

Arsenic contamination in groundwater system of Viterbo area (Central Italy)

Maurizio Barbieri¹, Angela Nigro¹, Giuseppe Sappa²

¹Department of Earth Science, Sapienza University of Rome, P.le A. Moro, 5 - 00185 Rome, Italy

²Department of Civil, Building and Environmental Engineering, University of Rome "Sapienza", Via Eudossiana - 00184 Rome, Italy

***Corresponding author:** Prof. Maurizio Barbieri, Department of Earth Science, Sapienza University of Rome, P.le A. Moro, 5 - 00185 Rome, Italy, Tel.: +39-06 4991 4593; e-mail: maurizio.barbieri@uniroma1.it

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Abstract

In the last years the presence of arsenic in groundwater became an urgent environmental issue. The As maximum concentration in drinking water has been changed from 50 µg/l to 10 µg/l, mainly due the effect observed on populations exposed to drinking water rich in arsenic. Since many springs and wells of the Cimino-Vicano area exceeds the limits provided by Council Directive 98/83/EC, arsenic has become the most urgent issue of local governments bodies. The aim of this paper is to investigate about the presence of this element in groundwater and to contribute understanding of the behaviour of this in aquatic environment. In this project have been analyzed 44 waters samples, with temperatures ranging from 15° C to 62° C, and they have been compared with data obtained from paper of Sappa et al., 2014 [1], relative to water supply network. The results show that the predominant specie of As in agricultural and thermal water in reducing conditions is arsenite As (III) while the predominant specie present in drinking water in oxidant conditions is arsenate As (V).

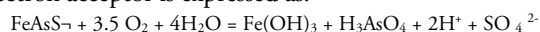
Keywords: Arsenic contamination, groundwater, pH-Eh diagram

1. Introduction

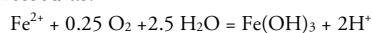
Arsenic is a metalloid whose presence is widely detected in many environmental matrices. The problem of the As presence in the water has been known since the 80s, when numerous studies have found high levels of As in groundwater resources, leading to the World Organization Health (WHO) to fix the level in drinking water at 10 µg/L. Nowadays, the countries in which are reported high levels of As in groundwater are Afghanistan, Bangladesh, Nepal, Pakistan, Mexico, Argentina, Chile, Hungary, Romania [2]. The high levels of As in groundwater are mainly of geological origin, while anthropogenic sources result of industrial activities, the use of pesticides, herbicides and fertilizers [2]. In Italy high levels of arsenic have been detected in groundwaters in many municipalities of Emilia Romagna and Lombardy [3,4], in some municipalities of Veneto [5] and in the Campi Flegrei area (Naples) [6], as well as in

spring waters and lakes of northern Lazio. Most of these investigations have shown such as the presence of this element is linked to natural processes of releasing of minerals in aquifers. Arsenic can exist in four oxidation states (-3, 0, +3 and +5). In the case of environmental exposure, toxicologists are primarily concerned with arsenic in the trivalent and pentavalent oxidation state. Under reducing conditions, the state of valence +3 (AsIII), as arsenite, is the dominant form, while the valence +5 (AsV), such as arsenate, is the most stable form under oxidizing conditions [7]. In groundwater, arsenic is found as hydrolyzed of acid arsenious and arsenic. A primary source of As in nature is the oxidation of Assulphides like arsenopyrite, FeAsS, and As-rich pyrite. The minerals can be oxidized by O₂, Fe³⁺, and NO₃⁻. The rate of arsenopyrite oxidation by Fe(III) is about 10 times faster than the rate of pyrite oxidation [8].

