



Study of environmental pollution caused by natural processes on soil, water and plants in metallogenic zone of northern Ardebil

Gholamreza Ahmadzadeh^{a*}, Alireza Saffari^b, Sahar Mostafaei^c

^a Department of Geology, Faculty of Science, University of Mohaghegh Ardabili, Ardabil, Iran

^b Department of Geology, Faculty of Natural Science, University of Tabriz, Tabriz, Iran

^c Masters student in watershed management, Tarbiat Modares University, Tehran, Iran

ABSTRACT

Mineral and alteration zone of north Ardebil, located at 27 kilometers of north west of Meshkinshahr. Given that a large part of the North West of the country, particularly along the zone of the garehDagh- Tarom are altered and mineralized, so study of this area can be very useful. Based on a sampling and chemical analysis of water, soil and plants, the heavy metals changes were evaluated and Practical solutions for the protection of environmental resources of study area and improve their conditions were proposed. heavy metals are one of The most important sources of water, soil and planet pollution that originate from rocks destruction. Toxic heavy metals eventually accumulate in the soil and enters through plants and water to the food chain of animals and humans. Mineralization and related altration processes in the study area led to extensive chemical and physical changes in igneous rocks and thus affected the distribution of metallic elements in the environment. A comparison between the total concentration of trace elements with sulfur, aluminum, iron plus manganese and particles smaller than 63 Mykrvmeter indicate The existence of a negative correlation between these elements with sulfur and the other hand existence of a positive correlation between these elements with Al and small particles of soil. However, the role of sulfides and fine particles is essential in absorption and enrichment of them in environment.

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*corresponding author

E-mail address:
g_ahmadzadeh@uma.ac.ir
(Gh. Ahmadzadeh)

1. Introduction

The purpose of this project is to investigate the level of soil, water and plant pollution in the study area caused by heavy metals and also to determine the source of these contaminants. Given that the elements are toxic in certain oxidation states, it is very important to determine their classification. Rock degradation in mineralization and alteration areas can be considered as a center for decentralized natural pollution, since the Qara Dagh-Tarom zone in the northwest of the country is a metallogenic zone (With extensive mineralization and alteration areas) and extensive mining activities have been carried out or are being carried out in some of its areas.

It is necessary to study the possibility of pollution of such areas from an environmental point of view and the problems that have arisen in their water and soil resources. This seems to be because heavy and toxic metals eventually accumulate in the soil and enter the animal and human food cycle through plants or water (Colin, 1995). Oral reports from district health officials, as well as field studies of indigenous peoples, indicate that one of the leading causes of death in rural areas is fatal gastrointestinal and lung diseases, especially cancer. Several cases of MS and skin diseases have also been reported in the area over the past few years.



Due to the large number of diseases and illnesses in a village with a small population (approximately 1000 people), the importance of

environmental studies in the region becomes clearer.

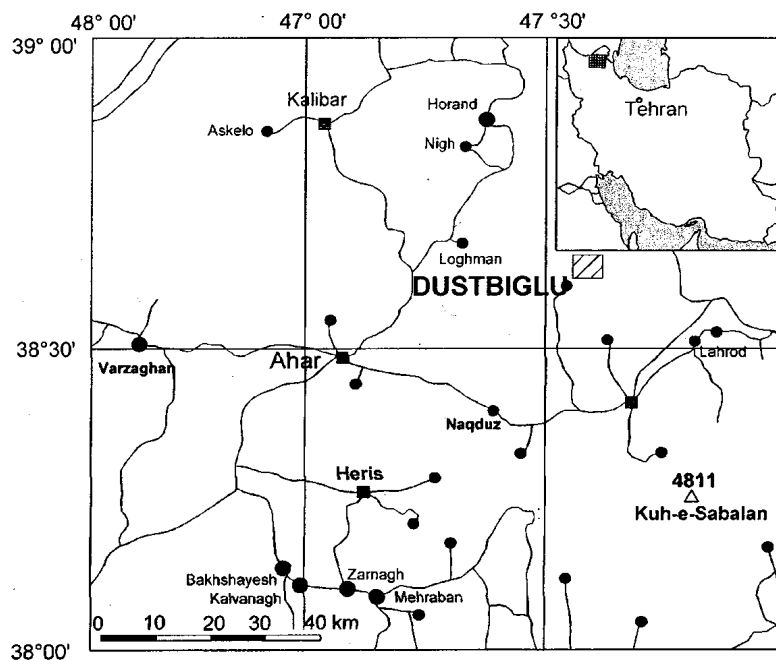


Fig. 1. Map of the study area (the rectangular figure shows the study area)

