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REVIEW PAPER

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THE SOURCE, CHARACTERISTICS AND DISTRIBUTION OF ARSENIC IN THE ENVIRONMENT

Arsenic is an ubiquitous element found in natural materials and in industrial products. The range of its concentrations found in the environment is large. Arsenic can occur in several oxidation states and is found in inorganic and organic forms. It is relatively mobile. The presence of arsenic in the environment, even at low levels, has negative effects on human and animal health. The investigation of arsenic content and behaviour in different type of waters and environment is important for chemistry and environmental protection. This paper represents a short review of scientific and expert investigations on the source, characteristics and distribution of arsenic in the environment.

Key words: Arsenic, Source, Characteristics, Distribution, Water.

SOURCE OF ARSENIC IN THE ENVIRONMENT

The source of arsenic in the environment can be natural and anthropogenic.

Natural sources

Arsenic occurs in the Earth's crust, soil, sediments, water, air and living organisms. The average concentration of arsenic in the Earth's crust, in igneous and sedimentary rocks is 2 mg/kg. In most rocks it ranges from 0.5 to 2.5 mg/kg [1]. Arsenic naturally occurs in over 200 different mineral forms, of which approximately 60% are arsenates, 20% sulfides and sulfosalts and the remaining 20% include arsenides, arsenites, oxides, silicates and elemental arsenic (As). The most abundant arsenic mineral is arsenopyrite (FeAsS) together with other As minerals such as realgar (AsS), orpiment (As₂S₃) and enargite (Cu₃AsS₄) [2]. The concentrations of arsenic in soils depend on the geological structure of the area. In soils of various countries they range from 0.1 to 40 mg/kg (mean 5 mg/kg). The natural level of arsenic in sediments is usually less than 10 mg/kg, dry weight, and varies considerably all over the world [3].

The concentration of arsenic in natural water varies by more than four orders of magnitude and under natural conditions the highest concentrations of arsenic are found in groundwaters, up to 5000 µg/L. Seawater ordinarily contains 1–8 µg/L of arsenic. The concentration of arsenic in unpolluted fresh waters typically ranges from 1–10 µg/L, rising to 100–5000 µg/L in areas of sulfide mineralization and mining [4]. High

levels of arsenic have been detected in waters from areas of thermal activity in New Zealand, up to 8.5 mg/L. Geothermal water in Japan contains 1.8–6.4 mg/L. Concentrations of arsenic above 50 µg/L have been identified in groundwaters from alluvial sediments in the southern part of the Great Hungarian Plain of Hungary and neighbouring parts of Romania [5]. Since it is a part of the large Danube basin, an increased concentration of arsenic was expected in Vojvodina. According to data from the "Vinca" institute the concentration of arsenic in Vojvodina ranges from 0–310 µg/L. Just in the region of the town of Zrenjanin it is found that this concentration varies from 50 to 250 µg/L [6]. That was the reason for scientific investigations in our country of arsenic compounds and the possibilities of their removal from water [7–9].

The maximal permissible concentration of arsenic in drinking water is 50 µg/L and the value recommended by the EPA and WHO is 10 µg/L [10,11].

Concentration of arsenic in air is low and ranges from 0.4 to 30 ng/m³ [12]. Among natural sources, volcanic emissions can cause increased concentrations of arsenic. Typical arsenic levels for the European region are currently quoted as being between 0.2 and 1.5 ng/m³ in rural areas and no more than 50 ng/m³ in industrial areas [13].

Arsenic is present in bioorganisms. Its concentration varies from less than 0.01 to about 5 µg/g. Among marine animals (coelenterates, some molluscs, crustaceans, shellfish) arsenic was found to be accumulative, in animal tissue, to levels from 0.005 to 3 mg/kg. Some shellfish may contain more than 100 µg/g of arsenic. The average arsenic content in freshwater fish is 0.54 µg/g. In mammals arsenic accumulates primarily in the hair and nails. Domestic animals contain lower amounts of arsenic, about 0.3 µg/g, than wild animals. Human organisms generally contain less than 0.3 µg/g of arsenic.

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Anthropogenic sources

Man influences the content of arsenic in nature directly, by using arsenic compounds for different purposes, and indirectly, by his activities, influencing the mobility of arsenic from different natural sources. Industrial plants and technologies in which arsenic is used, consumed or disposed influence the increased content of arsenic in the environment. Such sources of arsenic are the products of melting and fossil-fuel combustion, products used in agronomy such as pesticides and mineral compost which contain arsenic compounds. Arsenic compounds are used in bronze production, for wood conservation, in pyrotechnics, in the production of pigments, pesticides, insecticides, poisons and drugs. Wastewaters from industry may contain high arsenic concentrations and if they come in to natural recipients without purification, they can cause tremendous damage to living organisms.

