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Investigation of physicochemical properties of water in downstream areas of selected dams in Aras catchment and water quality assessment

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Abstract: The aim of this study was to evaluate the physicochemical properties of downstream water of Aras River dams. Sampling was performed from early 2018-2019 in selected stations. Heavy metals were measured by atomic absorption spectrometry. Nitrate, nitrite and total dissolved solids concentrations were also measured by spectrophotometer. Concentrations of Ca, Na and K were measured with a Flame Photometer and the rest were measured with specialized devices. The results showed that the lowest electrical conductivity in the measured samples was 0.789 and the highest was 4.346 µs/cm, which basically indicates the high limit of soil and water for irrigation of plants. On the other hand, total solids with 1211 ppm indicate a moderate limit for salinity. Also; regarding pH, the average recorded for the study area is 8.17, which is within the national permissible and standard range of the world health organization. Nitrate and nitrite are both above the permissible and standard range. Potassium is within the permitted and standard range. Calcium, according to the average obtained in the study area (64 ppm) can be said that this parameter is within the allowable and standard range. In the case of lead (0.09 ppb), it can be said that this parameter is within the allowable and standard range. In the case of cadmium (0.8 ppb), it can be said that this parameter is within the allowable and standard range, 4 parameters nitrate, nitrite, EC and TDS have an average higher than the national standard and the other parameters are lower than the standard in terms of average. It seems that the only way to deal with the pollution caused by the industries around the Aras River is to apply the approach of environmental law by the Commonwealth.
Keywords: Aras River, Heavy metals, Physicochemical, Pollution load.

1. Introduction

The necessity of human social life requires optimal resource management and pre-crisis control of resource scarcity, the issue of "water" and consequently "pollution of water resources" is one of the major challenges facing human life, especially in Iran. These challenges in the future can threaten the areas of public order and social services at large levels and therefore require the presence, intervention and supervision of the government. Pollution generally means the introduction or introduction of harmful, toxic or energetic substances (heat or sound) into the human, animal or plant environment, in excessive amounts and beyond their biological potential, which endangers biological resources, and endangers the life and health of living things (Rostamabadi & Jalali, 2014). Water pollution is the most important threat to both developed and developing countries (Chakravarty et al., 2010; USEPA, 2017).

Today, the protection of water resources is the first priority of environmental organizations. Access to unpolluted freshwater will be one of the greatest challenges facing humanity in the years to come. Surface water quality provides important data on the resources available to support life in this ecosystem (Manikannan et al., 2011). The physicochemical composition of surface water is affected by various factors and parameters such as natural factors (rainfall, regional geology, climate and topography) and human factors (urban wastewater, industrial and agricultural activities). Aquatic ecosystems are naturally the final recipients of heavy metals (Peng et al., 2009). Some metals are carcinogenic to humans. The study of the chemical quality of water resources is a suitable indicator to determine the capability of various uses, including agriculture, industry, services and washing and cleaning (WHO, 2006). Decreased quality of water resources also affects other natural resources in many ways, including reducing agricultural production, disrupting soil structure, changing climate conditions, and creating problems for human health (Farhadi et al., 2020).

The entry of pollutants into aquatic ecosystems endangers both natural areas and the health of the inhabitants of the surrounding area. Pollutants that enter the environment from mining activities and effluents containing heavy metals penetrate into the soil and groundwater aquifers and have negative effects on the health of the region and the people. Ignoring such pollution will not only endanger the health of local people, but also endanger the health of a large part of the community. Heavy metals refer to any metal chemical element that has a relatively high density and is also toxic at low concentrations (Mansouri et al., 2020). Heavy metals are the building blocks of the earth's crust and do not degrade or erode (Jhajharia et al., 2011). Given the importance of heavy metals in aquatic environments, it is necessary to determine the concentration of these metals in environments such as freshwater rivers (Oihang et al., 2015; Imanpour Namin et al., 2011). Numerous studies have been conducted worldwide on the amount of heavy metals in aquatic ecosystems and their consequences, including the following:-Concentrations of copper (Cu), lead (Pb), nickle (Ni), cadmium (Cd), mercury (Hg), and arsenic (As) were collected in samples collected from the Liangyang River. The results showed that the concentration of heavy metals is high in the rainy season and low in the dry season. The concentration of copper in the surface waters of the region was 2.4 to 131 times the reference concentration and after Cu copper, Ni, Cd, Pb, Hg, and As had the highest concentrations, respectively. However, compared to the Chinese environmental standard, first Cd cadmium, Hg, Pb, and Cu copper were identified as the most harmful elements, respectively. The concentration of Cu copper in sedimentary samples was 3.2 to 429 times the reference concentration and after Cu copper, Ni, Hg, Pb, Cd, and As had the highest concentrations, respectively (Guo et al., 2009).