2. Material and Methods

2.1. Office studies

During these studies, after collecting previous information, altered areas and mineralization using topographic maps 1: 250000, 1: 50000 and aerial photographs with scale 1: 20,000 was prepared with geological information. In these maps, while drawing the homogeneity of different lithologies and the phenomena of mineralization and alteration resulting from them, important tectonic structures such as faults were identified. While studying the aerial photographs and existing topographic maps, a hydrographic map of the area was prepared and rivers, streams, springs and water wells were shown.

2.2. Field studies

2.2.1. Soil, water and plant sampling stage and preparation

2.2.1.1. Soil: For chemical analysis of agricultural, garden, rangeland and barren soils, tampered samples were selected from about 70 points selectively. After harvesting soil samples weighing approximately one kg, 500 g was stored as a control sample and 500 g was transferred to the laboratory for chemical

analysis. The samples were chemically analyzed by ICP-Ms method and the amounts of heavy metals were measured with an accuracy of parts per million.

2.2.1.2. Water: 20 water samples were collected from wells, springs, waterways and Qarasu river in alteration and non-alteration areas on a case-by-case basis. These samples are chemically (CO_3^{-2} , HCO_3^- , SO_4^{-2} , K^+ , Na^+ , Mg^{+2} , Ca^{+2} , pH, EC, TH, TDS and Cl^-) were analyzed.

2.2.1.3. Plant: In this research, plant sampling has been done in two stages:

A) Herbarium specimens: The main rangeland plant species and some crops were transferred to herbarium after collection and pressing and after drying, they were pasted on the relevant sheets. All information about each plant was written on the side form and identified using available botanical sources.

B) Sampling for chemical analysis: 12 species of main plants were selected from the identified species and about 5 kg were collected from their aerial parts. Plant samples were stored in perforated, disposable plastic bags. The shoots collected from each plant were washed and dried separately. Then, they were transported to the laboratory by sample bags to prepare ash and perform chemical analysis by ICP method.

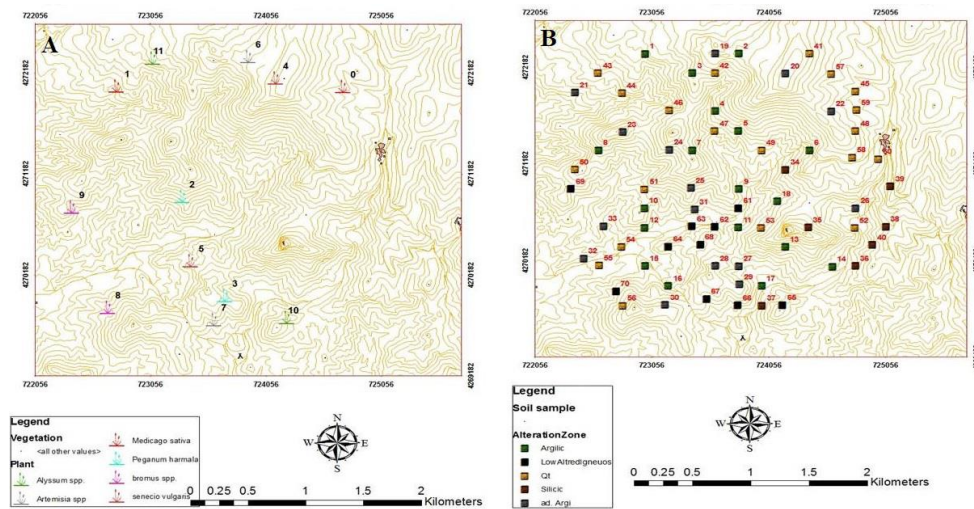


Fig. 2. Position of soil and plant samples

2.3. Analysis of results

2.3.1. Soil: In order to study the contamination of soil samples in different alteration zones, the amounts of heavy metals were compared with the existing standards for soils and the severity of their contamination was determined. The enrichment factor is also calculated based on the ratio of the concentration of an element to its average concentration in the Earth's crust. These factors are more calculated than elements such as aluminum, iron, titanium or zirconium that are less mobile. In this study, the titanium enrichment factor is calculated as follows:

