Vol. 10

Original Research Paper

Impact of Arsenic on Environmental Geochemistry of South East of Kurdistan, Iran

Artimes Ghassemi Dehnavi, Ramin Sarikhani* and D. Nagaraju**

Department of Mining, Safashahr Branch, Islamic Azad University, Safashahr, Iran

*Department of Geology, University of Lorestan, Khoramabad, Iran

**Department of Studies in Geology, University of Mysore, Manasagangothri, Mysore- 570 006, India

Nat. Env. & Poll. Tech. Website: www.neptjournal.com

Received: 4/12/2010 Accepted: 31/12/2010

Key Words: Hazardous materials

Environmental problems Arsenic, Alteration rocks

ABSTRACT

Contamination of the environment by arsenic is one of the major environmental problems. Arsenic is usually present in small amounts in all rocks, soil, dust, water, air and biological tissues. However, the knowledge of its source, pathways and hydrogeochemistry are still matters of research and study. The aim of present study is the arsenic occurrence in sediments and groundwater in the south eastern Kurdistan, Iran that has caused serious health problems in rural population in the area, especially children, who are running the risk of hazardous effects of arsenic compounds in environment. The goal of this paper is to present objective and systematic data on this problem in south eastern of Kurdistan, Iran. Chemical analyses of groundwater and sediment samples indicate high levels in near alteration rocks.

INTRODUCTION

The occurrence of high concentrations of arsenic (As), one of the most hazardous chemical elements in drinking waters, has been recognized over the past two or three decades as of great public health concern in several parts of the world, including Argentina, Bangladesh, India, Pakistan, Mexico, Mongolia, Germany, Thailand, China, Chile, the USA, Canada, Hungary, Romania, Vietnam, Nepal, Myanmar and Iran (Anwar et al. 2003). However, the most widespread arsenic enrichment of groundwater occurs in a large region covering portions of West Bengal in India and Bangladesh. Even low levels arsenic exposure can cause a variety of cancerous (skin, lung, bladder) and non-cancerous (diabetes mellitus, vascular hypertension, dermal lesions) diseases (Lottermoser et al. 1999). Arsenic is ubiquitous in the earth's crust, although generally constituting less than 1% of most rocks, coals and soils (Casiot et al. 2007). Higher arsenic concentrations are associated with alluvial/lacustrine deposits in semi arid regions, volcanic deposits, alteration rocks and geothermal systems. The major arsenic containing minerals are arsenopyrites (FeAsS), realgar (As₄S₄), orpiment and arsenic trisulfide (As₂S₃). Arsenic combined with oxygen, chlorine or sulphur is referred to as inorganic arsenic, whereas arsenic combined with carbon-based molecules is referred to as organic arsenic. In general, arsenic in groundwater is released from minerals and organic matters. Naturally occurring arsenic in groundwater aquifers is a result of various factors, including physico-chemical properties, regional climate and geological conditions. The causes of

natural leaching-out of arsenic to groundwater are considered to be oxidation or reduction. The oxidation theory suggests that causing oxidization of minerals, including pyrite, reaches out arsenic to groundwater. Also sediments are usually an efficient means of accumulation and transport downstream of inorganic contaminants. Arsenic and heavy metals originate from altered rocks, volcanic rocks and mine wastes (tailings) either as particulate matter or acid mine drainage (Tamaki et al. 1992). Arsenic associated with geothermal waters also has been reported in several parts of the world and Iran. In most of these cases, the origin of arsenic was attributed to natural sources associated with the regional geological and hydrological background such as the reducing character of the water, its long residence time, the low water flow and a potential impact on the aquifers of the hydrothermal activity manifested in an adjacent area (Chormann 1985, Woo et al. 2001)). The arsenic in Kurdistan, Iran may originate in a natural enrichment process by geothermal activities and alteration in the study area. The primary source and release mechanism of arsenic from alteration rocks and sediments into groundwater is still not well understood. The objective of this paper is to carry out arsenic analysis of drinking waters and sediment samples from wells and springs in domestic and rural areas of southeastern Kurdistan and to check if its levels comply with International Standards for sediments and drinking water (Rose et al. 1979).

MATERIALS AND METHODS

The Study Area

The study area lies between latitudes $34^{\circ}50'$ to $35^{\circ}30'$ N and longitudes $47^{\circ}15'$ to $48^{\circ}10'$ E and located between Hamadan and Sanandaj. The total geographical area extends in the study area is about 500 sq. km², and is bordered by Bijar on the north, Kermanshah town on the south and Hamadan on the east (Fig. 1).