Huang et al. (2015) investigated the effects of electrical waste disposal on aquatic environments in Accra, Ghana. The results showed that the amount of heavy metals such as lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) in aqueous samples is very high. Also, the old methods of recycling electronic waste lead to the release of these heavy metals. The rate of heavy metals and pollutants released from electronic wastes that adhere to sediments and thus enter aquatic environments is highly dependent on pH (Huang et al., 2015). Song et al. (2013) investigated the environmental impact of heavy metals released from e-waste recycling in China. They concluded that four types of heavy metals, copper, lead, cadmium and chromium, were released from electronic waste. To protect the environment, the recycling of electronic waste, which leads to the release of heavy metals into the environment, must be controlled (Song et al., 2013).

Some legislators, such as France, Hungary, and Czechoslovakia, see water pollution control as part of the overall water issue, while countries such as Switzerland, the Netherlands, and Belgium consider it separately from other water issues. The need to prevent and reduce water pollution is one of the most important concerns of many European countries, and gradually over time, many laws have been enacted to protect the environment or control water pollution. Few countries today do not have specific or general laws on preventing water pollution. Considering that Aras catchment area covers three northwestern provinces of the country and is an important water source for this region, and considering the multiplicity and diversity of industrial and agricultural activities along the river, in this study, the physicochemical characteristics of this river has been examined. The purpose of this study is to determine the parameters, concentrations of elements and heavy metals and finally to measure and evaluate the current situation for various uses by comparing with national and international standards.

Materials and Methods

Study area

Aras River is one of the most important rivers in Iran, which is located in the northwestern border of Iran. The river originates from the heights of Min Gul in the south of Erzurum in Turkey and flows through the three countries of Iran, Armenia and Azerbaijan with a distance of 1072 km to the Kora River in Azerbaijan and then to the Caspian Sea (Bagirov & Bravarnik, 2005). Aras River has coarse-grained bedding materials with relatively high slope, shallow depth and in some cases wide width, generally located in the middle basin or mountainous area. The area of Aras catchment is 102000 square kilometers, of which 41% (39478 square kilometers) belongs to the lands of Iran, The highest point in this basin is Sabalan peak with 4811 meters and the lowest point with a height of 20 meters is located at the outlet of Aras river located on the border of Iran and the Republic of Azerbaijan. The Aras River catchment area in Iran constitutes 22% of the Caspian Sea catchment area (Farabi et al., 2014). The water regime of this river is mainly due to snowmelt as well as streams obtained from rainfall and the existence of numerous natural springs. The maximum measured discharge of Aras River in normal years is 1100 cubic meters per second at Aras dam and 1600 cubic meters per second at

Mill Moghan diversion dam and the minimum river discharge in dry years at Aras dam is 32 cubic meters per second. The average flow of this river is 183 cubic meters at Aras dam and about 250 cubic meters per second at Mil Moghan diversion dam. Figure 1, shows the location of the Aras catchment. The study area of this research is the industries and dams located in the border area of Iran and Armenia and downstream of this area.

Fig. 1- Location of the study area

Methodology

This research is of applied type and by survey method and through sampling and laboratory studies. Sampling was performed from early 2018 to mid-2019 in selected stations. Since the studies and measurements of pollutants have been done in a one-year ruling period, as a result, seasonal changes have been observed in it. The study area included the Aras River catchment located in Iran. Based on the visits made, as well as the study of documents and reports, these areas were considered as the centers of distribution of industrial and agricultural pollutants. Table 1 shows the names and specifications of the studied stations.