$$EF = \frac{\left(\frac{X}{Ti}\right)_{\text{Soil}}}{\left(\frac{X}{Ti}\right)_{\text{Crust}}} \quad (1)$$

2.3.2. Water: In order to study the geochemical characteristics of the waters of the region, the simplest method is to draw chemical diagrams. In the second stage, comparing the concentration of copper in the water with the existing standards clarifies the severity of their pollution. In this study, the effect of alteration zones on the quality of water resources in two separate sections, the effects of geochemical and chemical (Chemical parameters of water such as pH, EH, cations and anions) are investigated and Water chemistry diagrams are drawn for water samples.

2.3.3. Plant: For more and more accurate study of plants, in addition to comparing the concentration of heavy metals with existing standards, different coefficients have been used, which are mentioned below:

A) Calculating the transfer coefficient of elements to the plant: The transfer coefficient of partial elements to the plant (TF), also known as the biological accumulation rate (BR) is a good

way to determine the amount of absorption of elements by the plant. This coefficient is calculated by dividing the concentration of the element in the aerial tissue of the plant by the total concentration of the element in the topsoil (root penetration):

$$(My) \text{ Element concentration in soil} / (Mx) \text{ Element concentration in the plant} = (TF) \text{ transfer coefficient}$$

B) Calculation of Bioconcentration Factor (BCF): This factor, which shows the accumulation of metal elements in a plant organ, has been calculated to assess the absorption and contamination of elements in the plant:

$$BCF = \frac{Tecp \left(\frac{mg}{kg}\right)}{Tecw \left(\frac{mg}{l}\right)} \quad (2)$$

Tecp: Concentration of a metallic element in the aerial parts of the plant

Tecw: Concentration of metallic element in groundwater (average concentration)

3. Results and discussion

3.1. Contamination and enrichment of metals in the soil

The results obtained from the decomposition of soils in the region with the allowed values and existing environmental standards showed that the contamination of soils with heavy metals is severe and the concentration of these elements is higher than the standard values. According to Jung (2001) contamination index values, 55.7% of the samples are infected with $PI > 1$. Also, due to the widespread use of enrichment factor, as a suitable method in determining soil contamination (Kabata-

Pendias and Pendias, 2001; Swartjes, 1999), this coefficient has been calculated for all soil samples. Based on this parameter, most of the soils of the region can be considered contaminated, so that the concentration of most toxic elements in more than 50% of the soil samples in the region is completely concentrated. Considering the similarities

between the results of comparing the concentration of toxic elements with the standards and their permissible limits, enrichment factors and pollution indices, it can be concluded that most of the samples decomposed from the soil of the region are contaminated.

