

Hydrochemistry of Arsenic in Groundwater Pollution in Eastern U. P.

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Abstract

The presence of arsenic (As) in water and its effect on human health through both drinking and agricultural practices is of serious concern worldwide. Arsenic rich groundwater mostly occurs in the Bengal Delta Plain, covering the state of West Bengal, the adjoining country of Bangladesh and extending to Jharkhand, Bihar, Uttar Pradesh, Assam, and other North-eastern states of India and the neighbouring country of Nepal. The number of people at risk of arsenic poisoning, through drinking water from sunken wells, may be considerably larger than previously thought of. This article conceptualizes by reviewing the As sources, major occurrences, mechanisms of arsenic mobilization and process of contamination in groundwater of Ganges–Brahmaputra river basin of India through an integrated approach. In groundwater, inorganic As commonly exists as arsenate (As^{5+}) and arsenite (As^{3+}). Inter-conversion of As^{5+} and As^{3+} takes place by oxidation of As^{3+} to As^{5+} and reduction of As^{5+} to As^{3+} . There is another mode of occurrence of arsenic, namely organoarsenic, which is mostly less toxic than both As^{3+} and As^{5+} . Organoarsenic is formed from inorganic arsenic by a process called biomethylation.

Keywords : Arsenic contamination, arseneous acid, Ganges–Brahmaputra river basin, groundwater.

Introduction

Arsenic is a natural constituent of the earth's crust and is the 20th most abundant element. The average concentration of As in the continental crust is 1–2 mg/kg. processes such as weathering and volcanic eruptions, and may be transported over long distances as suspended particulates and aerosols through water or air. Arsenic emission from industrial activity also accounts for widespread contamination of soil and groundwater environment. Many authors have reported As emissions to the atmosphere on global, regional and local scales^{32–34}. Once introduced into the atmosphere, As may circulate in natural ecosystems for a long time depending on the prevailing geochemical environment.

Major As occurrences in groundwater

In groundwater, inorganic As commonly exists as arsenate (As^{5+}) and arsenite (As^{3+}). Inter-conversion of As^{5+} and As^{3+} takes place by oxidation of As^{3+} to As^{5+} and reduction of As^{5+} to As^{3+} . There is another mode of occurrence of arsenic, namely organo arsenic, which is mostly less toxic than both As^{3+} and As^{5+} . Organoarsenic is formed from inorganic arsenic by a process called biomethylation. Organoarsenic occurs in various organisms such as plants, fish, crab and the human body. Biological methylation or biomethylation is performed by heavy-metal bacteria or fungi which are devoid of chlorophyll, such as prokaryota (bacteria) and akaryota (fungi). High concentrations of arsenic tend to occur in sulphide minerals and metal oxides, especially iron oxides. Several studies suggest that the As-rich groundwater is mostly restricted to the alluvial aquifers of the Ganges delta comprising sediments carried from the sulphide-rich mineralized areas of Bihar and elsewhere surrounding the basin of deposition. However, recent studies indicate that the vast tract of Indo-Gangetic alluvium extending further to the west and the Brahmaputra alluvium have elevated concentrations of As in wells placed in the late Quaternary and Holocene aquifers. Arsenic released during the weathering of sulphide minerals is generally adsorbed onto the surface of iron oxy hydroxides that precipitated under oxidizing conditions generally prevailing during the deposition of the Holocene sediments. However, redox processes in the sediments trigger the reductive dissolution of iron oxides that transfers substantial amounts of As in aqueous phases through biogeochemical interactions. As-containing groundwater in Ganges–Brahmaputra river basin is hosted by the sediments deposited by the rivers during the late Quaternary or Holocene age. Lithology of these late Quaternary sediments include sands, silt and clay. Mineralogical composition of these sediments consist of quartz, feldspars and kaolinite and the fine-grained overbank facies are rich in organic matter. There is thick layer of newer alluvium containing sand, silt and clay, which spreads out by numerous rivers that originate from the Himalayas both in the north and northeast. Most environmental arsenic problems recognized today are the result of mobilization under natural conditions.