THE CHARACTERISTICS AND DISTRIBUTION OF ARSENIC SPECIES IN WATER

Arsenic is an ubiquitous element found in all parts of the Earth, in lower or higher concentrations. However arsenic has the greatest influence on living organisms through water ecosystems. One of the most current problems in the world is the pollution of water and decreased natural sources of fresh and quality drinking water. Therefore, in this paper special attention will be paid to arsenic in water ecosystems.

Arsenic was not traditionally on the list of elements routinely tested by water-quality testing laboratories and thus many high-arsenic water sources may have been missed. Concentrations of arsenic in fresh water vary by more than four orders of magnitude depending on the source of arsenic, the available amount and the local geochemical environment. Under natural conditions, the greatest range and the highest concentrations of arsenic were found in ground waters as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favourable for arsenic mobilization and accumulation [5]. This factor is important because, in many countries, groundwaters are potential sources of drinking water. Taking chemical and technological aspects, into account it is necessary to emphasize that arsenic can occur in water in different forms and that the toxicity and mobility of arsenic depend on the present form.

Arsenic is especially interesting for investigation because of its abilities of mobilization in the range of pH values typically found in natural waters and under both oxidizing and reducing conditions. It can occur in the environment in several oxidation states (+5, +3, 0 and -3), but in natural waters it is mostly found in inorganic

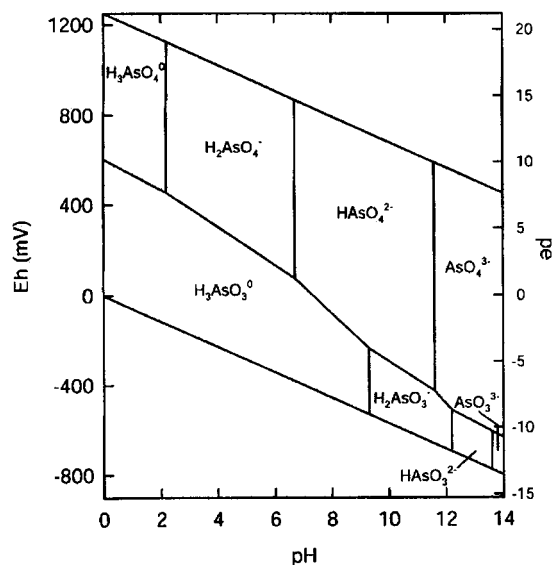


Figure 1. E-pH diagram for aqueous As species in the system As-O₂-H₂O at 25°C and 1 bar total pressure [15]

form as oxyanions of trivalent arsenite As (III) or pentavalent arsenate As (V). Under reducing conditions at pH lower than about 9.2, the uncharged arsenite species H₃AsO₃⁰ predominates (Fig. 1) [14,15]. The distributions of arsenic species as a function of pH are given in Fig. 2 [5].

Organic arsenic forms may be produced by microbiological activity, mostly in surface water. Organic forms may, however, occur where waters are significantly impacted by industrial pollution. The dominant organic forms found in significant concentration, especially during the summer months, are dimethylarsinic acid (DMAA; (CH₃)₂AsO(OH)) and monomethylarsonic acid (MMAA; CH₃AsO(OH)₂). The redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidising condition, H₂AsO₄⁻ is dominant at low pH (less than about pH 6.9), whilst at higher pH, HAsO₄²⁻ becomes dominant. Molecular species H₃AsO₄⁰ may be present in water extremely acidic conditions and AsO₄³⁻ may be present in extremely alkaline conditions as shown in Fig. 1.

As already stated, the drinking-water limit for arsenic is very low compared to the overall abundance of arsenic in the natural environment. Fortunately, arsenic is mostly immobilised by various minerals, particularly Fe oxides, and is thus not available for abstraction. Two categories of processes largely control arsenic mobility in an aqueous environment: (1) adsorption and desorption reactions and (2) solid-phase precipitation and dissolution reactions. The attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, the detachment of arsenic from such a surface,