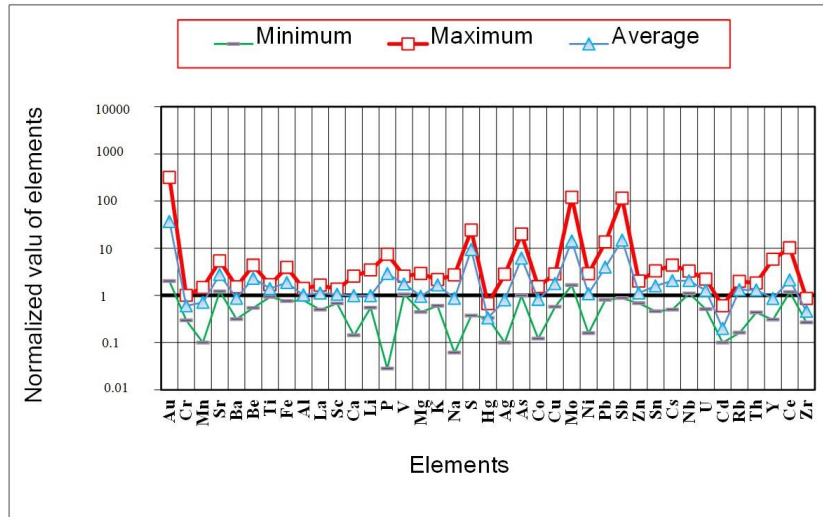


Fig. 3. Comparison of normalized concentrations of elements with standard values

3.2. Estimation of Bioconcentration factor in plants

From the types of plant species found in the study area, 6 types of plants that constitute a large amount of vegetation in the study area and are grazed by livestock are selected, and for further study, two of each Samples were sampled at different locations in the area. Each of the samples contains different elements that

X can be poisonous for grazing livestock and the plant itself. Also, in order to identify the species that can store toxic elements in their roots and thus prevent these elements from entering the biological cycle through grazing, botanical studies were conducted on other plant species in the study area. Table 1 shows the types of plant species selected from the study area and the characteristics of the harvest site.

Table 1. Plant samples (genus) selected from the research site and characteristics of the harvest site

Row	scientific name	Type of cover	Soil origin
1	Medicago sativa	Crop and garden	Quaternary deposits
2	Medicago sativa	Crop and garden	Quaternary deposits
3	Peganum harmala	Rangeland	Advanced argillic
4	Peganum harmala	Rangeland	Igneous rocks
5	Senecio vulgaris	Rangeland	Advanced argillic
6	Senecio vulgaris	Rangeland	Igneous rocks
7	Artemisia spp.	Rangeland	Argylic
8	Artemisia spp.	Rangeland	Igneous rocks
9	Bromus spp.	Rangeland	Igneous rocks
10	Bromus spp.	Rangeland	Igneous rocks
11	Alyssum spp.	Rangeland	Igneous rocks
12	Alyssum spp.	Rangeland	Argylic

Plants easily absorb minor elements in both ionic and complex states, Kabata-Pendias and Pendias (2001) showed that pH, regenerative

conditions, organic matter and the presence of competing elements (such as calcium, magnesium and phosphorus) affect the

bioavailability of minor elements in the soil. Under oxidation conditions characterized by a pH of approximately 3, the bioavailability of cadmium, cobalt, copper, nickel, and zinc is high (Kabata-Pendias, 2004). The availability of other trace elements (including arsenic) is lower under similar conditions. The plant species collected from the area show the Bioconcentration of heavy metals. The main cause of Bioconcentration of these elements in plants is lack of nutrients, which increases the absorption of some metallic elements by these plants (Bhattacharya et al., 2006). Among cations, arsenic is absorbed by plants more than the solid phase than the aqueous phase, because arsenic can also be present as an anion (Bhattacharya et al., 2006). The values of Bioconcentration factor (BCF) calculated for Aerial organs of plants in the study range indicate a significant accumulation of toxic elements in them. Despite soil pollution, the high concentration of these elements varies in different species of the region. Increasing the concentration of toxic metals in plants is only accepted to increase it by $\frac{1}{2}$ to $\frac{1}{10}$ in the soil (Bohn, McNeal and O'Connor, 1994), so the concentration of arsenic multiplication to several tens of times in the plants of the region indicates Severe pollution in them. Animal poisoning problems usually occur when infected plants are their only food. Therefore,

livestock whose grazing is limited to the contaminated areas under study are expected to exhibit the most severe effect of toxic metal accumulation. The results also show that the amount of heavy and toxic metals that are deposited on plants through the air and dust and then enter the bodies of livestock and locals, is much higher than the amount that is absorbed by plants and drinking water.

3.3. Measurement, classification

Determining the classification is important because some elements are toxic in certain states, in other words, the overall concentration of the metal obtained by the decomposition apparatus does not well determine the toxicity of the metal. In fact, it must be determined whether the metal produces toxicity in free form or in combination with other ligands. Due to the fact that the methods used to directly determine the classification are not EPA approved, special thermodynamic software such as MINTQA2 for measuring the classification based on inputs such as total metal concentration and pH is prepared according to the basic data available in these systems as well as the defined reactions that can determine the classification. Based on this, the total concentrations and pH of the samples were entered into the software and the results of Table 2 were obtained. Which is calculated as a sample for the copper element.

