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## ***Investigation of Hydrogeochemical Characteristics of Hajilarchai Basin and Origin of Trace Elements***

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### **1-Introduction**

Water resources are vital to living things because of their essential. Therefore, the issue of water pollution is of special importance. The type and concentration of major elements, sub-elements, and trace elements in water depend on aspects e.g. geographical conditions, the availability of rock and soil elements, the origin of rocks and soil in contact with water, and dissolution reactions between rock and water. Contaminants of surface and groundwater resources of natural or geogenic origin may be caused by volcanic activity, natural rock erosion, or anthropogenic activities for instance agriculture, animal feed, mining, and the entry of municipal and industrial wastewater. Beyond the amount of elements of the standards is known as pollution. Some metals (copper, iron, zinc) are essential in small amounts for living organisms, and their deficiency interferes with the body's normal functioning, but is toxic in large quantities, leading to organ damage and poisoning. Trace elements can enter plant and animal tissues through water contact with soil and eventually into the food chain .

Mining, mineral processing, and metallurgical extraction are the three main activities of the gold mining industries that can produce waste. Metallurgical extraction breaks the crystallographic bonds in the ore mineral to recover the desired element or compound. Large amounts of waste may be generated during this activity. Especially in gold mines that release more than 99% of the extracted ore as waste in the environment.

Cyanide used in gold mines is another significant environmental concern. Cyanide is a group of nitriles composed of carbon and nitrogen and is found naturally in some fruits e.g. most bitter seeds, apple seeds, peach kernels, plums, bitter almonds, bamboo shoots, and cassava roots. Cyanide products are used in various industries such as gold and silver

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mines and metallurgical plants. Cyanide ions can enter the environment through wastewater and pollute soil, air, and water sources, which are of great importance due to their high toxicity. Current studies have studied aspects of cyanide behavior in environmental considerations in gold-related mineral processing operations. In the discharge of cyanide solution into the environment, the cyanide concentration is naturally reduced by various mechanisms such as complexation, volatilization, sulfidation, adsorption, precipitation, and biological conversion.

The emission rates of these metals and cyanide compounds have increased in the twentieth century due to the development of mining activities. As the emission of these metals increases, their impact on the lives of plants and animals has enhanced. Therefore, in recent studies, the origin of elements and compounds affected by the mining and industrial activities in water has been investigated to determine the extent of emissions from anthropogenic and geogenic sources and their fate. The present paper examines the hydrochemical properties of the area and then uses multivariate statistical techniques to identify possible sources of elements.

## **2-Methodology**

### **2-1-Hydrogeological, geological characteristics of the Study**

The study area is located in East Azerbaijan province, in the north of Tabriz and the western part of Varzeqan city and with an approximate distance of 26 km from Varzeqan. The study area consists of 5 sub-basins of Goy Chai, Boyerk Chai, Miverood, Eri Chai, and Hajilarchai, which finally join the Aras River and flow into the Caspian Sea. Due to the location of the Zarrin Dagh Astarcan Gold Factory in the mountainous lands of the basin, with relatively sharp topographic conditions, there is a possibility that the factory will affect the catchment area. According to the Emberger method, the region is known as a semi-arid and cold climate with an average annual temperature of 10.06 ° C. The study area is located in the division of tectonic-sedimentary units of Iran in the Alborz-Azerbaijan zone. The zone of Azerbaijan is covered with Mesozoic to Quaternary sediments, Tertiary-Quaternary volcanic zone, Neogene-Quaternary Intermountain basins. The oldest rock units found in this basin are related to limestone, sand, and Paleozoic shales of the Devonian and Carboniferous periods of Qarahdag Mountain.

In this study, graphic methods such as Piper and Steve diagrams and multivariate statistical methods were used to investigate the hydrochemical properties of water resources to find the source of existing abnormalities. Piper and Stiff diagrams are used to determine the chemical characteristics and source rock of the elements, respectively. Factor analysis and cluster analysis are the most common multivariate statistical techniques used to detect source trace elements and their relationship patterns.

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### 3-Results and Discussion

The location of the samples in the piper diagram shows that the types of water studied are calcium and bicarbonate with temporary hardness except for sample 10. The predominant type of sample 10 is mixing. Stiff diagrams were used to determine the origin of water samples. Based on the stiff diagram drawn for sampling and matching pattern samples, samples 1, 2, 3, 4, 5, 6, 7, and 8 have limestone origin, sample 9 has an igneous origin, and samples 10 and 11 have the origin of limestone. The reason for the high chloride in samples 10 and 11 obtained from factory piezometers is probably the use of calcium hypochlorite in soil treatment activities .

The factor analysis method has been used to determine the factors affecting the water quality of the Hajilarchai basin. Four main factors for the hydrochemical process were identified in the study area. The first factor that is more effective on water quality includes potassium, calcium, parameters of sodium, magnesium, bicarbonate, chlorine, sulfate, barium, EC, cobalt, lead, zinc, nickel with a positive factor loading and pH, with a negative factor loading. This factor reflects the general trend of water and the effect of evaporitic and saline formations. The high factor loads of the trace elements cobalt, nickel, lead, zinc, and bromide shows that these metals are of geogenic origin. The second factor includes nitrate, ammonium, and fluoride with a high operating load. The presence of the nitrate parameter shows the anthropogenic origin of this factor. The third factor includes cyanide and copper. The fourth factor includes manganese with a positive factor loading and arsenic with a negative factor loading. These two factors seem to be of geogenic origin.

Hierarchical clustering (HC) was used to classify the data. HC analysis was conducted once for the parameters and once for the samples. The samples were split into three categories, the first and third clusters representing the origin of geogenic and the second one representing anthropogenic activities. The parameters were divided into two clusters and five sub-clusters. The parameters in each sub-cluster indicate their common origin and high correlation.

### 4-Conclusions

The results of this study showed that the watercourse of the study area has high amounts of calcium and bicarbonate. It was also found that lithology plays a major role in hydrochemistry and water quality. The outcomes of multivariate statistical analysis indicate the impact of geological formations and anthropogenic activities on watercourses in the region. The origin of trace element concentrations in water sources was identified using factor and hierarchical cluster analysis methods. The effect of anthropogenic activities is also visible in the basin.

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**Keywords:** hydro chemistry, multivariate statistical analysis, trace elements, Hajilar Chai Basin, Northwest of Iran.

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