The overall reaction of arsenopyrite oxidation with O₂ as electron acceptor is expressed as:



Ferric hydroxide plays a much more important role in controlling dissolved As concentration. Its precipitation can be expressed as:



This reaction is important for As migration, because both As(+V) and As(+III) are adsorbed on Fe(OH)₃. According to Pierce and Moore, 1982 [9], a pH of about 7.0 is the adsorption optimum for arsenite and a pH of about 4.0 is the adsorption optimum for arsenate. The arsenic cycle 'expanded as a result of human interference and because of this large amounts of arsenic into the environment and in organisms. As mainly issued by manufacturers of copper, but also stems from the production of lead, zinc and use of products used in agriculture. Arsenic, once it has entered the environment, cannot be destroyed so it can spread and have adverse effects on the health of humans and animals. Arsenic is toxic to both plants and animals and inorganic arsenicals are proven carcinogens in human; the effects of this element for human health range from skin lesions to cancer on the brain, stomach and kidney [10]. The legislation on quality of drinking water has evolved over time as a function of progress knowledge about the substance present in water [11]. Until 1985 in Italy the only law which concerned the characteristics of drinking water was a R.D of 1934, which required that the water distributed for human use had to be good quality. This common law has been kept until 1958 when the WHO provided "International standard of drinking water" which established a maximum admissible concentration of As less than 200 mg/L. Subsequently, the Italian State has approached the problem of pollutants in the water with a D.P.C.M. 1985. Later with a Presidential Decree of 1988 which has required for the arsenic maximum concentration of 50 µg/l. With D.Lgs. n. 31 2001 Italy has transposed the Directive of CE of 1998 and it ordered mandatory compliance to the values given in the decree from 25 December of 2003. The As maximum concentration is 10 µg/l. The decree required more possibility: First exception of 3 years (2006) keep within the maximum values established of Health Department; Second exception of other 3 years (2009) upon agreement of Health Department; Third exception of other 3 years (2012) upon agreement of Health Department and approval of CE. The entry into force of the law occurred January 1, 2013.

In this paper are compared arsenic data of Viterbo area (Central Italy) relative to wells and springs used for various use (agricultural water supply) and thermal water, with data published to Sappa et al., 2014 relative a domestic water supply network.

2. Geological framework

The area investigate comprises the Cimino and Vico volcanic complexes located between the Tyrrhenian sea and Central Apennines mountains in the Latium region. The surface geology is characterized by volcanic products of the series potassium regarding Cimino and highly potassic regarding Vicano [12]. The activity of the district Cimino, which is placed in a time interval between 1.5 Ma and 0.8 Ma ago, was characterized by emissions of acidic viscous lava from fractures of the earth's crust that gave birth to the very steep hills. The products of Cimino complex are mainly composed of latites and trachytes [13]. Vico complex is situated south of the Cimino volcanic-complex and consist of a strato-volcano with a central caldera depression housing Lake Vico. The activity of the volcanic Vicana began around 0.8 Ma ago and ended 0.09 but does focusing at a building-layer volcanic characterized by explosive activity [14]. This activity gave rise to several different products: trachyphonolitic tuffs, tephritic-phonolitic and trachytic lavas, ignimbrites of several compositions varying from trachyte, phonolite to tephryte, and deposits from hydromagmatic activity [13,15,16]. The substrate of volcanic deposits Cimini and Vicani is represented by sedimentary formations of marine origin, in particular limestone-marl-clay sediments, flysch Tolfa, dating back to the Pliocene-Pleistocene sedimentary formations and of continental origin villafranchiana. Other formations found in the area under consideration are travertine, mainly located at the hot springs, and alluvial deposits, both dating back to the Pleistocene-Holocene. The substrate beneath the Cimini and Vico volcanics consists of sedimentary rocks: a Pliocene-Pleistocene sedimentary complex including conglomerates, sandstones, sands and clays; the Upper Cretaceous-Oligocene flysch (Ligurian Units) consisting mainly of shale, marls, calcarenites, marly limestones and sandstones; the Triassic-Paleogene carbonate rocks (Tuscan-Umbrian-Marche Units), several thousand meters thick, including limestone, marly limestone, marls, dolomitic limestone, dolostone and anhydrites [17].