Table 1: Name of the studied dams in Aras catchment

Row	River name	Province
1	Baba Ahmad	Azarbayjan Gharbi
2	Aghzaman	Ardabil
3	Anar	Ardabil
4	Inanloo	Ardabil
5	Beig Baghloo	Ardabil
6	Chokho Razmi	Azarbayjan Sharghi
7	Zenooz	Azarbayjan Sharghi
8	Sheikh Ahmad	Ardabil

Sampling containers were made of 1 liter polymer which was thoroughly washed before sampling. Samples were taken from a distance of 2 m from the water's edge and 20 cm from the river. 3 water samples were taken in each station. One for the measurement of heavy metals, one for the measurement of nitrate (NO_3^-), nitrite (NO_2^-), electrical conductivity (EC), total dissolved solids (TDS), biochemical oxygen demand (BOD), and the other for the measurement of minerals such as sodium (Na), calcium (Ca), and potassium (K). The sample for heavy metals using concentrated nitric acid was pH less than 2 acidic. To prevent the possible deposition of captions and the growth of microorganisms and also to minimize surface adsorption by the walls of the container. The samples were then transferred to a trusted laboratory. Heavy metals, iron (Fe), Pb, Cd, Cu, chromium (Cr), Zn, manganese (Mn), and cobalt (Co) were measured by atomic absorption spectrometry. NO_3^-, NO_2^-, and TDS concentrations were also measured by spectrophotometer. Concentrations of Ca, Na and K were measured with a Flame Photometer and the rest were measured with specialized devices. All samplings were repeated four times and the average number for each station was announced.

Contamination coefficient is obtained from the ratio of element concentration from the sample taken to the concentration of the same element in the background sample (Abrahim & Parker, 2008).

Equation (1)

$$CF = \frac{C_{sample}}{C_{background}}$$

The pollution load coefficient is also calculated from the following equation:

Equation (2)

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \ldots . CF_n}$$

Where CF: Pollution coefficient; n: Number of metals; $C_{background}$: amount of pollution concentration in the whole field of water; C_{sample}: The element concentration is taken in the sample.

CF>1: Indicates contamination in sediments. CF<1: It means no pollution.

If PLI is close to 1, it indicates that the load or concentration of heavy metals is close to the base concentration, and if it is more than 1, it indicates that the sediment is contaminated (Wang et al., 2013). SPSS.18 software was used to investigate the data distribution and Spearman test was used to determine the correlation. Bivariate correlation analysis was also used to describe the relationship between the parameters. High correlation coefficient (close to +1 and -1) means high correlation between two pairs of variables and values close to zero indicate no correlation between the two variables at a significant level of $P < 0.05$. Explicitly, the parameters that show r greater than 0.7 are considered strong correlations, r between 0.5 to 0.7 moderate correlations, and r less than 0.5 weakly correlations. Strong correlations between elements indicate similar input sources or similar geochemical behavior of ions. In order to analyze and interpret the results, comparative comparison of data with standard tables of pollutants was used. Table 2 shows the standard of pollutants and parameters.

Table 2: Quality standards for water parameters (Release to surface waters and agriculture)

Parameter / standard	WHO Standard	National limit	National optimal limit
Nitrate (ppm)	50	50	70
Nitrite (ppm)	0.5	0.5	1
pH	6.5 - 8.5	7 – 8.5	6.5 - 9
TDS	1400	1000	1500
Na (ppm)	200	200	200
K (ppm)	12	12	14
Ca (ppm)	200	200	350
Pb (µ/l)	10	10	20
Cd (µ/l)	3	3	5
Fe (ppm)	300	300	400
Mn (ppm)	400	400	400

(World Health Organization and National Standard) (Nooshady et al., 2009)