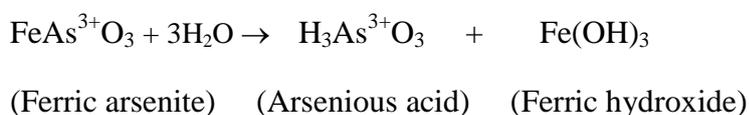
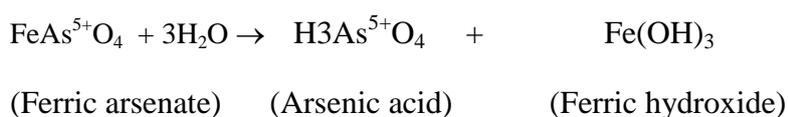
Materials and Methods

Sampling sites: Ballia is an eastern district of the state of Uttar Pradesh, India covering an area of 3000 sq.km. and having a total population of about 27 lakh (density of 925 per sq.km). The district is bounded on two sides by river Ganga and Ghagra. Drinking water in the district occurs under unconfined and semi confined conditions. Study focused and undertook a detailed survey of villages in Belhari block along with two other blocks, Dubhar and Rewati with a (population 0.1 million during the year 2012). Drinking water and blood samples collection: 100 water

samples were collected from drinking water sources and handpump at different depth. All these sources of drinking water from the sampling area were cemented. The depth of sources ranged between 10-60m, drawing water from different alluvial aquifers. For 100 wells, information regarding the age and depth of wells were collected from the users. The depth of drinking water sources varied according to distribution and requirement of villagers. Human blood samples (100 no) were collected from both arsenic affected area or from site where arsenic concentration in drinking water greater than standard value ($10 \mu\text{g l}^{-1}$). The polypropylene tubes for blood sample collection were previously decontaminated with nitric acid (10%) and then kept in deionized water. A 5 ml of blood was collected into decontaminated sample tubes for determining arsenic level (APHA, 2005).

Results and Discussion

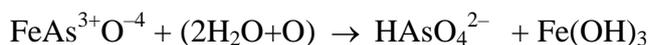
Iron arsenate (FeAsO_4) may be tentatively regarded as the direct and immediate source of arsenic, because it is easily formed from scorolite [$\text{FeAs}_4, 2\text{H}_2\text{O}$] and pitticite (hydrated mixture of arsenate and sulphate), which are common alteration products of arsenopyrite. Since arsenopyrite can contain As^{3+} ions in small proportion with ions of As^{5+} which is the dominant constituent, it is quite likely that arsenic in the alluvium occurs as ferric arsenate (FeAsO_4), with ferric arsenite (FeAsO_3) in minor proportion. Due to hydrolysis under conditions of low pH and high Eh, ferric arsenate is dissociated into the strongly poisonous arsenic acid (H_3AsO_4) with ferric hydroxide, whereas ferric arsenite breaks down into arsenious acid (H_3AsO_3) and ferric hydroxide. The relevant equations for such hydrolysis are as follows:



Ferric hydroxide is soluble in acidic aqueous environment, but it is precipitated in alkaline and reducing conditions at low Eh. Thus, if the acidity of the solution decreases (pH increases), colloidal precipitation of ferric hydroxide take place. Some As^{5+} and As^{3+} ions being absorbed on the particles of $\text{Fe}(\text{OH})_3$ may be co-precipitated with the latter. This reduces arsenic content of water. However, precipitation of As^{5+} and As^{3+} is not simultaneous because As^{3+} is 5 to 10 times more soluble than As^{5+} and its stability in aqueous solution increases with the alkalinity of water and reducing character of the environment. Thus, even after colloidal precipitation of As^{5+} ions

with ferric hydroxide, the aqueous solution may contain As^{3+} ions in large amount. In mildly acid to neutral solution ($\text{pH} = 7$) or even in mildly alkaline solution under oxygenated condition at $\text{Eh} > 0$, breakdown of ferric arsenate and ferric arsenite by hydrolysis can produce As^{5+} bearing arsenic acid (HAsO_2) and As^{3+} bearing arsenious acid (H_3AsO_3) respectively, together with ferric hydroxide in both cases.

