Journal of Radiation Researches, vol.4, No.1, 2017, Baku

UDC: 543.3;543.32/34

ESTIMATION OF RIVER WATERS QUALITY IN AZERBAIJAN

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***Abstract*:** In a qualitative analysis of water collected from different rivers of Azerbaijan, 29 water samples were analyzed to assess water quality and suitability for domestic, livestock and irrigation usage. The pH of the river water varied within 7.79-9.34. Electrical conductivity of all collected water samples were within the range of 279-2738 µS/cm indicating low to high salinity. Total dissolved solids ranged from 166-4047 mg/L. The anion chemistry in water samples was dominated by HCO_3^-, Cl^- and SO_4^{2-}, respectively. The cation chemistry indicated that among 29 water samples, 16 showed dominance sequence as Ca > Na > Mg > K, 5 samples as Na > Ca > Mg > K, 6 samples as Ca > Na > K > Mg and 2 sample as Na>K>Ca>Mg. The quality assessment showed relatively high values of EC, TDS, HCO_3^-, Cl^- and SO_4^{2-}, in the number of water samples, which would make them unsafe for drinking, livestock and irrigation purposes.

Key words: river waters, electrical conductivity, hydrochemical analysis

1. Introduction

Water quality management is the surface water and groundwater quality control at any time for supplying water at a required quality for a specific use. For water quality control it is necessary to know physical, chemical and biological characteristics of the river. To reach this objective, it is necessary to have proper monitoring of water quality. Having enough data without proper interpretation cannot help water quality management adequately /1/.

The capacity for water resources to meet the various needs has been over-stressed and this as led to its scarcity. Various reasons can be advanced for this and they relate to population increase, climate change, environmental degradation, weak and inadequate institutional capacities, and the growing poverty levels in the country. The rapid population increase has subjected the limited available water resources to a lot of pressure in efforts to meet the various needs. Climatic variability and change has also significantly altered the rainfall patterns and amounts, thereby affecting the replenishment rate of water bodies /2.3/. Hydro chemical analysis and subsequently water quality evaluation often reveals quality of water that is suitable for domestic consumption, agriculture and industrial purposes, as well as aiding in management of the water resource. Furthermore, it is possible to understand the change in water quality due to rock water interaction or anthropogenic influence. Water often consists of seven major chemical ions which include cations Ca^{2+}, Mg^{2+}, Na^+, K^+ and anions Cl^- , HCO_3^- , SO_4^{2-}. Other parameters include pH, Color, Turbidity, Free Carbon Dioxide and Total Dissolved Solid. These chemical parameters play a significant role in classifying and assessing water quality.

In the present study, waters collected from different sources of Republic of Azerbaijan were analyzed and compared to water quality standards for domestic, industrial, livestock and irrigation usage. Republic of Azerbaijan is one of the countries in the South Caucasus and has a territory of 86,600 km2. The Republic borders with Russia in the north for 289 km along Samur River, 340 km with Georgia in the northwest, 766 km with Armenia in the west and southwest, 11 km with Turkey, and 618 km with Iran in the south. The length of its Caspian Sea coastline from the Astara River to Samur River is 825 km.

The range of elevation within the Republic varies from 4,480 m. in the Major Caucasus Mountains (Bazarduzu crest) to –26.0 m (Caspian Sea level). The average altitude of the area is 384 m with 18 per cent of the area below sea level, 39.5 per cent is between 0 and 500 m, 15.5 per cent is between 500 and 1,000 m., and 27 per cent is greater than 1,000 m. Sharp changes of altitudes due to the orographic structure of the Major and Minor Caucasus Mountains and the location of the Kur-Araz lowlands form the unique climate in the country. Climate conditions and relief of the area plays special role in formation of the water resources of the republic.

Geology. The territory of the Republic of Azerbaijan forms a constituent geological part of the Alpine folded belt. Sedimentary deposits embracing the south-western parts of the Major and Minor Caucasus, including the intermountain Kura-River trough, as well as the Mid- and South Caspian basins consist of diversity fold systems. The Earth's crust thickness in Azerbaijan varies in the range from 38 to 55 km. Its maximum thickness is observed in the Minor Caucasus area, while its minimum thickness is typical for the Tallish foothills. Geological setting of the area consists of sedimentary, volcanic-sedimentary, volcanic and terrestrial deposits embracing almost entire stratigraphic range beginning from pre-Cambrian period up to Holocene time.