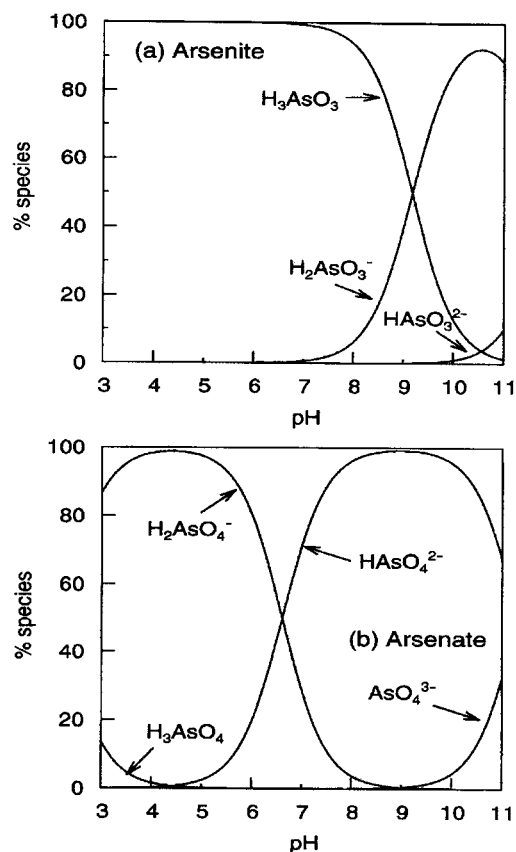


Figure 2. (a) As(III) and (b) As(V) speciation as a function of pH [5]

is an example of desorption. Solid-phase precipitation is the formation of a solid phase from components present in aqueous solution. The precipitation of the mineral calcite, from calcium and carbonate present in ground water, is an example of solid-phase precipitation. The dissolution of volcanic glass within an aquifer is an example of solid-phase dissolution. Arsenic adsorption and desorption reactions are influenced by changes in pH, the occurrence of redox reactions, the presence of competing anions, and solid-phase structural changes at the atomic level. Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including the pH, redox state and chemical composition [16]. An abundant source of Fe oxides with surface-bound and coprecipitated arsenic provides a ready source of arsenic that may be released given an appropriate change in the geochemical conditions. Under aerobic and acidic to near-neutral conditions, typical of many natural environments, arsenic is very strongly adsorbed by oxide minerals as the arsenate ion. As the pH increases, especially above pH 8.5, arsenic desorbs from the oxide surfaces, thereby increasing the concentration of arsenic in solution. This effect can be demonstrated by some model calculations. The arsenate ion concentration as a

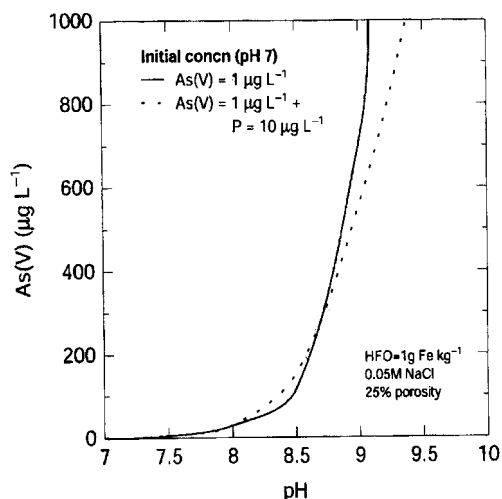


Figure 3. Calculated increase in As concentration when the pH of a sediment containing 1 g kg⁻¹ Fe as HFO is increased from its initial value of pH 7 under closed-system conditions [17]

function of pH, for defined conditions, is given in Fig. 3 [17].

There is a sharp increase in the porewater arsenic concentration above pH 8.5. Above pH 9, the arsenate concentration can exceed 1000 µg/L. This system assumes no competing anions in solution. But in natural waters there are other anions (e.g. phosphate, bicarbonate and silicate) that will compete for the sorption sites on the hydrous ferric oxide (HFO) and thereby reduce the initial arsenic loading. The example of phosphate in water with the arsenate ion is shown in Fig. 3. In the absence of other specifically adsorbed anions, arsenite adsorption by Fe oxides is practically independent of pH. This differs to the arsenate described above. But in natural waters some pH dependence in arsenite adsorption will be induced by secondary interactions arising from the pH dependence of other specifically adsorbed and competing ions such as phosphate and even arsenate. So, desorption at high pH is the most likely mechanism for the development of ground-water arsenic problems under oxidising conditions and would account for the observed positive correlation of arsenic concentrations with increasing pH [18,19].