2. Results

The results of physicochemical parameters of the studied samples downstream of the selected dams of Aras River are presented in Table 3. According to the research findings, the concentration range of NO_3^- was 26 to 717 ppm with an average of 323. The highest amount of NO_3^- was recorded in station number 7 (Zenooz dam) and the lowest amount of nitrate was recorded in station number 1 (Baba Ahmad dam). In the case of NO_2^-, the minimum level was 0.02 ppm in station number 1 (Baba Ahmad dam) and the highest level was 0.98 ppm in station number 7 (Zenooz dam), the average was 0.67. Regarding EC, the lowest measured amount was 789 µS/cm in station number 2 (Aghzaman), the highest amount belonged to Zenooz station with 2364 µS/cm, and the average was 1645 µS/cm. Regarding pH, the lowest value of 7.64 belonged to Aghzaman Dam and the highest value belonged to Zenooz Dam with 9.23 and the average was 8.17. In the case of Na, the lowest amount of 49 ppm belonged to Aghzaman dam and the highest amount of 90 belonged to Chokho Rzami dam and the average was 67 ppm. In the case of K, the lowest amount of 5.8 ppm belongs to Baba Ahmad Dam and the highest amount of 8.2 ppm belongs to Zenooz Dam, the average of this parameter was 7.5. Also; In the case of Ca, the lowest level of 38 ppm belonged to Zenooz dam and the highest level of 81 ppm was measured in Baba Ahmad dam, the average of this parameter was 64. The TDS were measured with the lowest amount of 568 ppm in Baba Ahmad Dam and the highest amount in Zenooz Dam with 1920 ppm.

Table 3: Descriptive statistics of physicochemical parameters of samples extracted from downstream of the studied dams in Aras River (Sample number = 4)

Parameter	Unit	Minimum	Maximum	Average	Standard deviation
NO_3	ppm	26	717	323	187.64
NO_2	ppm	0.02	0.98	0.67	0.45
EC	µS/cm	0.789	4.346	3.145	345.66
pH	-	7.64	9.23	8.17	0.43
Na	ppm	49	90	67	11.1
K	ppm	5.8	8.2	7.5	0.56
Ca	ppm	38	81	64	11.46
TDS	ppm	568	1920	1211	469.07
Pb	ppb	0.05	0.2	0.09	23.2
Cd	ppb	0.02	1.78	0.8	15.11
Cu	ppb	0.6	29.1	11.7	5.97
Mn	ppb	6.7	88.16	7.9	18.63
Cr	ppb	9.66	38.26	12.45	9.67
Co	ppb	12.78	181.36	57.89	34.74
Fe	ppb	7.6	292.31	88.92	87.17
Zn	ppb	1.9	69.87	11.87	11.53