Table 2. Distribution of copper element among its different species in the aquatic environment (percentage)

Row	$\text{CuCO}_3(\text{aq.})$	$\text{CuSO}_4(\text{aq.})$	$\text{Cu}_2(\text{OH})_2^{+2}$	$\text{Cu}(\text{OH})_2(\text{aq.})$	CuOH^+	Cu^{+2}	other
1	53.9	3.1	1.4	-	12.4	25.2	1.3
2	76.8	-	3.3	1.1	11.2	8.8	1.8
3	65	5.2	1.3	-	11.6	15.1	1.8
4	69.3	3.3	-	1.3	13.2	11.6	1.3
5	61.2	4.7	-	1.1	14.8	17.3	0.9
6	67.4	1.6	1.5	3.8	17.9	6.9	0.9
7	50	3.5	1.3	-	15.8	28.1	1.3
8	52.6	10.9	6.4	-	12.2	16.1	1.8

The water conditions of the region are such that among inorganic complexes, metal-carbonate complex is predominant and hydroxide complexes are of secondary importance (Table 2), considering that copper has a high tendency to form organic and inorganic complexes, The percentage of free Cu^{+2} is low, so the toxicity of copper should be lower than expected, because the total concentration of copper metal alone does not determine its toxicity. In other words, a small percentage of all copper in the waters of the region is free and toxic.

Discussion

Soil pollution cannot be excluded from environmental pollution because soil is one of the most important pillars of the environment and contaminated soil can also pollute surface and groundwater. Plants can also be contaminated by absorbing metallic and mineral elements from the soil. Below we examine the key factors in the transfer of elements from soil and water to plants and thus the food cycle of humans and animals. Plants usually derive their

mineral components from the soil. The minor exceptions are nitrogen and sulfur gases, which are absorbed directly from the atmosphere by the leaves, as well as ions that enter the plant through dust caused by fertilizer spraying on the leaves. Under natural conditions, the main factors in the absorption of nutrients by plants can be the presence or absence of the element in the soil, the degree of composition and rate of extraction from solid soil phases, the activity of soil microorganisms and Differentiation of plant roots while absorbing nutrients from the soil (Bohn, McNeal and O'Connor, 1994). In this article, only the first case and small amounts of elements from the point of view of toxicity concentration will be discussed. Although it is very difficult to define toxic values for plants or animals that feed on these plants, many researchers have tried to define standard values for most of the metallic elements present in soils and thus separate contaminated soils. Murrman and Koutz (1972) report the natural concentrations of elements in the soil that are considered toxic. The average limit of a number of elements whose increase in concentration to more than the mentioned values is considered toxic is presented by Quick, 1988, ZarriKafsh, 1997. Also, most of the elements of different pollution categories based on their concentration have been prepared and published by Gieseler (1987) and the Department of Environment (1980). Other standards are suggested, as shown in Tables 8 and 9 of the Appendix. There is no definitive answer to the question of what concentrations of elements are poisonous to plants because the concentrations of toxic agents in them are unknown to most plants and also change with growing conditions. However, plants are far more resistant to high concentrations of trace metals than livestock, Soil accumulation, plant root inhibition, and limited mobility to plant aerial parts all prevent trace metal ions from entering the animal food chain, but the concentration of elements in many plant species has been proven (Bohn, McNeal and O'Connor, 1994). Vinogradov (1977) investigated the ability of plants to concentrate some trace elements and identified two types of group and selective concentration in plants. In the concentration of the first type, all plants that grow in a certain area have higher amounts of some specific chemical elements, which depends on the presence of these elements with relatively high concentrations in the soil and in