Geological Setting

To the north of the geosuture originating from the collision between the Arabian and the Eurasian plate, occurred an extensive volcanism (mainly calc-alkaline) starting from Middle Eocene. The end of this volcanism was not synchronous all along the volcanic belt. In fact, while in Central Iran the calc-alkaline activity ended in Oligo-Miocene times, in Eastern Anatolia and probably Western Iran it lasted up to Quaternary times, giving rise to large central volcanoes. The continuing andesitic volcanism in the region facing the apex of the Arabian block has been interpreted as the local remnant of the calc-alkaline activity from the subduction of the Arabian plate under Eurasia, which ended in this sector in Upper-Lower Pliocene times. After the collision of the northern continental margin of Arabian with the Eurasian block in Pliocene, the Anatolian and Iranian micro plates came into being as a sequel to the further northward penetration of the Arabian plate.

In the study area (Western Iran), two distinct volcanic cycles have been recognized. The first one of Upper Miocene age consists of high-K calc-alkaline volcanic rocks interpreted as final products the calc-alkaline Tertiary phase of central Iran. The second one, mostly of Pleistocene age consists of undersaturated, mainly potassic, alkaline products. As the lava of this last phase is slightly fractionated, the chemical differences shown by these rocks have been interpreted as primitive features related to the physical conditions governing the partial melting in the mantle and/or the mantle heterogeneity. In a volcanic centre contemporaneous basic and acid magmas have been found, and interpreted as derived from two different and independent sources. The alkaline basic volcanism affected the western margin of the Iranian plate after the Pliocene. Mio-Pliocene and Quaternary deposits in East Province, are almost horizontal is disposed. In north and northeast Mehdikhan and south Qararhbolagh villages, Quaternary igneous magmatic activities occur as outcrops. Around Delbaran and Maloojeh, Pliocene highly porous tuff (Pt) show large-scale development. Other sedimentary and Quaternary deposits like marly limestone, travertine, marls and sandy tuff are shown in Fig. 2 (Geological Survey of Iran 1999, 2002).

Methodology



Fig. 1. Location map of the study area and sampling locations.

The fieldwork included sampling of the groundwater, as well as stream sediments and Quaternary sediments. In addition, samples from altered rocks were also collected. Sampling was performed after the rainy period, during normal flow conditions (infiltration period with enrichment by dissolution-spring season), and a dry period (no precipitation-summer season). Acidified samples were analysed for heavy metals and trace elements using inductively coupled plasma atomic emission spectrometry (ICPAES).

Stream sediment samples: Forty six samples of sediments were collected following the standard procedures along the streams in the study area. Samples were collected with a plastic spade, transferred to pre-cleaned plastic bags, sealed and brought to the laboratory (Agresti 2002). All soils and sediments were oven-dried at 70°C and powdered prior to analysis. Samples were homogenized (Kolker & Nordstrom

