

Hydrological and geochemical processes controlling the origin and transport of Arsenic in the Pangi area (NW Torbat Hydarieh, Iran)

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Abstract—In this study, arsenic concentration and pollution in water resources of Pangi area (Kadkan, NW Torbat Hydarieh), adjacent to Sarhang- Golbou ophiolitic zone, is investigated. Results of this study indicate high concentrations of arsenic in local water resources as arsenic concentration is 12 times greater than standard values in Golbou. Aquifer lithology, hydrological gradient, and water geochemistry of Roudeshour and adjacent areas show that the same processes control arsenic concentrations in surficial and ground water resources. As-bearing sulfide minerals especially pyrite and arsenopyrite are the main origin of arsenic in water resources. In spite of that, arsenic remaining time and mechanism of diffusion in water phase is controversial. According to geochemical studies, arsenic can be released at and close to surface of aquifer and then during geochemical reactions it can be transferred to depth. States of arsenic diffusion in aqueous phases depend on oxidation of As-bearing solid materials and displacement of antagonistic ligands. In presence of sulfides and reducing conditions, thioarsenic is dominant form of arsenic but in oxidizing conditions arsenate is dominant form. Thus, solution of Fe oxy-hydroxides together with arsenic diffusion, is the main agent of high concentration of arsenic in local water resources.

Keywords—Arsenic, Ophiolite, Pangi, Sulfide Minerals

I. INTRODUCTION

Arsenic is a metalloid of environmental concern due to its toxic properties that is found as trioxide and pentaoxide [8]. It is one of the most dangerous inorganic pollutants for the environment and human health, Minerals containing arsenic

are mostly observed in hydrothermal deposites [23]. Furthermore, it's observed in some volcanic rocks [6]. Arsenic can attain high concentrations in sulphide ore assemblages, where it is mainly found in sulphides and sulphosalts, such as arsenopyrite, arsenical pyrite, orpiment, realgar, enargite and tennantite, which are typically concentrated in metalliferous deposites. Mining of these deposites derives into arsenic pollution. Weathering and erosion of As-bearing minerals releases arsenic into surface water and ground water resources [20] that finally arsenic can remain in solution or be trapped by adsorption on secondary phases and colloids or by coprecipitation reactions [17]. Arsenic occurs in four oxidation states that include arsenic (0), arsenic (3⁻), arsenic (3⁺), and arsenic (5⁺) [13]. The possible mobilization of arsenic in the soils, and subsequent leaching into ground or surface water or entry into the human food chain, should always be considered as a serious hazard [6]. Based on WHO, a number of water resources has been identified with geogenic arsenic concentration exceeding 10 µg/L, WHO Guidelines [30] in most of the affected regions in the world. However, concentration of arsenic in drinking water is advised to be lower than 5 ppb [24], As well as, according to Institute of Standards and Industrial Research of Iran (ISIRI-1053) [1], the maximum permissible levels of arsenic in drinking water is 10 micrograms per liter.

The arsenic contamination has been acknowledged as a major public health issue by the World Health Organization [29]. Based on epidemiological data, arsenic is classified as a Group A and Category 1 human carcinogen by the US Environmental Protection Agency [27]. According to EPA, Chronic effects of disease in human may occur after long-term exposure to drinking water containing arsenic at levels even

less than 3 ppb [25]. Toxic effects of arsenic have long been known and affect almost every major bodily function and metabolic pathway. As-contaminated environments are characterized by limited species abundance and diversity. The presence of arsenic in groundwater in pernicious concentrations for human health constitutes a worldwide high-priority ground-water quality problem [9]. Long time exposure to arsenic may cause various diseases including skin disorders [26], circulatory system problems [15], cardiovascular disease [27], neurological complications [19], reproductive disorders, respiratory effects (18), diabetes mellitus [21]] and an increased cancer risk, especially of the skin, bladder, lungs and kidneys [15].

II. GEOLOGICAL SETTING

Ophiolitic melanges in the studied area include mantle (harzburgite, lherzolite, and pyroxenite) and crustal (isotropic gabbros, microgabbros, slaty diabasic dykes, and pillow lavas) sequences. Andesites, volcanosedimentaries, hialoclastic breccias, tuffs (dacitic, andesitic and vitric tuffs) are the main volcanic units in the area. As well, Abundance of serpentinitic units in comparison with others is a significant characteristic of ophiolites in the studied area (fig. 1) [2]. Mineralogical investigation of these units by scanning electron microscope (SEM) exhibits the presence of Fe-sulfide minerals (pyrite) and nickel in gabbros and serpentinites containing opaque minerals respectively [22].

