppm)	12.1	0.084	0.047	14	0.077	0.084
Sr (ppb)	996.1	0.096	0.056	1132.7	0.085	0.054

* Lilliefors test statistic ($\alpha = 0.05$)

In this study, despite calculating the NBL of many groundwater chemical variables, an attempt has been made to focus more on some of them. These elements include SO₄, F, As, Fe, and Mn. The selection of these elements is based on previous studies by authors in this area and does not mean that other chemical components are insignificant.

Table 4 Calculated NBLs by statistical (i.e. Iterative 2 σ and CDF) and deterministic (95th percentile) approaches

Parameter	Iterative 2 σ				CDF				95th		Final NBL
	Min.	Max.	Mean	Normality	Min.	Max.	Mean	Normality	2 σ	CDF	
EC (μ S/cm)	355	1080	700	YES	355	1170	762.5	YES			1170
SO ₄ (ppm)	0.5	88	42.2	YES	0.5	125.5	63	YES			125.5
F (ppm)	0.07	0.85	0.5	YES	0.07	1.02	0.5	YES			1.02
Cl (ppm)	6.1	45	22.5	NO	6.1	53.9	30	NO	42.5	81.9	81.9
HCO ₃ +CO ₃ (ppm)	78.5	590.7	295.4	NO	78.5	552.7	315.6	NO	546.8	542.43	546.8
Ca (ppm)	20.3	126.6	69.5	NO	20.3	135.6	78	YES			78
K (ppm)	1.34	4.26	2.7	YES	0.78	5.81	3.3	YES			5.81
Mg (ppm)	15.6	59.2	36.7	YES	15.6	73.1	44.4	YES			73.1
Na (ppm)	12.2	61.7	35.3	YES	12.2	80.2	46.2	NO			61.7
B (ppm)	0.1	1.8	0.9	YES	0.1	1.9	1	YES			1.9
Br (ppm)	0.1	0.83	0.4	YES	0.1	1.3	0.7	NO			1.3
Al (ppb)	10	70	40	NO	10	70	40	NO	60	60	60
As (ppb)	0.35	6	2.7	NO	0.35	8.45	4.4	YES			8.45
Ba (ppb)	44.6	157.7	100.1	NO	34.7	168.7	10.7	YES			168.7
Fe (ppb)	10	570	263.6	YES	10	260	255	YES			570
Li (ppb)	0.7	30.3	12.2	YES	0.7	24	12.4	YES			30.3
Mn (ppb)	0.01	70	23.59	NO	0.01	80	40	NO	70	80	80
Si (ppm)	6.46	12.03	9.2	YES	5.14	13.61	9.4	NO			12.03
Sr (ppb)	349.4	989	669.1	YES	280	1111.5	659.8	YES			1111.5

Hydrogeochemical analysis of this aquifer shows that Ca-HCO₃/SO₄ is the predominant groundwater facies, which indicates the general fresh groundwater. However, the UA may in some places be affected by salinity or freshening due to the change of seasons and changes in the aquifer recharge. In some places, mechanisms such as cation exchange reactions between water and aquifer solid materials, mixing with saline groundwater derived from dilute brine, and possibly dissolving salts in the unsaturated zone can cause salinization and increase the concentration of some major elements such as Na, Cl, and SO₄ in some samples.

Calculation of NBL of SO₄ as a chemical variable that can be of human and natural origin shows that both Iterative 2 σ and CDF methods can provide a normal distribution of background values (Table 4). Based on the results of the Kolmogorov-Smirnov test, as the computed p-value

(0.618) is greater than the significance level ($\alpha=0.05$), the NBL calculated by the Iterative 2σ approach for SO_4 follows a Normal distribution (Fig. 3).

The results show that in the Iterative 2σ method, the computational NBL is between 0.5 and 88 ppm (with an average of 42.2 ppm). On the other hand, in the CDF method, NBL has a higher upper limit (125.5 ppm) and mean (63 ppm) compared to the first method. However, based on the results of the Kolmogorov-Smirnov test, as the computed p-value (0.42) is greater than the significance level ($\alpha=0.05$), the NBL calculated by the CDF method for SO_4 follows a Normal distribution (Fig. 3). Therefore, given that both methods have a lower t -statistic than the t -crit., the upper limit of the CDF method (125.5 ppm) can be considered as the final NBL. In Fig.3, the NBL calculated for SO_4 by Iterative 2σ and CDF methods as well as distribution fitting on background values are shown.