Sample ID	$X(UTM)^1$	Y(UTM)	Geology Units	Arsenic (ppm)	Standard Limit (ppm)
1	751547	3930966	Pt	106	40
2	751991	3928047	Plm+Qtr+Qal	27	40
3	754025	3918796	Qc+Plm	32	40
4	746744	3926407	Qc+Plm	110	40
5	755933	3913374	Qc+Qtr+Qal	114	40
6	756230	3909045	Qal+Qft1+Plm+TRJd	44	40
7	756427	3931659	Plm	24	40
8	762018	3925117	Plm+Qt1	21	40
9	759780	3927992	Plm+Qal	24	40
10	766189	3923172	Plm+Plb+Qft2	10	40
11	764752	3913970	Qft1+Plm	28	40
12	771628	3916009	Pt+Qal	32	40
13	769358	3914423	Plb+Plm+Qal	29	40
14	764893	3910871	Qc+Plms	139	40
15	771373	3910132	Qal+Plm	19	40
16	769395	3906040	Qal+Plm	22	40
17	764093	3917187	Plt	22	40
18	768204	3917168	Plb+Plm+Otr+Pcg	25	40
19	762548	3920862	Oc+Otr	22	40
20	756667	3916714	Oc+Otr+Plb+Plm	36	40
21	742740	3929839	Oal+Plm	202	40
22	767401	3902051	Pt+Oal	70	40
23	772481	3892997	Oal+Oft2	71	40
24	771988	3900733	Oal+Plm	64	40
25	771151	3896941	Oal+Plm	129	40
26	769973	3900392	Oft1+Plm	64	40
27	740031	3929593	Plm	137	40
28	735756	3930328	Oc+Pt+Otr	22	40
29	739809	3920324	Oc+Plm	14	40
30	736323	3912922	Oc+Plm	13	40
31	746905	3903209	Oal+TRJc+TRJd	14	40
32	751492	3901690	Oal+dg+g+TRJ11+di+TR	11	40
33	748851	3895310	g+dg+Oft2	5	40
34	742376	3899723	TRJ11+TRJ12+Oal	10	40
35	729786	3916860	Oal+Plm	7	40
36	763087	3907863	Plm+Oft2+Oal	38	40
37	762182	3900114	Oft1+Plm	7	40
38	731412	3928808	Pt+MPa	28	40
39	732802	3926080	Oc+Pt+MPa+Plms	92	40
40	737711	3922558	Oft2+Pt	104	40
41	739917	3923903	Oal+Pt+Oft?	70	40
42	733083	3921525	Plm	115	40
43	728688	3922564	Plm	17	40
44	748917	3910550	Oal+Otr	16	40
45	745737	3913265	Qal+Plm	19	40
46	762689	3890181	Qal+TRIschl+TRId	15	40
.0	. 02007	5070101	Xui i i aboiii i i itaa	15	07

Table 1: Arsenic analysis of sediments (ppm) in THE study area.

UTM-Universal Transverse Mercator



Fig. 2. Geological map of the study area (after Ghomashi, Geological Survey of Iran1999).

2001), quartered and dry-sieved through 165-mm nylon mesh.

Groundwater samples: Natural water samples were collected from the wells and springs that supply water to rural

areas of east of Kurdistan. About 50 groundwater representative samples were collected from 50 sampling points of east of Kurdistan with the help of global positioning system (GPS). The water samples were collected in well stoppered



Fig. 3: Comparison of arsenic pollution of groundwater with international standards.



Fig. 4: Comparison of sediment pollution with international standards.

polyethylene plastic bottles previously soaked in 10% nitric acid for 24 h and rinsed with ultra pure water. All water samples were filtered in the field. Samples for cation analysis were acidified (concentrated HNO₃ to pH = 2), whereas non-acidified samples were collected for anion and stable isotope analysis.

RESULTS AND DISCUSSION

The main study of arsenic contamination is focused on both highly contaminated and non-contaminated regions of east of Kurdistan. Exposures to arsenic can result in a wide range of natural, industrial and biological effects depending on the level and duration of exposure. Varied effects are reported by range of doses in the developing foetus and infants, the latter being more sensitive than the adults. High levels of exposure may result in toxic biochemical impairment in humans which in turn cause problems in the synthesis of haemoglobin, kidneys, gastrointestinal tract, joints and reproductive system, and may result in acute or chronic damages to the nervous system. Average arsenic is estimated 10-50 µg and 1-40g. The majority of rural people in the eastern of Kurdistan use groundwater from wells and springs. Arsenic in the environment is derived from both natural and anthropogenic sources. Exposures can occur through drinking water, air, soil and dust and also from old paintings containing arsenic. In the study area the major exposure is from geological sources through sediment, soil and water. Chemical industries too affect the environmental contamination, but

Artimes Ghassemi Dehnavi et al.