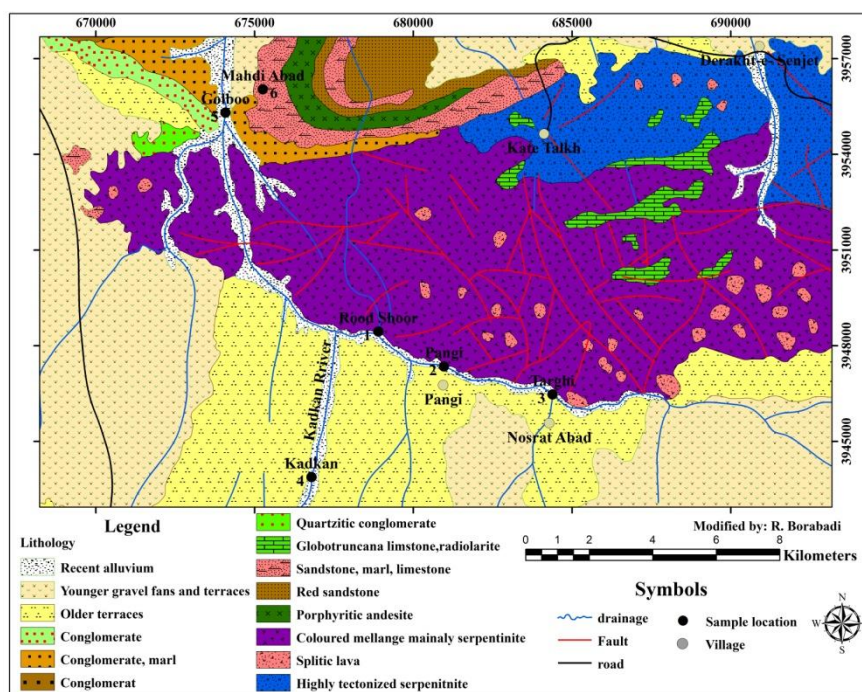


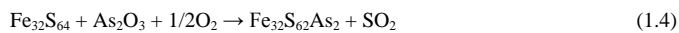
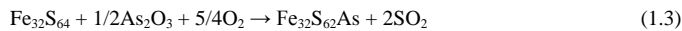
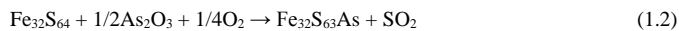
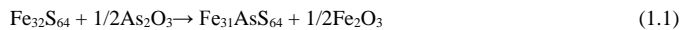
Fig. 1 Geological map of Pangi area (modified from Torbat Hydariieh 1:250000 map) and location of water samples

III. SAMPELIG METODS

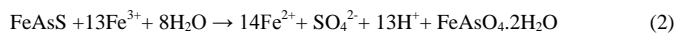
Six water samples were collected to determine the concentration of heavy metals and measuring physical and chemical properties of water samples. Measured physical parameters were pH, electrical conductivity (EC), redox potential (Eh). To determine the chemical properties of water resources, 250 CC water were taken by a polyethylene container. After filtering, 5 CC nitric acid was added to stabilize heavy metals in the water samples. These Samples were analyzed by graphite furnace atomic absorption spectrometry (GFAAS, GTA-110 model) for arsenic, heavy metal cations as well as anions concentrations determinations in the Geological Survey of Mashhad.

IV. DISCUSSION AND CONCLUSIONS

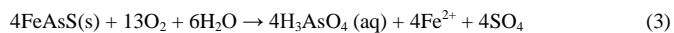
Studied area is a part of ophiolitic melange in northwestern of Torbat Heydariye which is surrounded by heavily serpentinitized ophiolitic exposures, and can be considered as a geogenic source of arsenic in water resources. Weathering of pillow lavas and diabasic dykes enriched with As-bearing sulfide minerals, especially arsenopyrite and pyrite is apparently responsible for the observed highly concentration of arsenic in the studied area. In oxidizing conditions, pyrite and arsenolite (As_2O_3) can interact and create $Fe_{31}AsS_{64}$ as indicated in reaction (1), Specific types of substitution are indicated in the following reactions [7].