Geography and Climate. As a predominantly mountainous country, Azerbaijan is surrounded by the Major Caucasus, Minor Caucasus, Tallish and North Iranian Mountains. The Kur-Araz Lowland, between the Greater and Lesser Caucasus, stretches to the Caspian Sea in the eastern part of the country. The Greater Caucasus, situated in the north of the country and stretching from the northwest to the southeast, protects the country from direct influences of northern cold air masses. That leads to the formation of a subtropical climate on most of the foothills and plains of the country. Other mountain chains surrounding the country also impact air circulation. The complexity of the landscape causes non uniform formation of climatic zones and creates vertical climate zones.

Physiographic conditions and different atmosphere circulations admit 8 types of air currents including continental, sea, arctic, tropical currents of air that formulates the climate of the country. The maximum annual precipitation falls in Lenkeran (1,600 to 1,800 mm.) and the minimum in Absheron (200 to 350 mm.). The maximum daily precipitation of 334 mm was observed at the Bilieser Station in 1955.

Eight out of 11 existing climate types including semi-desert, arid steppe and mountain tundra are present in the country. The annual average air temperature is approximately 14.6 ^{0}C in the Kur-Araz lowlands and 0^{0}C in the mountains. The absolute minimum temperature observed was –33.0^{0}C (in Julfa and Ordubad) and absolute maximum temperature of +46.0^{0}C was again observed in Julfa and Ordubad.

2. Methodology

2.1 Sample collection and analysis. In this study, 29 river water samples were collected during April 2014 to August 2014 as shown in Table1. The water samples were collected after 30 minutes of pumping to avoid stagnant and contaminated water. The white plastic containers were rinsed out 3-4 times with the water to be sampled. Then the containers were filled up to the brim and were immediately sealed to avoid exposure to air. After the collection, the containers were labeled for identification and brought to the laboratory. During sample collection, handling, and preservation, standard procedures recommended by the EPA methods were followed to ensure data quality and consistency.

The water samples were analyzed in the Laboratory. All these samples were analyzed for pH, Total Dissolved Solids (TDS), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sulphate (SO_4^{2-}), chloride (Cl^-) and carbonate (CO_3^{2-}), bicarbonate (HCO_3^-). Among the analyzed parameters, Na^+, K, Ca^{2+} and Mg^{2+} were determined by using flame atomic absorption spectrometer.

3. Results and discussion

The results of the geochemical analysis of water samples collected from rivers of Azerbaijan is given in Table 1. The general statistics of major ion chemistry of collected water is summarized in Table 2.

The pH of water samples varied from 7.79 to 9.34 with a mean value of 8.46 indicating alkalinity of water. On the basis of the measured pH of waters, 76% of all samples under the investigation area were not problematic in of drinking and irrigation and usage (Table 1). All samples have pH upper than 7.79 indicating were unsuitable for livestock usage. The electrical conductivity (EC) of all collected water samples were within the range of 279 to 2738 μS cm^{-1} with an average value of 434 μS cm-1. There were wide spatial variations observed in the EC in different rivers, only 2 samples have EC upper than 750 μS/cm. The total dissolved solids (TDS), which is the sum of the dissolved ionic concentrations, ranged between166 to 4047 mg/L (average 522 mg/L). In regard to TDS, 6 water samples under the investigation area were problematic for drinking and livestock usage, and all samples were found suitable for irrigation usage.

The anion chemistry of the analyzed water samples shows HCO_3^- , Cl^- and SO_4^{2-} to be the dominant anions at the investigation area. The concentration of HCO_4^- - was within the range of 97 to 720 mg/L with a mean value of 173 mg/L (Table 1). With respect to HCO_3^- content all water samples were found suitable for drinking (except 3 samples) and livestock usage but all water samples exceeded the recommended limit for irrigation. Chloride concentration in water samples varied from 0.31 to 667 mg/L with an average value of 43.2 mg/L. (Table 1).

In regard to Cl^-, all water samples under the investigation area were found suitable for drinking (except 2 samples) and livestock purpose and only samples were found unsuitable for irrigation usage (Table1). The SO_4^{2-} content in water samples ranged from 25 to 1676 mg/L with a mean value of 198 mg/L (Table 1). Maximum permissible limit of SO_4^{2-} in irrigation water is 20 mg/ L /4/. Considering this limit as standard, all samples, were above the limit, those may be problematic for irrigation. On the other hand, all water samples under the investigation area were suitable for drinking and livestock (except 4 samples) usage in respect of SO_4^{2-} content (Table 1).