Fig. 3 NBL calculated for SO_4 by Iterative 2σ (upper) and CDF (lower) methods.

As shown in Table 5, the NBL calculated for SO_4 is less than the reference values (REF). Therefore, although SO_4 is known as one of the dominant groundwater anions in this aquifer and

has a high concentration in some samples if we consider only the role of natural/geochemical activities, this anion will have concentrations lower than REF and will not pose a risk to human health.

Table 5 Comparison of REF, NBL, and TV for studied variables

Parameter	REF	NBL	TV
EC ($\mu\text{S}/\text{cm}$)	n.d.	1170	1086.1
SO_4 (ppm)	400 ^a , 250 ^b	125.5	88.1
F (ppm)	1.5 ^a , 2 ^b	1.02	0.9
Cl (ppm)	250 ^{a,b}	81.9	45.1
HCO_3+CO_3 (ppm)	n.d.	546.8	592.6
Ca (ppm)	300 ^a	78	145.1
K (ppm)	12 ^a	5.81	4.3
Mg (ppm)	30 ^a	73.1	76.4
Na (ppm)	250 ^a	61.7	61.7
B (ppm)	1 ^c	1.9	1.9
Br (ppm)	n.d.	1.3	0.8
Al (ppb)	50 ^b	60	79.4
As (ppb)	10 ^b	8.45	9.6
Ba (ppb)	2000 ^b	168.7	169.1
Fe (ppb)	200 ^b	570	558.4
Li (ppb)	n.d.	30.3	30.3
Mn (ppb)	50	80	72.2
Si (ppm)	n.d.	12.03	12.1
Sr (ppb)	n.d.	1111.5	1132.7

^a (WHO 2011), ^b (EPA 2011), ^c (Bulut et al. 2020), n.d: not defined

The study of this area shows that intensive agricultural activities can increase the concentration of some compounds due to the use of agricultural fertilizers. The results of geophysical studies show that with increasing depth, one can see an increase in electrical resistance, which can be interpreted as a relative decrease in solute concentration. Therefore, most samples with high levels of solutes are affected by surface currents (such as agricultural return water and effluents of residential and industrial units). These changes have also been confirmed by isotopic and geochemical studies (Amiri et al. 2017, 2016).

Amiri and Berndtsson (2020) showed that by studying the concentration of F in 58 and 84 groundwater samples in both wet and dry seasons, 15 and 23% of the samples had a F concentration higher than the standard drinking water recommended by WHO (2011). The results show that high concentrations of F are often measured in shallow wells, which may be

due to human activities such as industrial and agricultural effluents. On the other hand, the interaction between groundwater and geological formations also plays an important role in controlling the F content in groundwater. Some of these high F samples are located in the vicinity of volcanic rocks. Besides, they showed that children at risk for non-carcinogenic diseases due to groundwater consumption had high F concentrations.

Therefore, considering the importance of studying the role of human and natural factors in changing the F concentration in this part of the Urmia aquifer, this study has tried to calculate the NBL of this anion. The results of NBL of F show that similar to SO_4 , both Iterative 2σ and CDF methods can provide a normal distribution of background values (Table 4). The results of the Kolmogorov-Smirnov test indicate that as the computed p-value (0.702) is greater than the significance level ($\alpha=0.05$), the NBL calculated by the Iterative 2σ approach for F follows a Normal distribution (Fig. 4).

Fig. 4 NBL calculated for F by Iterative 2σ (upper) and CDF (lower) methods.