Table 2: Arsenic	analysis of	f groundwater	(ppb) in study area.
	~	0	AT A

Sample ID	Туре	X(UTM)	Y(UTM)	Arsenic (ppb)	Standard Limit (ppb)
1	well	776704	3889920	195.3	50
2	well	784289	3891780	137.1	50
3	spring	786085	3893648	123.3	50
4	well	783696	3891524	121.2	50
5	well	776244	3888453	226.6	50
6	well	779594	3895586	242.3	50
7	spring	784268	3899931	245.3	50
8	well	779917	3900856	72.3	50
9	well	776158	3898270	275.3	50
10	spring	774952	3898708	187.9	50
11	spring	776859	3896307	25.96	50
12	spring	772508	3904742	245.2	50
13	well	770666	3910461	179.3	50
14	well	769558	3913189	216.3	50
15	spring	764219	3908625	145.6	50
16	well	735082	3916875	43	50
17	well	733174	3918553	54	50
18	spring	730995	3922493	87	50
20	well	728406	3922057	102.2	50
21	spring	726523	3925126	136	50
22	well	727565	3926324	98.6	50
23	spring	727395	3929749	87.4	50
24	spring	727518	3931476	64.63	50
25	well	723940	3935092	25.73	50
26	well	723177	3933442	34.84	50
27	well	720424	3932109	37.72	50
28	spring	719254	3931180	32	50
29	well	717103	3927677	125.6	50
34	spring	755225	3918184	220.6	50
35	well	755570	3917857	154.8	50
36	well	755212	3917557	180.4	50
37	well	760355	3919879	18.3	50
38	spring	760001	3919428	123.6	50
40	spring~	744984	3921054	32.4	50
41	well	743791	3925018	52.4	50
42	spring	744053	3926216	65	50
43	well	747191	3907442	15	50
44	well	733374	3942050	8.7	50
45	well	732970	3948047	32	50
46	spring	729753	3948537	25	50
47	spring	723617	3943151	252.6	50
48	well	722210	3943523	54	50
49	well	713718	3944946	21	50
50	spring	723805	3943655	165.3	50
	· · · · · · · · · · · · · · · · · · ·				

1- Universal Transverse Mercator (UTM)

we can't see any manufacturing and industrial activities in this area that increases pollution. The study indicates that the main source of arsenic contamination in the environment in Kurdistan is natural. The metals exist naturally in the bedrock, and are released through weathering. In water, the metals exist in different forms, both dissolved and suspended, depending on hydrogeochemical environment resulting in varying solubility, transportation and toxicity.

Groundwater contamination: Arsenic can enter the drinking water through the entire distribution system including mains, service lines, in-house plumbing, water coolers, and plumbing fixtures within houses, schools and other buildings. The results of this study can be applied for an efficient tool for pollution handling, their sources and evaluating the environmental impact from the transport of contaminants into groundwater causing pollution. We have analysed the arsenic concentration in the saturated zone. In the study area, the maximum concentration of arsenic occurs at the centre of the NW and SE tract. All sites were carefully screened to eliminate obvious data bias. The selected sites were present



Fig.5: Groundwater pollution map of arsenic of study area.

in a naturally contaminated zone with geologic formation (Matsumoto et al. 2000, Pellicori et al. 2005). This screening resulted in a final dataset of 50 representative groundwater samples collected from the selected sites and included wells in new residential establishment, older residences and rural areas and also from springs that are used for drinking water. Fig. 1 shows the site locations and Table 2 shows the number and arsenic concentration of the samples in the wells and springs. Fig. 6 shows distribution of arsenic in the study area.

Sediment contamination: Arsenic is mobile within units consisting of larger-grained particles that have higher hydraulic conductivities (sand, gravel). Compounding the contamination problem within the sand unit are the physical characteristics of its aquifer and surface drainage. The relatively high hydraulic conductivity of the sand unit, coupled with short residence time for contamination is responsible for arsenic mobility.

Groundwater recharges through stream base flow. Thus, any contaminant entering groundwater within the sand and gravel unit will flow in the general direction of the surface drainage and would enter a surface stream within a relatively short time due to the high drainage density. Another significant finding is the presence of elevated concentrations



Fig.6: Sediments pollution map of arsenic of study area.

of arsenic within the groundwater of the clay and silty clay geologic units, as mobility of metals in clay is generally believed to be very low. Factors of significance are very high concentrations of arsenic within the clay soil units; cracks within the clay unit allowing some downward migration of contamination and the long duration and continuous deposition of arsenic within these areas due to the alteration rocks of the watershed (EPA 1999).

CONCLUSIONS

Data on representative arsenic concentration in 50 groundwater samples and 49 stream sediment samples were used to define arsenic distribution statistics for groundwater and stream sediments in the region and map its occurrence and distribution in southeastern of Kurdistan. Significant sources of arsenic include those that occur naturally in groundwater and sediments. The groundwater and sediments typically have higher frequencies of elevated arsenic in the study area. Stream sediments acquire arsenic from both alteration of rock and anthropogenic sources, and stream sediment statistics for arsenic are correlable with lithology units and geologic activities. The correlations indicated by the analysis of arsenic distributions in stream sediments and groundwater indicate that rocks are most likely the dominant

sources of arsenic to most sediments and groundwater. High content of arsenic in sediments and groundwater samples are noted in a NW toward SE tract in the study area. The content of arsenic in these areas is greater than the standard levels. Arsenic concentrations are, in general, low in the common rocks and sediments. However, in the vicinity of the ore deposits, altered rocks and sediments may be rich in arsenic. In general, arsenic stems are mostly from alteration of rocks and smelting of sulfide ores in the study area. Arsenic-containing ores and alteration zones may heavily pollute the surroundings, groundwater and stream networks.