The cationic chemistry of the water samples collected from rivers of Azerbaijan is dominated by calcium, sodium, magnesium and potassium (Table 2). Out of 29 water samples,16 showed dominance sequence as Ca > Mg > Na >K, 5 samples as Na > Ca > Mg > K , 6 samples as Ca > Na >Mg > K, and 2 sample as Na>K>Ca>Mg. Weathering of rock forming minerals and cation exchange processes normally control the levels of these cations. High concentration of Ca and Mg in the waters are attributed to the weathering of crystalline dolomitic limestones and Ca-Mg silicates (amphiboles, pyroxenes, olivine, biotite and others /5/. Sodium and potassium in the aquatic system were derived from the atmospheric deposition, evaporate dissolution and silicate weathering. The weathering of Na and K silicate minerals like albite, anorthite, orthoclase and microcline may be the possible source of Na and K in waters /6-8/. The content of Ca in water samples varied from 23.68 to 148 mg/L with an average value of 75 mg/L. Irrigation water containing less than 800 mg/L Ca was suitable for irrigating crops /4/. On the basis of Ca content, all water samples could safely be used for irrigation and would not be affected by soils of the study area. On the other hand, according to /9,10/ all water samples (except 1 sample) could also be safely used for drinking purpose (Table 1). The concentration of Mg in water samples was found within the range of 3.99 to 240 mg/L with a mean value of 25.63 mg/L (Table 2). According to /4/ irrigation water containing below 120 mg/L Mg was suitable for crops and soils. In the investigated rivers, all water samples (except 1 sample) were within the recommended limit for drinking and irrigation usage, and could safely be used for drinking and irrigation purposes with respect to Mg content. Sodium concentration in the study area varied from 4.26 to 820 mg/L with an average value of 72.84 mg/L. According to /4/, irrigation water generally containing less than 920 mg/L Na is suitable for crops and soils. On the other hand, maximum permissible limit of Na in drinking water is 50 mg/L /9,10/. With respect to Na content, all water samples under investigation area could safely be used for drinking (except 4 samples for drinking purpose) as well as for long-term irrigation without any harmful effect on soils and crops.

The concentration of K present in the water samples collected from rivers of Azerbaijan varied from 0.979 to 17.64 mg/L with a mean value of 4.08 mg/L (Table 2). The maximum permissible limit of K in irrigation water is 2.0 mg/ L /4/ while for drinking water is 100 mg/L /9,10/. In the investigated area, all water samples were within the recommended limit for drinking water quality but 15 water samples were above the recommended limit of irrigation water quality.

Table 1

Geochemical parameters in the water samples compared to desirable standard values for drinking, livestock and irrigation use

Parameters	Range	Mean	Max.desirable value for drinking water	Max.desirable value for livestock drinking water	Max.desirable value for irrigation
pH	7.79-9.34	8.46	7.0-8.5	6.8-7.5	6.0-8.4
ES(μS/cm)	279-2738	483	750	-	-
TDS(mg/L)	166-4047	522	500	<500	-
HCO_3^-(mg/L)	97-720	173	200	<400	92
SO_4^-(mg/L)	25-1676	198	200	<250	20
Cl^-(mg/L)	0.31-667	43.2	250	-	142
Ca^{2+}(mg/L)	23.68-148	48.74	75	-	800
Mg^{2+}(mg/L)	3.99-240	25.63	30	-	120
Na^+(mg/L)	4.56-820	72.84	50	-	920
K^+(mg/L	0.979-17.64	4.08	100	-	2.0

The suitability of water for irrigation purposes is dependent on its mineral constituents. Several criteria for judging its suitability have been proposed by /11,12/. Irrigation water containing large amounts of sodium is of special concern due to sodium's effects on the soil and possibility to pose a sodium hazard. The high concentration of sodium in irrigation water may negatively affect the soil structure and decrease the soil hydraulic conductivity in fine-textured soil. The degree to which sodium will be absorbed by a soil is a function of the amount of sodium to divalent cations (Ca and Mg) and is regularly stated by the sodium adsorption ratio (SAR) /13/. The Sodium Absorption Ratio (SAR) which can be calculated from the ratio of sodium to calcium and magnesium (Asadollahfardi et al. 2011). The equation is expressed as follows:

$$SAR=\frac{Na^+}{\sqrt{(Ca^{2+}+Mg^{2+})/2}}$$

Where, all the ions are expressed in meq/L.