In the Iterative 2σ method, the NBL varies between 0.07 and 0.85 ppm (with an average of 0.5 ppm). On the other hand, in the CDF method, NBL has a higher upper limit (1.02 ppm)

compared to the first method. However, the Kolmogorov-Smirnov test demonstrates the normal distribution for NBL calculated by the CDF method, as the computed p-value (0.77) is greater than the significance level ($\alpha=0.05$) (Fig. 4). Therefore, given that both methods have a lower t -statistic than the t -crit. The upper limit of the CDF method (1.02 ppm) can be considered as the final NBL. In Fig. 4, the NBL calculated for F by Iterative 2σ and CDF methods as well as distribution fitting on background values are shown.

As shown in Table 5, the NBL calculated for F is less than the REF value. Therefore, although the concentration of F in some samples is higher than international standards, the results show that natural/geochemical factors cannot increase the concentration of F above the recommended value for drinking. Therefore, any increase above 1.02 ppm could be due to human contamination.

Sohrabi et al. (2020) examined groundwater quality in UA by focusing on potentially toxic elements. The results showed that some elements such as Fe, Ba, and Al have the highest concentrations compared to other elements. However, some elements such as Cr and Cd also have the lowest concentrations among these elements. Besides, As, as one of the most important elements that can have irreversible effects on human health, in some samples has a concentration higher than the value recommended by WHO (2011). This element can be at an alarming level and can pose risks such as carcinogenic and non-carcinogenic diseases in children and adults. According to the results, the most important factors controlling the concentration of As in these waters is the reductive dissolution of Fe (hydro)oxides and clay minerals. Also, the use of agricultural fertilizers, especially phosphate fertilizers, can play a role in reducing the concentration of As due to an increase in its adsorption rate.

Therefore, the determination of NBL of As can be of great help in identifying human and natural factors controlling its concentration, as well as performing water resources management measures and preventing health problems through drinking water consumption. On the other hand, due to the role of Fe and the close relationship of this element with Mn and its high concentration in groundwater sources, the NBL determination of these two elements has received more attention compared to other chemical compounds.

Calculation of NBL of As in these groundwater samples shows that only the CDF method can provide a normal distribution of background values (Table 4). In the Iterative 2σ method, the NBL varies between 0.35 and 6 ppm (average 2.7 ppm). On the other hand, in the CDF method,

NBL has a higher upper limit (8.45 ppm) and mean (4.4 ppm) value compared to the first method. However, as the computed p-value (0.288) is greater than the significance level ($\alpha=0.05$), the normality test verifies the normal distribution of NBL calculated by the CDF method for As. Therefore, given that the CDF method has a lower t -statistic than the t -crit., the upper limit of the CDF method (8.45 ppm) can be considered as the final NBL. Fig. 5 shows the NBL calculated for As by Iterative 2σ and CDF methods as well as distribution fitting on background values.

Fig. 5 NBL calculated for As by Iterative 2σ (upper) and CDF (lower) methods.

The NBL calculated for As is less than its REF value (Table 5). Therefore, although the concentration of As in some samples is higher than international standards, the results show that natural/geochemical factors cannot increase the concentration of As above the recommended value for drinking. Therefore, any increase greater than 8.45 ppm could be due to human effects.

Based on the computational NBL for Fe, both Iterative 2σ and CDF methods can provide the normal distribution of background values (Table 4). In the Iterative 2σ approach, as the

computed p-value (0.462) is greater than the significance level ($\alpha=0.05$), the NBL calculated by this method for Fe follows a Normal distribution. The results show that in the Iterative 2σ method, the computational NBL changes between 10 and 570 ppm (with an average of 263.6 ppm). On the other hand, in the CDF method, NBL has a lower upper limit (260 ppm) and mean (255 ppm) values compared to the first method. However, as the computed p-value (0.806) is greater than the significance level ($\alpha=0.05$), the NBL calculated by the Iterative 2σ approach for Fe follows a Normal distribution (Fig. 6).

Fig. 6 NBL calculated for Fe by Iterative 2σ (upper) and CDF (lower) methods.

Therefore, given that both methods have a lower t -statistic than the t -crit., the upper limit of the Iterative 2σ method (570 ppm) can be considered as the final NBL. Figure 6 shows the NBL calculated for Fe by Iterative 2σ and CDF methods as well as distribution fitting on background values.

As shown in Table 5, the NBL calculated for iron is less than the REF value. The results show that natural/geochemical factors cannot increase the concentration of Fe above the recommended value for drinking.