Within the thermal area of Viterbo, an uplifting of the units underlying the volcanic rocks was detected, confined by N-S and E-W oriented faults (Fig. 2).

Additional faults, oriented NW-SE and NE-SW, further subdivide the deep structures, controlling the locations of eruptive volcanic centres [18].

3. Materials and method

The hydrogeochemistry of the aquifer of Viterbo geothermal system was investigated by sampling 44 samples from springs and private wells (fresh and thermal water). The sampling was performed during March until

July 2012. In the present research, these data were compared with existing data (for 231 individual domestic water supply wells and springs), obtained from "Geochemical modelling and multivariate statistical evaluation of trace elements in arsenic contaminated groundwater systems of Viterbo Area, (Central Italy)" by Sappa et al., 2014. The analysis have been conducted in according to standard methods [19]. Water's temperature, electrical conductivity and pH values were determined in the field. Bicarbonate was determined by titration with 0.1 N HCl.

Each water sample were divided into two subsamples: the first were stored at 4 °C for the major ions analysis, the other were transferred to clean acid-washed polyethylene bottles, acidified with concentrated nitric acid (Ultrapur) to pH <2 and stored at 4 °C for the trace elements analysis. Major ions were determined with a Dionex DX-120 ion chromatograph (reliability $\pm 2\%$).

A Dionex CS-12 column was used for determining cations (Na, K, Mg, Ca), whereas a Dionex AS9-SC column was used for anions (F, Cl, NO₃, SO₄).

Trace elements concentrations were measured using ICP-MS (X Series 2 Thermo Fisher Scientific), the analytical accuracy of these methods ranged from 2% to 5%. All the analysis was conducted in the Earth Science Department, Sapienza University of Rome, Italy.

4. Results and discussion

Physicochemical parameters and major constituents

Table 1 shows summary statistics of physicochemical parameters (mean, median, maximum, minimum values and standard deviation values) of wells and spring water samples and guideline values of WHO (2006) for drinking water. In this table waters are divided in two groups: waters with T<25°C and waters with T>25°C. In the first group the values of temperature range from 15.1°C to 24.2°C, the E.C values range from 289 $\mu\text{S}/\text{cm}$ to 1501 $\mu\text{S}/\text{cm}$, pH values range from 6.32 to 8.01 pH units and

Eh values range from -0.07 to 0.14 Volts. The ionic dominance pattern of the water samples for cations and anions is Ca>Na>K>Mg and HCO₃>SO₄>NO₃>Cl>F. Some samples shows high concentrations of NO₃ with maximum value equal to 283 mg/l, this depends on the agricultural activities present in the area. The second groups shows a temperature values range from 25.3°C to 62.7°C, the E.C values range from 266 $\mu\text{S}/\text{cm}$ to 3400 $\mu\text{S}/\text{cm}$, pH values range from 5.79 to 7.08 pH Units and Eh values range from -0.315 to 0.089 Volts. The ionic dominance pattern of the water samples for cations and anions is Ca>Mg>K>Na and SO₄>HCO₃>Cl>NO₃>F. These samples belong to thermal waters for this reason show a greater concentrations of SO₄ that present a maximum value equal to 2579 mg/l.

Traces elements

A series of various trace elements (Table 2), including Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Mo and U, were determined in the studied of groundwater. Same elements are investigated in paper of Sappa et al. (Table 2) for evaluate the safety of water for drinking. Table 2 shows the mean values of samples divided in two groups on based to temperature values. In the first group arsenic shows a mean value equal to 83.0 $\mu\text{g}/\text{l}$ certainly greater of WHO limit. In the samples with T>25°C the elements that exceeds the WHO limits are B with mean value equal to 910 $\mu\text{g}/\text{l}$ and As. Arsenic presents a mean value equal to 197 $\mu\text{g}/\text{l}$. Table 3 show the value of trace elements reported in paper of Sappa et al. and highlight that the mean values of As concentration are minor respect to concentrations measured for this research. Greater concentrations of As are found in springs and wells with T>25°C that are recharged by hydrothermal aquifer, while for water with T<25°C the presence of As and other trace elements such as V, Mo, U, B, F, Sr are probably related to the circulation of groundwater in the superficial volcanic formations. Analysis of tables 2 and 3 shows that the As is present both in wells and springs sampled by us, that in springs and wells used for drinking waters.