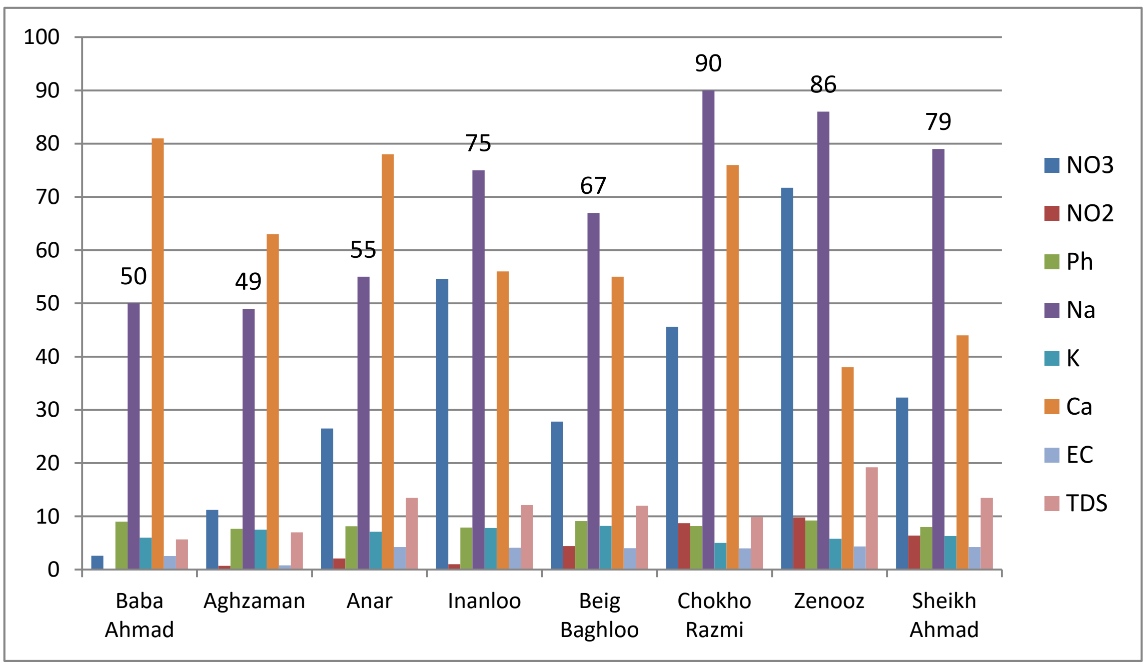

Fig. 2- Comparative diagram of measured parameters in selected stations (Source: Research Findings)

According to the Pearson correlation analysis of measured parameters in the study area, there is a significant correlation between EC, TDS and heavy metals parameters at the level of 0.01. On the other hand, there is also a correlation between the parameter of Fe and EC at the level of 0.01. There is, moreover, a correlation between Ca and K parameters at the level of 0.01. On the other hand, there is a correlation between NO_3^-, NO_2^-, Na, Ca, K, and TDS. However, the pH parameter had no correlation with other parameters.

3. Discussion

Rivers have historically been one of the main resources of water used by humans; current water is considered in terms of biology and fishery. Surface water has a great potential for contamination human societies and industrial centers (Jalili, 2020). Since water salinity is a function of two parameters of EC and TDS, EC less than 0.7 µs/cm does not limit plant growth and the range between 0.7-3 µs/cm indicates average limit and rate higher than 3 µs/cm indicates a high limit, by comparing the research results, it is determined that the lowest EC in the measured samples is 0.789 and the maximum is 4.346 µs/cm, which in principle indicates a high limit of soil and water for irrigation of plants. The Wilcox diagram is plotted for the relationship between electrical conductivity and sodium parameters (Fig. 3).

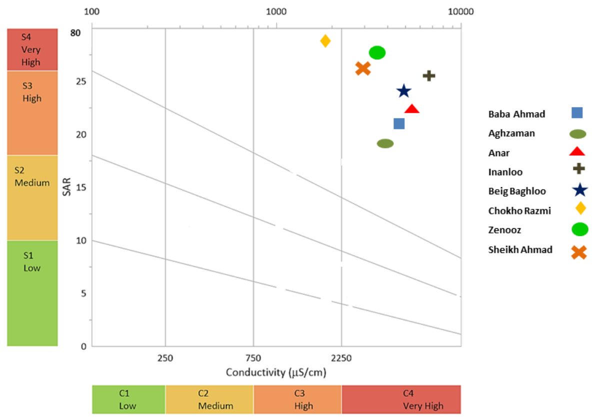

Fig. 3- Wilcox diagram for the relationship between electrical conductivity and sodium parameters (Source: Research Findings)

On the other hand, TDS are also considered as the second parameter affecting water salinity. Accordingly, if the measured rate is less than 450 ppm, it indicates no limit and the range between 450-4000 ppm indicates a moderate limit and above 2000 ppm indicates a severe limit. The results show that the mean measured for this parameter in the study area is 1211 ppm, which indicates a moderate limit for salinity. However, the results indicate that with the exception of Baba Ahmad Dam, other areas have moderate to high limits for this parameter. In addition, the national allowable limit for this parameter is 1000 ppm and the optimum national limit is 1500 ppm, the average result (1211 ppm) is beyond this range. Also; regarding pH, the recorded average for the study area is 8.17, which is within the national permissible and standard range of the WHO, but in 2 points (Beig Baghloo and Zenooz) was above the national permissible and permissible range. In the case of NO_3^-, the permissible limit of the WHO and the national standard is 50 ppm, the average of which was 323 ppm, and in the case of NO_2^-, the permissible limit of the WHO and the national standard is 0.5 ppm, which is the average. Measured is 0.67 ppm. Both cases indicate that it is higher than the allowable limit, which naturally requires the use of treatment methods for use as drinking water or irrigation for agriculture.