The potential for sodium hazard increases in waters with higher sodium adsorption ration SAR values. The sodium absorption ration (SAR) content in study area has shown variation from 0.156 to 10.4 with an average value 1.53 (table 2). Sodium Absorption Ratios for all water samples (except sample from Devechichay river) of study area are less than 10 indicate excellent quality for irrigation and sample fall in excellent (S1) category while Sodium Absorption Ratios for water sample from Devechichay river are within range 10-18 indicate good quality for irrigation and samples fall in good (S2) categore (table 2.).

Soluble Sodium Percent (SSP) is also used to evaluate sodium hazard. SSP is defined as the ration of sodium to the total cations. Water with a SSP greater than 60 /14,15/:

$$SSP=\frac{Soluble(Na^{+}+K)*100}{Total\ cations\ concentration}$$

Where, all the ionic concentrations are expressed in meq/L.

The Soluble Sodium Percent (SSP) values less than 50 or equal to 50 indicates good quality water and it is more than 50 indicates the unsuitable water quality for irrigation. The values of Soluble Sodium Percent (SSP) ranges from 6.61 to 66.53 an average 25.1. 96.6% Soluble Sodium Percent (SSP) for water of study area are less than 50 and indicate good quality water for irrigation purpose while remaining 3.4% is more than 50 % may result in sodium accumulations that will cause a breakdown in the soil’s physical properties (table 2).

Table 2.
Classification of water on the basis of SAR, KR, SSP and RSC

Parameter	Range	Water Class	Samples	% age
SAR	<10 10-18 18-26 >26	Excellent (S1) Good (S2) Doubtful (S3) Unsuitable (S4)	28 1	96.6 3.4
SSR	<50 >50	Good Bad	26 3	89.7 10.3
KR	<1 >1	Good Unsuitable	26 3	89.7 10.3
RSC	<1.25 1,25-2.5 >2.5	Good Doubtful Unsuitable	29	100

KR: Sodium measured against Ca^{2+} and Mg^{2+} is used to calculate Kelley׳s ratio. The formula used in the estimation of Kelley׳s Ratio /14,15/

$$KR=Na^{+}/(Ca^{2+}+Mg^{2+})$$

A Kelley׳s Ratio (KR) of more than one indicates an excess level of sodium in waters. Hence, waters with a Kelley׳s Ratio less than one are suitable for irrigation, while those with a ratio more than one are unsuitable for irrigation. The values of Kelley׳s Ratio (KR) ranges from 0.059 to 1.93 an average 0.43. 89.7 % a Kelley׳s Ratio values for the water of study area are less than 1 and indicate good quality water for irrigation purpose while remaining 10.3 % is more than 1 indicate the unsuitable water for irrigation (table 2).

Residual sodium carbonate (RSC): The Residual Sodium Carbonate (RSC) were also calculated and used for irrigation water quality assessment. This parameter is used for the assessment of the effect of carbonate and bicarbonate on the quality of water for agricultural purposes. RSC is calculated as follows:

$$RSC=(CO_3^{2-}+HCO_3^{-})-(Ca^{2+}+Mg^{2+})$$

Where, all the ions are expressed in meq/L.

The potential for sodium hazard is increases as RSC increases, and much of the calcium and the magnesium are precipitated out of solution when water is applied to the soil. Salts become concentrated when soil dries out, as less soluble ions (as $Ca2^{+}$ and Mg^{2+}) tend to precipitate out of solution /16/. The values of Residual sodium carbonate ranges from –11.72 to 0.283 with average value -1.734 (table 1). In the study area, the RSC is negative (except 2 samples) showing that Na^{+} buildup is unlikely with practically no Na+ hazard and therefore classified as fit for irrigation. The water having less than 1.25 or equal 1.25 epm of RSC is safe water for irrigation purpose, water is having from 1.25 to 2.5 epm of Residual sodium carbonate is marginally suitable for irrigation purpose whereas water having more than 2.5 epm of RSC is not suitable for irrigation purposes. Based on Residual sodium carbonate (RSC) values, all the samples of study area having values less than 1.25 epm and were safe for irrigation (table).