Table1: WHO limits and Statistics of physicochemical parametres and majorions.

		Water T<25°C					Water T>25°C					
WHO		Mean	Median	Min.	Max.	Std. Dev		Mean	Median	Min.	Max.	Std. Dev
N.S	T°C	19.2	19.3	15.1	24.2	2.15	T°C	48.7	53.1	25.3	62.7	12.9
6.5-9.2	pH	7.13	7.16	6.32	8.01	0.53	pH	6.32	6.25	5.79	7.08	0.31
1500	E.C.	648	658	289	1501	310	E.C.	2690	2995	266	3400	830
75-200	Ca ppm	64.6	58.6	17.6	229	46.1	Ca ppm	323	318	158	605	97.4
50-150	Mg ppm	16.1	9.48	1.24	119	23.4	Mg ppm	110	114	73.5	155	23.4
200	Na ppm	35.4	29.8	12.0	129	24.2	Na ppm	38.1	38.3	30.8	48.1	4.18
200	K ppm	28.8	25.7	6.39	59.4	13.5	K ppm	42.7	39.5	34.9	71.1	8.59
250	Cl ppm	30.8	22.4	4.08	114	25.6	Cl ppm	17.2	14.9	3.40	54.9	10.7
250	SO ₄ ppm	110	67.7	14.8	484	120	SO ₄ ppm	1638	1742	389	2579	610
N.S	HCO ₃ ppm	371	307	88.5	824	210	HCO ₃ ppm	969	976	427	1373	253
1.5	F ppm	4.60	1.40	0.20	53.0	11.1	F ppm	2.74	2.34	0.57	9.79	2.01
50	NO ₃ ppm	47.7	32.2	<0.01	283	67.0	NO ₃ ppm	6.79	0.15	<0.01	52.0	17.3
	Eh (V)	0.002	-0.009	-0.07	0.14	0.047	Eh (V)	-0.079	-0.116	-0.315	0.089	0.193

Table2: WHO limits and Mean of traces elements for water samples.

WHO	(µg/l)	T<25°C		T>25°C	
		Mean		Mean	
N.S	Li	23.5	Li	54.7	
N.S	Be	0.704	Be	1.44	
500	B	273	B	910	
200	Al	46.6	Al	40.1	
N.S	V	21.9	V	3.88	
50	Cr	0.709	Cr	0.35	
400	Mn	3.18	Mn	24.8	
300	Fe	159	Fe	44.8	
N.S	Co	0.83	Co	3.15	
20.00	Ni	2.14	Ni	1.3	
2000	Cu	2.34	Cu	3	
3000	Zn	124	Zn	38	
10	As	83	As	295	
N.S	Rb	131	Rb	120	
N.S	Sr	1058	Sr	5758	
7	Mo	1.7	Mo	0.249	
15	U	5.82	U	3.64	

Dependence of arsenic speciation on environmental parameters.

Although the aquatic environment, arsenic can exist in four oxidation states (-3, 0, +3, +5), and in organic or inorganic form, the predominant species in groundwater are trivalent arsenic [As (III)] and pentavalent [As (V)] in inorganic form; organic forms are present in very low amounts in groundwater and, since their formation requires biological activity, may be essentially detected in correspondence of favourable conditions as in lacustrine environments [20]. In addition, considering the typical pH range of groundwater (between 6 and 9), and whereas the groundwater intended for human consumption have a positive redox potential (corresponding to a good oxygenation), it follows that H_3AsO_3 , $H_2AsO_4^-$ and $HAAsO_4^{2-}$ are the most important chemical species of arsenic in drinking water and that most of the arsenic is in the form pentavalent. Both redox potential (Eh) and pH impose important controls on arsenic speciation in the natural environment [19]. Figure 1 shows the pH-Eh diagram for inorganic arsenic compounds. Under oxidant