REFERENCES

- Agresti, A. 2002. Categorical Data Analysis. John Wiley and Sons, Hoboken, NJ.
- Anwar, H.M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., Safiullah, S. and Kato, K. 2003. Geochemical occurrence of arsenic in groundwater of Bangladesh: Sources and mobilization processes. J. Geochem. Explor., 77: 109-131.
- Casiot, C., Ujevic, M., Munoz, M., Seidel, J.I. and Elbaz-poulichet, F. 2007. Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (Upper Orb Basin, France). Appl Geochem. 22: 788-798.
- Chormann, J.R., F.H. 1985. The Occurrence of Arsenic in Soils and Stream Sediments in Town of Hudson, New Hampshire. Unpubl. Master's Thesis, Univ. of New Hampshire, Durham.
- EPA 1999. National Primary Drinking Water Standards. EPA 810-94-001, United States Environmental Protection Agency.
- EPA 1999. National Recommended Water Quality Criteria Correction. EPA 822-Z- pp. 99-100, United States Environmental Protection Agency.
- Fergusson, J. E. 1990. The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon, New Zealand.
- Geological Survey of Iran 2002. Distribution map of acidic hydrothermal alteration zones of Iran.

- Geological Survey of Iran 1999. Qorveh geological map, Geological Maps of Iran 1:100000, A. Ghomashi.
- Kolker, A. and Nordstrom, D.K. 2001. Occurrence and microdistribution of arsenic in pyrite. In: Proceedings of the USGS Workshop on Arsenic in the Environment, February 21-22, Denver, Colorado Extended Abstracts. Available online at URL http://wwwbrr.cr.usgs.gov/Arsenic/ Final- AbsPDF/Kolker.pdf.
- Lottermoser, B.G., Ashley, P.M. and Lawie, D.C. 1999. Environmental geochemistry of the Gulf creek copper mine area, north-eastern New South Wales, Australia. Environ. Geol., 39(1): 61-74.
- Matsumoto, T. and Hosoda, T. 2000. Arsenic contamination and hydrogeological background in Samta village, western Bangladesh. Abstract, Pre-Congress Workshop (Bwo 10), Arsenic in Groundwater of Sedimentary Aquifers. 31st International Geological Congress, Rio de Janeiro, Brazil.
- Pellicori, D.A., Gammons, C.H. and Poulson, S.R. 2005. Geochemistry and stable isotope composition of the Berkeley pit lake and surrounding mine waters, Butte, Montana. Appl. Geochem., 20: 2116-2137.
- Rose, A.W., Hawkes, H.E. and Webb, J.S. 1979. Geochemistry in Mineral Exploration. Second ed., Academic Press, New York.
- Stollenwerk, K.G. 2003. Geochemical processes controlling transport of arsenic in groundwater: A review of adsorption. In: Welch, A.H. and Stollenwerk, K.G. (Eds.), Arsenic in Ground Water: Geochemistry and Occurrence. Kluwer Academic Publishers, Dordrecht, pp. 67-100.
- Smedley, P.L. and Kinniburgh, D.G. 2002. A review of the source, behavior and distribution of arsenic in natural waters. Appl. Geochem., 17: 517-568.
- Tamaki, S. and Frankenberger, J.R. 1992. Environmental biochemistry of arsenic. Rev. Environ. Contam. Toxicol., 124: 79-110.
- WHO 1996. Guidelines for Drinking Water Quality, Health Criteria and Other Supporting Information. 2nd ed., Environmental Health Criteria on Arsenic and Arsenic Compounds. Environmental Health Criteria Series, No. 224, Arsenic and Arsenic Compounds, World Health Organization, Geneva.
- Woo, N.C. and Choi, M. J. 2001. Arsenic and metal contamination of water resources from mining wastes in Korea. Environ Geol., 40(3): 305-311.