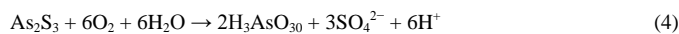
Fe arsenates especially scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) that is stable in acidic media, can directly be formed by arsenopyrite based on reaction (2) [19]:



As well as, oxidation of arsenopyrite is occurred based on reaction (3) which arsenic, iron and sulfate enter the solution [19]:



Oxidation of arsenides and arsenosulfides such as realgar and orpiment in geological formations can release arsenic and sulfate to water resources. For instance, inorganic trivalent arsenic can be produced by oxidation of orpiment according to reaction (4) [13]:



With respect to the above reactions, oxidation of As-bearing sulfide minerals such as pyrite and arsenopyrite during

weathering leads to arsenic release. Arsenic released can distribute in the environment as FeAsO_4 and $4\text{H}_3\text{AsO}_4$. Relationship between springs and alteration hydrothermal zones can be understood well provided that chemistry of springs and alteration hydrothermal zones investigates. For example, elevated amount of sulfate in samples is attributed to sulfide oxidation that sometimes is together with gypsum sedimentation. Elevated concentration of arsenic and sulfate in water is probably related to sulfide minerals oxidation and interaction between stone-water during argillic alteration because ions like potassium and sulfate are promoted in this type of hydrothermal alteration. In fact, oxidation of realgar and orpiment, and interaction between stone-water lead to release elements like As, K, Sb, Li, and also sulfate into water [14]. According to results of this study, arsenic concentration is several times greater than permissible values. arsenic concentrations and pH and EC values are given in table I as well as, bar diagrams in fig. 2 indicate arsenic concentration in sampling points. Arsenic concentrations is increased along water flow especially after crossing ophiolites and finally concentration attains 124 ppb in Golbou. This matter indicates that ophiolites are resources of arsenic in water, and arsenic solubility is governed by hydrological and hydrochemical processes.

Table I. Results of physical and chemical parameters

Sample	1	2	3	4	5	6
As (ppb)	14.2	115.9	119.3	111.4	124	27.3
pH	9.1	8.8	8.1	8.2	8.7	7.9
EC ($\mu\text{s}/\text{cm}$)	4441	557	773	4650	995	543

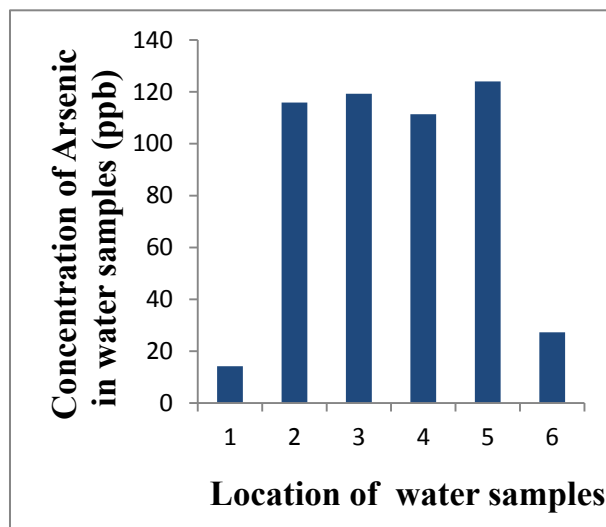


Fig. 2 The concentration of arsenic in water

The highest concentration of arsenic is in pH values ranging from 6.5-8.5. Arsenate (As^{5+}) and arsenite (As^{3+}) are the main forms of arsenic in surficial and ground water [11]. Thermodynamically, Free arsenic is just stable in low reducing potential. The increase of pH influences soluble arsenite

concentration in water resources. In oxidizing media having pH values higher than 9.4, arsenic can be adsorbed on cloidal iron oxides [16]. Stabilization realm of arsenite compounds is showed at Fig. 3.