On the basis of literature data it is known that arsenite is more toxic and mobile, and also more difficult to remove from drinking-water supplies than arsenate. Therefore, it is important not only to determine the arsenic concentration in water, but also to determine the species of arsenic compounds [16]. Consequently, various speciation procedures have been proposed and reviewed [20]. The procedures for As (III), As(V) and DMA selective determination in natural water samples are given in Fig. 4 [21].

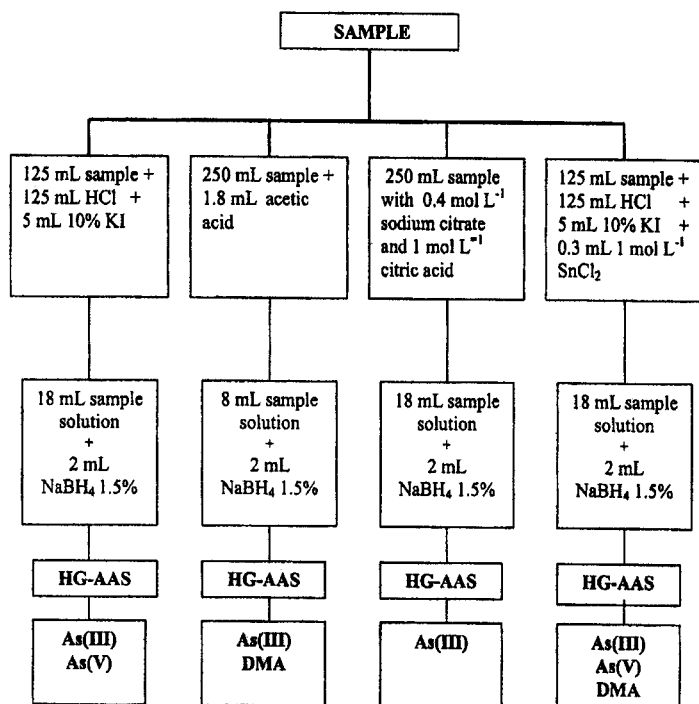


Figure 4. Procedure for As (III), As (V) and DMA selective determination in natural water samples [21]

Arsenite alone was measured in 0.4 mol/L citrate buffer (pH = 4.4); arsenite plus arsenate were determined together in 6.0 mol/L hydrochloric acid after a pre-reduction with potassium iodide, and arsenite plus dimethylarsinate species were determined in 0.12 mol/L acetic acid. Total arsenic could be determined in 6.0 mol/L hydrochloric acid following a pre-reduction step of the arsenate and dimethylarsinate species with a potassium iodide – stannous chloride mixture. Sample storage in the reduction media proposed for the selective reduction speciation enabled a storage period of up to seven days for the different species studied [21].

CONCLUSIONS

On the basis of a review of the source, characteristics and distribution of arsenic in the environment, it may be concluded that arsenic is a widespread element in nature and that its compounds have a bad influence on the health of people and animals. The recognition of this fact and knowledge about the toxicity of arsenic are significant stimulation for the permanent monitoring of arsenic (concentration and form) in the environment. On the basis of literature data it may be concluded that antropogenic sources of arsenic influence the presence of this element in nature. A current world problem is the presence of arsenic in wastewater, which in natural cycles gets into the groundwater which represents a basic natural source of fresh water.

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IZVOD

PORIJEKLO, SVOJSTVA I RASPODJELA ARSENA U ŽIVOTNOJ SREDINI

(Pregledni rad)

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Arsen je rasprostranjen u prirodi, nalazi se u atmosferi, zemljištu, stjenama, prirodnim vodama i organizmima. Opseg koncentracija u kojima se može naći u prirodi je širok (u prirodnim vodama od 0,5 do 5000 µg/L). Zastupljen je u neorganskim i organskim jedinjenjima u valentnim stanjima -3, 0, +3 i +5. Relativno je mobilan i ima ga u tragovima u svim materijalima. Pored prirodnih materijala, nalazi se u industrijskim proizvodima jer se koristi u: medicini, poljoprivredi, elektronici, industriji i metalurgiji.

Prisustvo arsena u životnoj sredini, čak i u niskim koncentracijama, ugrožava zdravlje ljudi i životinja. U organizam dospjeva vodom ili preko lanca ishrane. Ispitivanje sadržaja i ponašanja arsena u raznim vrstama voda i uopšte u životnoj sredini od velikog je značaja za hemiju i zaštitu životne sredine. Ovaj rad predstavlja kratak revijalni pregled naučnih i stručnih saznanja o porijeklu, svojstvima i raspodjeli arsena u životnoj sredini.

Ključne riječi: Arsen, Porijeklo, Svojstva, Raspodjela, Voda.