Table 3: Mean values of trace elements for a domestic water supply network by Sappa et al., 2014

	Monitored wells (MeanValues)						
	MJ1	MJ2	MB1	MB2	MB3	MB4	MB5
Li	9.80	9.00	66.9	16.2	30.4	66.1	33.3
Be	0.350	0.450	1.19	0.350	0.440	1.12	0.770
B	93.0	79.6	832	145.1	320	841	381
Al	5.40	11.9	18.0	4.60	6.40	7.00	10.3
V	33.8	38.5	32.5	40.0	34.3	27.9	44.8
Cr	0.610	1.40	0.070	0.370	0.200	0.100	0.070
Mn	0.160	0.35	111	30.7	11.5	99.9	99.1
Fe	2.40	11.3	114	322	4.60	36.8	815
Co	0.29	0.28	1.84	0.38	0.93	1.82	0.810
Ni	0.00	5.96	0.92	0.01	0.00	1.91	0.060
Cu	0.43	91.6	2.47	0.00	0.00	0.46	0.740
Zn	0.01	16.6	2.76	13.05	0.00	1.03	71.5
As	16.7	14.4	13.1	14.5	7.70	14.11	15.1
Rb	30.9	34.6	169.6	73.7	124	165.6	101.3
Sr	325	273	1229	200	586	1083	532.9
Mo	2.34	2.17	1.35	1.30	0.70	1.10	2.65
U	6.26	2.71	12.9	3.38	7.63	10.7	6.76

conditions (High values of Eh) and $pH > 2$ Arsenic found as $H_3AsO_4^-$; for pH values range from 2 to 11, As found as $H_3AsO_4^-$ and $H_3AsO_4^{2-}$. At low Eh values (reducing conditions), H_3AsO_3 is the predominant inorganic arsenic species (iAsIII) under reducing conditions. If Eh values below mV exist in the environment, arsenic compounds such as As_2S_3 in the presence of sulfur or hydrogen sulfide can be formed but these conditions are not environmentally relevant [10]. The solubility of these compounds is very limited under neutral and acidic conditions [21]. Under very strong reducing conditions, arsine and elemental arsenic are formed but again, only rarely, if ever in the natural environment. The figures 1 and 2 show the pH-Eh diagrams of arsenic species. For samples with $T < 25^\circ C$ (Figure 1A) the predominant species is As III (H_3AsO_3); also samples with $T > 25^\circ C$ (Figure1B) show that the predominant species is As III. Figure 2 and table 4 shows the results obtained from Sappa et al., 2014. This figure, that present the pH-Eh diagrams for drinking water, shows that the predominant species is As V ($H_2AsO_4^-$ and $H_2AsO_4^{2-}$).

Table 4: Values of ph and Eh by Sappa et al., 2014

WHO guideline values		Wells					Springs				
		Mean	Median	Min.	Max.	S. Dev	Mean	Median	Min.	Max.	S. Dev
6.5-9.2	pH	6.00	8.70	7.00	7.00	0.50	6.20	8.10	6.90	6.90	0.400
-	Eh (V)	0.23	0.66	0.3	0.28	0.08	0.23	0.58	0.31	0.31	0.06

5. Conclusions

Arsenic is a metalloid which presence is widely detected in many environmental matrices.