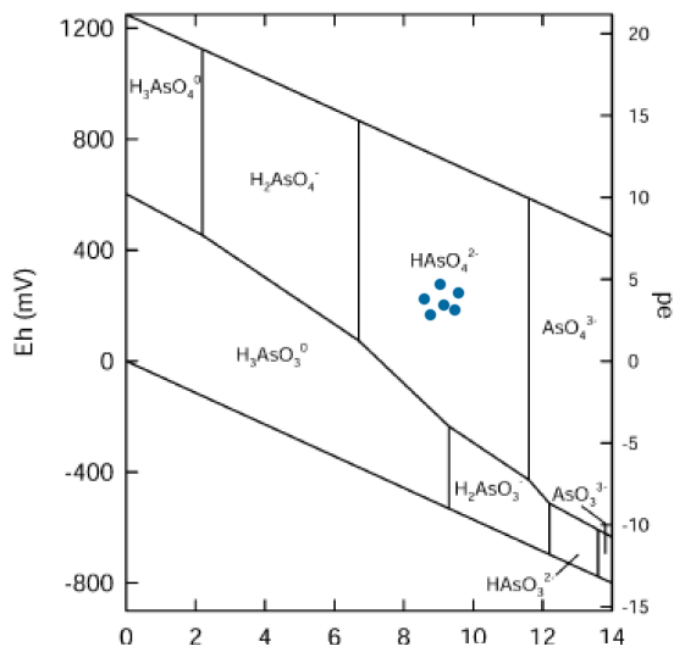


Fig. 3 pH-Eh diagram of Arsenic system in water resources

Oxidation of arsenic under alkaline conditions can lead to pollution of water resources. Measured pH values for water samples was ranging from 7.9 to 9.1, showing alkaline pH. Hence, there is potential condition for arsenic contamination. With respect to oxidizing condition of surficial waters in the area, and also Eh- pH diagram (Fig. 3), apparently HAsO_4^{2-} is the dominant arsenic sulfidic compound. It is well established that arsenic sorption on oxides is mainly pH dependent: arsenate is preferentially sorbed on hydrous oxides for pH values ranging from 4.0 to 7.0, whereas arsenite is preferentially sorbed for pH values ranging from 7.0 to 10.0. Distinction between arsenate and hydroxides occurs approximately in pH 8.0. Thus, pH variations control spatial and temporal fluctuations of arsenic (3+) and arsenic (5+) concentration in shallow ground waters, as domination of these species and their distribution between solid and liquid phases depends mainly on pH and Eh conditions [5]. So ability of arsenic solubility in water samples will increase as pH increases. Presence of arsenic together with sulfur and sodium is one of the noticeable properties of mineral brines in active hydrothermal zones. Average concentration of sodium and sulfate in local water resources is 258.5 and 219.9 respectively that is noticeable. According to WHO[26], permissible level of sodium and sulfate in ground water is 200 and 250 ppm

respectively. Therefore, local water resources, especially Pangli, have sulfate type and sodic facies. arsenic (5+) adsorption on some minerals is an effective process in mobility and stabilization of arsenic. Hydroxides, specially iron and manganese hydroxides that are abundant on the surface of some minerals, can interact with arsenic (5+) and adsorb it [12]. Oxy-hydroxides can effectively release arsenic in three ways: 1) Solution of arsenic minerals, 2) Arsenic adsorption on oxy-hydroxides, and 3) Arsenic release under high pH values. So Fe in high concentrations acts as an absorbent, and prevents arsenic to release into water body. Arsenic concentrations in local water resources are higher than standard values. Leaching As-bearing minerals in ophiolitic units and soils by streams and discharge to local rivers, especially Pangli, supply high concentration of arsenate in water resources. The biggest problem is observed in Golbou where arsenic concentration is 12 times greater than standard values. Arsenic concentration of water can be decreased by Identification of polluted areas and then detouring streams. Therefore, based on geochemical-sedimentary processes, arsenic concentration in water body can unlimitedly be conserved. arsenic concentration profile in Kate Talkh is reflecting arsenic displacement by aquifer and then discharge to Roud Shour river. Results of this study indicate that it's

easily possible to predict variations of arsenic concentration in local water resources using lithological, hydrological, and geochemical information.

VIII. CONCLUSION

Hydrochemical variables of water resources in Pangi area were evaluated in order to enhance an understanding of the most significant processes which impact the hydrochemical variations. Major conclusions of this study are drawn as follows:

- 1- Weathering of ophiolites is the most effective process on quality of water resources in the area due to this process, arsenic present in hydrothermal veins can be released to water resources.
- 2- Good correlation between arsenic, SO_4^{2-} , and Na^+ is related to sulfidic mineralization of pillow lavas and basic dykes in studied ophiolites.
- 3- Direct relationship between pH and arsenic concentration in water resources shows that arsenic is more stable in oxidation and alkaline conditions, and arsenic sulfides are mostly as HAsO_4^{2-} .
- 4- Regarding to results, arsenic concentration is increased along water flow. Concentrations are especially increased where ophiolites are crossed by streams, as the highest concentration of arsenic in Golbou reaches 12 times greater than the permissible level. Arsenic concentration is low in Mahdi Abad aqueduct because it's far from ophiolites.
- 5- Average concentration of arsenic in local water resources (86 ppb) is higher than the standard values.
- 6- The lowest arsenic concentration observed in Roud-E-Shour area (before contact with ophiolites). However, it's alternatively increased along water flow and after crossing ophiolitic formations.

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