4. Conclusion

River waters were sampled and analyzed for their hydrochemical characteristics and evaluation of the water quality for drinking and irrigation purposes. SAR values and the sodium percentage (Na %) in locations indicate that majority of the river water samples are suitable for irrigation. The hydrochemical analysis demonstrates that the water sample is typical of shallow fresh waters. The EC value in all eleven cities ranged from 279-2738 μS/cm. Similarly, the pH value of all the collected samples ranged from 7.79-9.34 against the recommended WHO guideline range of 6.5-8.5 for drinking water. The anion chemistry of the analyzed water samples shows HCO_3^{-}, Cl^{-} and SO_4^{2-} to be the dominant anions at the investigation area. With respect to HCO_3^{-}, SO_4^{2} content all water samples were found suitable for drinking (except 3 samples) and livestock usage but all water samples exceeded the recommended limit for irrigation. In regard to Cl^{-}, all water samples under the investigation area were found suitable for drinking (except 2 samples) and livestock purpose and only samples were found unsuitable for irrigation usage.

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ОЦЕНКА КАЧЕСТВА РЕЧНЫХ ВОД В АЗЕРБАЙДЖАНЕ

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Резюме: Для качественного анализа вод, собранных из разных рек Азербайджана, было проанализировано 29 образцов для оценки качества воды и пригодности для использования в домашних хозяйствах, животноводстве и ирригации. PH речной воды варьировался от 7,79-9,34. Электропроводность всех собранных образцов воды находилась в диапазоне 279-2738 мкСм/см, которая указывает на низкую и высокую соленость. Общее количество растворенных твердых веществ составило 166-4047 мг/л. В анионной химии в образцах воды доминировали HCO_3^-, Cl^- и SO_4^{2-}, соответственно. Катионная химия показала, что среди 29 образцов воды 16 показала последовательность доминирования как Ca> Na> Mg> K, 5 образцов в виде Na> Ca> Mg> K, 6 образцов в виде Ca> Na> K> Mg и 2 образца в виде Na> K> Ca> Mg. Оценка качества показала относительно высокие значения EC, TDS, HCO_3^-, Cl^- и SO_4^{2-} в ряде образцов воды, что сделало бы их небезопасными для целей питья, животноводства и ирригации.

Ключевые слова: речные воды, электропроводность, гидрохимический анализ

AZƏRBAYCANDA ÇAY SULARININ KEYFIYYƏTININ QIYMƏTLƏNDIRILMƏSI

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Xülasə: Azərbaycanın müxtəlif çaylarında su keyfiyyətini və onun məişətdə, heyvandarlıqda, suvarmada istifadə imkənlarını qiymətləndirmək üçün 29 çay suyu nümunəsi analiz olunmuşdur. Çay suyu nümunələrinin pH-göstəricisi 7, 79 - 9, 34 arasında dəyişir. Bütün götürülmüş su nümunələrinin elektrik keçiriciliyi 279-2738 µS/sm aralığında dəyişir və yüksək şoranlığın da olduğu müşahidə olunur. Ümumi həll olmuş maddələrin qatılığı 166-4047 mg/L arasında dəyişir. Su nümunələrində anion tərkibi uyğun olaraq HCO_3, Cl^- və SO_4^{2-} üstünlük ardıcıllığı təşkil edir. Kation tərkibinin analizi 29 su nümunəsindən 16-da Ca-Na> Mg> K kimi 5 nümunədə Na> Ca> Mg> K kimi, 6 nümunədə Ca> Na> K> Mg kimi və 2 nümunədə Na> K> Ca> Mg. paylanma ardıcıllığının olduğunu göstərir. Keyfiyyətin qiymətləndirilməsi zamanı bir sıra su nümunələrində EC, TDS, HCO_3^-, Cl^- və SO_4^{2-} parametrləri üçün nisbətən yüksək qiymətlər müşahidə olunur. Qeyd olunan parametrlər bu su mənbələrini içmək üçün, heyvandarlıq və suvarma məqsədləri üçün təhlükəli hala gətirir.

Açar sözlər: çay suları, elektrik keçiriciliyi, hidrokimyəvi analiz