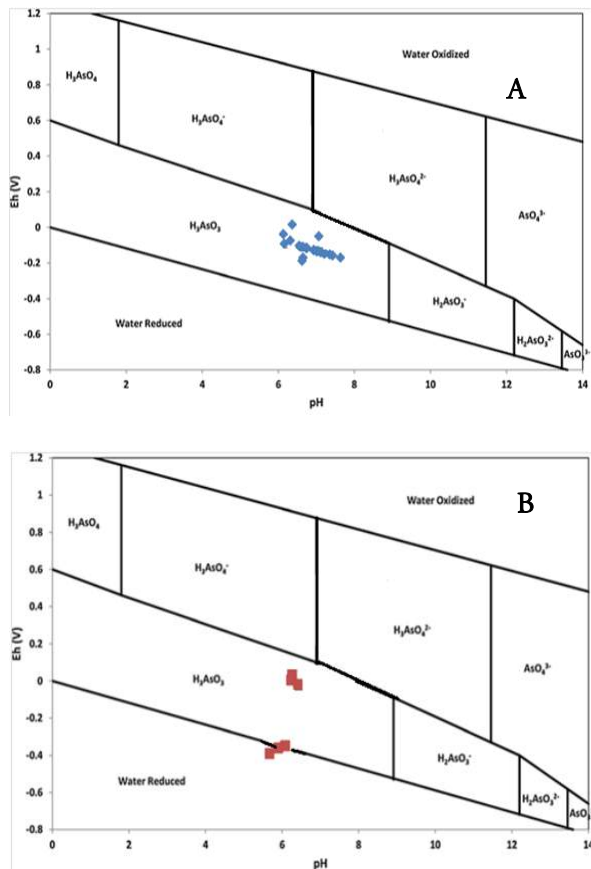


Fig. 1 Ph-Eh diagrams; Figure A samples with $T < 25^{\circ}\text{C}$, figure B samples with $T > 25^{\circ}\text{C}$.

The Cimino-Vicano area is one of the Italian place mainly affected by the presence of arsenic in groundwater. In 2010 the Viterbo area there have been more problems about numbers of municipalities interested and for the levels of contamination detected.

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The aim of this paper is to investigate about the presence of As in natural water and to contribute understanding of the behaviour of this element in aquatic environment. For this study have been reported the results obtained following a monitoring campaign relative to springs and private wells (fresh and thermal waters).

These sample shows a As concentrations definitely greater of WHO limit ($10 \mu\text{g/l}$) which amount to maximum

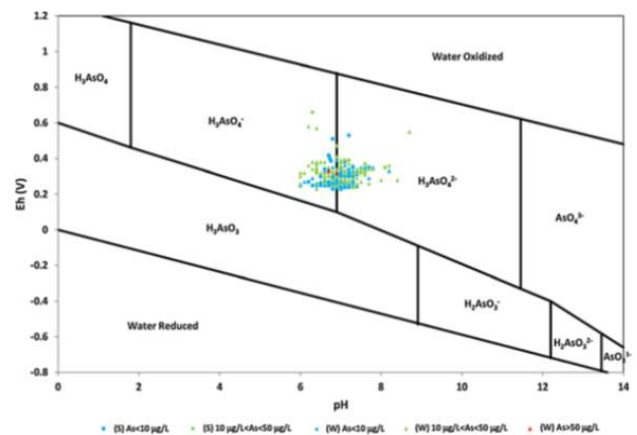


Fig. 2 Ph-Eh diagram by Sappa et al., 2014.

values in thermal water. Moreover were reported the data obtained to Sappa et al., 2014 relative to domestic water supply wells and springs which show a As concentration greater to $10 \mu\text{g/l}$. The pH-Eh diagram show that in fresh groundwater ($T < 25^{\circ}\text{C}$) the predominant species of arsenic is As (III) (H_3AsO_3) for pH values range from 6.32 to 7.13; also for waters with $T > 25^{\circ}\text{C}$ the predominant species is As (III) with values of pH and Eh more negative. Instead, in drinking water (where the As concentrations are minor to respect other samples) the predominant species is As (V) (H_2AsO_4^- and $\text{H}_2\text{AsO}_4^{2-}$).

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