the rocks below. In the concentration of the second type (selective), in certain plant species, the accumulation of special chemical elements takes place. Since there is a correlation between the distribution of trace and metallic elements in plants and bedrock and soil on them, the values of element anomalies in plants should be consistent with the geochemical anomalies of that element in bedrock and soils (Beus and Grigorian, 1977). Today, there is ample evidence to suggest excessive levels of trace elements in plants growing on contaminated soils. It should also be noted that different plant species usually differ significantly in the amount of accumulation of trace metal elements. This is indicated by the concentration coefficients of rare and trace elements in different plant species relative to the amount of these elements in the soil. Therefore, despite the soil contamination, the high (1994) concentration of elements in different species may be different. Bohn, McNeal and O'Connor emphasize that the increase in toxic metal concentration in plants is only by $\frac{1}{2}$ to $\frac{1}{10}$ the increase in soil. As a result, the concentration coefficients of different elements can be calculated for different plant species in infected and non-infected areas and then the plants that transfer the elements can be identified. There are no comprehensive statistical data on the distribution of trace metal elements in plants, but the available data can be used for general studies (Bohn, McNeal and O'Connor, 1994). Soil pollution caused by smelters, municipal and industrial wastes, pesticides as well as mineral areas can increase the concentrations of metallic elements in soil environments to toxic levels. However, animal poisoning problems usually occur when the infected plants are their only food. Therefore, livestock grazing in contaminated areas are expected to show the strongest effect of toxic metal accumulation. The amount of heavy and toxic metals that enter the body of livestock and locals through the air and dust on plants may be much higher than the amount that is absorbed by plants and drinking water, because of the low vegetation. Also, the softness and fineness of soil particles in these areas, especially in low rainy seasons, metal and toxic elements are dispersed in the air by atmospheric factors such as wind and rain along with soil particles and settle in the aerial parts of plants, easily enters the animals' bodies through food. Therefore, doubling the concentration of these elements in

the body of livestock in the region is not unexpected. Summarizing plant studies, it can be concluded that the accumulation of metals in plants is much more complex than rock, soil and water. The plant is a living organism and, depending on its needs, absorbs only certain elements in certain amounts and oxidation states. The absorption of metals varies greatly between different plant species as well as between different organs, making this issue much more complicated. Examination of the accumulation of metals in the studied plants also shows well that any plant accumulates a certain element. This feature of plants (selective accumulation) is widely used in the remediation of polluted environmental resources. This solution mostly uses plants that are resistant to poisoning as well as plants that concentrate toxic elements in their roots. Therefore, a more detailed study of plants in the region seems to be very useful and necessary both in terms of obtaining a more accurate estimate of the extent and severity of pollution and to provide a suitable method for improvement (green refining).

4. Conclusion

Samples collected from surface and groundwater, soil and plants in this study contain higher concentrations of heavy metals than the standard and conventional values set by the international institutions providing the values. High concentrations of arsenic in water (above 100 parts per billion) and soil (above 100 parts per million) are significant. The presence of large changes in the concentration of toxic elements indicates that both physical properties (grain size) and chemical properties (pH, secondary phases such as sulfides, iron oxides and clay minerals) play an important role in the dispersion of this element in the environment. Low pH dissolves heavy metals and transports them to more distant places. The calculated enrichment coefficient for soil samples is very high (above 120). Also, plant samples taken from different types show the accumulation of heavy metals in them. However, some plants that grow in the area (such as *Festuca rubra*) are resistant to metal poisoning. Therefore, green refinement can be considered as a potential improvement method. The presence of sulfide and oxide minerals such as pyrite, chalcopyrite, galena, sphalerite, molybdenite, hematite, magnetite, limonite, etc. in the area can be

effective in absorbing metal elements. XRD analysis of soils in the region indicates the presence of clay and aluminosilicate minerals such as kaolinite, Jarosite, illite and alunite as the main phase in the region. The large surface area and negative charge of these minerals can act as the main adsorbents of metals. Comparison of the results obtained from the decomposition of soils in the region with the allowable values and environmental standards showed that soil contamination with Gold, iron, vanadium, sulfur, copper, molybdenum, Plumbum, antimony, and arsenic are strong, and the concentrations of many other elements are higher than standard. Based on the values of contamination index, 55.7% of the samples are infected with $PI > 1$. Also, according to the calculated enrichment factor, most of the soils of the region can be considered contaminated, especially elements such as arsenic, copper, molybdenum, zinc, Plumbum, vanadium and antimony in more than 50% of the soil samples of the area are completely concentrated.

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