Regarding K, it can be said that the standard of the WHO and the national limit for this parameter is 12 ppm and the optimum national limit is 14 ppm. According to the mean obtained in the study area (7.5 ppm), it can be said that this parameter is within the allowable and standard range. Regarding Ca, it can be said that the standard of the WHO and the national limit for this parameter is 200 ppm and the optimum national limit is 350 ppm. According to the mean obtained in the study area (64 ppm), it can be said that this parameter is within the allowable and standard range. Even the maximum area limit (83 ppm) is within the allowable range. In the case of heavy metals; In the case of Pb, the WHO standard and the national permissible limit for this parameter are 10 ppb and the optimum national limit is 20 ppb. According to the mean obtained in the study area (0.09 ppb), it can be said that this parameter is within the allowable and standard range. Even the maximum area limit (0.2 ppb) is within the allowable range. In the case of heavy metals; In the case of Cd, the WHO standard and the national limit for this parameter are 3 ppb and the optimum national limit is 5 ppb. According to the mean obtained in the study area (0.8 ppb), it can be said that this parameter is within the allowable and standard range. Even the maximum range (1.78 ppb) is within the allowable range. Regarding Fe, it can be said that the standard of the WHO and the national limit for this parameter is 300 ppm and the optimal national limit is 400 ppm. According to the mean obtained in the study area (7.9 ppm), it can be said that this parameter is within the allowable and standard range. Even the maximum area limit (88 ppm) is within the allowable range. Regarding Mn, it can be said that the standard of the WHO and the national limit for this parameter is 400 ppm and the optimum national limit is 400 ppm. According to the mean obtained in the study area (88.92 ppm), it can be said that this parameter is within the allowable and standard range. Even the maximum area limit (292 ppm) is within the allowable range.

Considering the correlation between NO_3^- and NO_2^-, and their similar sources and conversion of NO_3^- to NO_2^- during the chemical process, it can be concluded that the high concentration of these variables is due to improper use of pesticides and chemical fertilizers used in agriculture and the entry of municipal wastewater and it can be industrial.

In the case of EC and TDS, the proximity of the variables affecting these two variables can indicate the same sources affecting them, most of which is pollution caused by the entry of municipal and industrial wastewater. The correlation between sodium and EC is due to the direct effect of Na on EC levels. In principle, Na is one of the main factors in the formation of EC.

As mentioned in the introduction, the main source of heavy metals entering the Aras River is factories and industries located in Azerbaijan and Armenia. In the meantime, it seems that dam construction causes an increase in nitrate and nitrite and other parameters.

The results of the present study are similar to some studies conducted in the study area, which include: Javadinehad et al., (2014) and Aazami & Taban (2019). As a recent study has shown, the amount of heavy metals in the Aras River at some stations has been higher than national and international standards. On the other hand, as the results of the Bakhtiari (2019) study show, other countries bordering the Aras River, especially Armenia, should make more commitments to protect the Aras River environment. Aspects of environmental rights in this river are not fully observed and all kinds of environmental pollution can be observed in it.

Conclusion

According to the research results, it is clear that the 4 parameters nitrate, nitrite, EC and TDS have an average higher than the national standard and the other parameters are lower than the standard in terms of average. However, in some stations, numbers higher than national and international standards have been seen. The highest level of pollution is observed in Zenooz and Chokho Razmi stations. It seems that the only way to deal with the pollution caused by the industries around the Aras River is to apply the approach of environmental law by the Commonwealth. The issue of water pollution is one of the serious dangers that threatens water resources and with the increase of population and the growing development of the country, not only this sensitivity has not decreased, but it has become more and more complex and its problems have become more serious and the need for basic planning to determine quality privacy, and makes the quality protection of water resources and the prevention of their pollution more obvious.

4. Conflict of interest

The authors declare that they have no conflict of interest.

5. Additional Information And Declarations

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Grant Disclosures

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Competing Interests

The author declare there is no competing interests, regarding the publication of this manuscript

Author Contributions

Ebrahim Safizadeh: Prposed the plan and analyzed the data.

Dariush Karimi: Conceived the experiments

Hamid Reza Ghafarzadeh: Authored or revised drafts of the paper

Seyed Abbbas Pourhashemi: Approved the final draft.

Ethics Statement

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