Calculation of NBL of Mn as an associated element influencing the adsorption and desorption mechanism of Fe and arsenic shows that none of the Iterative 2σ and CDF methods are suitable for calculating the NBL of this element because the remaining data do not follow the normal distribution. Based on the normality test, as the computed p-values for both Iterative 2σ and CDF methods (0.0002 and 0.001, respectively) are lower than the significance level ($\alpha=0.05$), the NBL calculated by these methods for Mn do not follow a normal distribution. Under such circumstances, the use of the 95th percentile of the remaining data (80 ppm) can be considered as the NBL of Mn (Table 4). Figure 7 shows the NBL calculated for Mn by Iterative 2σ and CDF methods as well as distribution fitting on background values. The NBL of Mn is greater than the REF value (Table 5). Therefore, natural geochemical factors can increase the concentration of this element so much that it is not suitable for consumption.

Fig. 7 NBL calculated for Mn by Iterative 2σ (upper) and CDF (lower) methods.

Results of NBL calculation for other chemical compounds including EC, Cl, HCO_3+CO_3 , Ca, K, Mg, Na, B, Br, Al, Ba, Li, Si, and Sr is provided in Tables 4, 5, and 6 and Supplementary Figs. S1-S14. These components, especially major ions, are generally controlled by natural factors and despite the actions taken in the pre-selection stage, in some cases, they are also affected by human factors. However, the NBLs calculated for these variables can be of great help in identifying natural and geochemical values and human impacts.

Conclusions

In this study, using statistical and graphical methods, the NBL of chemical compounds with high background value has been investigated. The number of 175 original samples was reduced to 140 in the pre-selection step based on the concentration of NO_3 and Cl. The purpose of this step is to remove samples that may have been contaminated by human activities. Then, the NBL of 19 chemical compounds was determined using Iterative 2σ and CDF methods. Thus, the NBL of 15 compounds was determined using these methods because the remaining data had a normal distribution and, besides, the t -statistic was lower than t -crit. Given that the condition for accepting the result obtained by these two statistical methods is the normal distribution of data, the NBL of the variables Cl, HCO_3+CO_3 , Al, and Mn cannot be calculated using Iterative 2σ and CDF methods. Therefore, the NBL of these elements was determined definitively (i.e. 95th percentile of remaining data). According to previous studies, the importance of components such as SO_4 , F, As, Fe, and Mn, their high concentration relative to the REF values, and their role in degrading the quality of water used by residents, has led to more focus on these elements in this study. Results showed that the upper limit of NBL calculated for SO_4 , F, As, Fe and Mn is about 125 ppm, 1 ppm, 8.5 ppb, 570 ppb, 80 ppb, respectively. Given that a study aimed at determining the NBL of various elements in groundwater has not been conducted in Iran, the results of this study can be a good roadmap for decision-makers and researchers to better manage this aquifer and other water resources in this country with limited freshwater resources.

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556 **Authors Contributions**

557 Vahab Amiri: Conceptualization, methodology, figures and tables preparation, literature search
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559 Mohammad Nakhaei: Literature search and evaluation, methodology, reviewing and editing of
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561 Razyeh Lak: Literature search and evaluation, reviewing and editing of the manuscript.

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565 **Competing Interests**

566 The authors declare that they have no known competing financial interests or personal relationships that could
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568 **Availability of data and materials**

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Figures

Figure 1

Geographical location of the study area. Green circles: included water samples, red circles: excluded water samples Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal

status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Identifying the outliers in nitrate data set by Q-Q plot, BW, and Grubbs test.

Figure 3

NBL calculated for SO_4 by Iterative 2σ (upper) and CDF (lower) methods.

Figure 4

NBL calculated for F by Iterative 2σ (upper) and CDF (lower) methods.

Figure 5

NBL calculated for As by Iterative 2σ (upper) and CDF (lower) methods.

Figure 6

NBL calculated for Fe by Iterative 2σ (upper) and CDF (lower) methods.

Figure 7

NBL calculated for Mn by Iterative 2σ (upper) and CDF (lower) methods.

Supplementary Files

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