The relevant equations are:



Arsenous acid (HAsO_4^{2-}) is the commonest of arsenate compounds in natural water as aqueous solution. In a mildly reducing environment, HAsO_4^{2-} is converted into As^{3+} bearing arsenious acid ($\text{H}_2\text{AsO}_3^{1-}$) and in a strongly reducing condition into arsenious acid (H_3AsO_3). The change can be shown by the following equations:



In the absence of As^{3+} in the source material (FeAsO_4)

As^{5+} bearing arsenic acid (HAsO_4^{2-}) can be formed by the hydrolysis of FeAsO_4 in a mildly alkaline and oxygenated environment and ferric hydroxide is produced at the same time. In the biomethylation process arsenic in the sediment is hydrolysed to arsenic acid and is further reduced by bacteria to $\text{As}^{3+}\text{O}(\text{OH})$ forms arsenite in solid state. Thus the first role of bacteria is to increase the ratio of $\text{As}^{3+}/\text{As}^{5+}$ in the sediment. This As^{3+} readily goes into aqueous solution to increase As toxicity of water. The next step of change brought about by bacteria is biomethylation of $\text{As}^{3+}\text{O}(\text{OH})$, resulting in the formation of $\text{CH}_3\text{As}^{5+}\text{O}(\text{OH})_2$ or methyl arsenic acid and $(\text{CH}_3)_2\text{As}^{5+}\text{O}(\text{OH})$, i.e. dimethyl arsenic acid or cacodylic acid, which is an extremely toxic compound. In each step, these substances are soluble in water to increase toxicity. In the fourth step, cacodylic acid is again biomethylated to form $(\text{CH}_3)_3\text{As}^{3+}$ or trimethylarsine by aerobic bacteria under oxidizing condition, whereas, anaerobic bacteria under reducing condition convert cacodylic acid to $(\text{CH}_3)_2\text{HAS}^{3+}$ or dimethyl arsine. Both are soluble in water and are toxic. The biomethylation process increases the proportion of organoarsenic, which is readily absorbed by plants and animals through soil and water. Thus, the arsenic content of soil and water is reduced. However, the unabsorbed part of the organo arsenic being toxic, pollutes the soil and water. Hence the practice of drawing arsenic contaminated groundwater from tube wells for irrigation purposes may ultimately lead to poisoning of surface soil and surface water, which

are normally arsenic-free even in arseniferous regions of West Bengal. The Brahmaputra alluvial basin is bounded by lower Himalayan mountains in the north and northeast. High intensity of rainfall in the catchment and plain areas has contributed to high sediment loads, which have developed the valley into a long stretch of recent and old alluvium. The alluvium near the river is more sandy and periodic fluvial action keeps the alluvium stratified. However, its influence has been gradually obliterated by climate as one moves from recent flood plains to old flood plains and then upland. As a result, there is deposition of coarse sand and coarser river-borne materials along with plant cells and other organic materials cells which may contain considerable amount of arsenic and other toxic elements. During the course of time, As elements get released in the reducing environment by the process of biomethylation and get shelter within silty and clayey sediments. Some studies also put forward the hypothesis that the burial of sediments rich in organic matter led to strongly reducing conditions in groundwater aquifer, which is facilitated by high water table, finegrained surface layers and widely practised wetland paddy cultivation, as well as microbial oxidation of sedimentary organic matter, depleting thereby the dissolved oxygen in groundwater. Arsenic is released when arsenic-rich iron oxyhydroxides, which are efficient arsenic scavengers, are reduced in anoxic groundwater. Such reduction is driven by concentrations of sedimentary organic matter. Most experts agree that the source of such high arsenic anomaly in groundwater is geological rather than from pesticide or other artificial sources. It is postulated that arsenic-bearing sulphide minerals, the commonest of which in nature is arsenopyrite (FeAsS) and/or their alteration products, had been transported in the geologic past possibly from those occurring along the foothills of the Himalayas and deposited with the alluvium in the Ganges–Brahmaputra basin. These extraneous arsenic minerals buried under the recent alluvium are considered to be responsible for contamination. However, arsenopyrite and its alteration products are less toxic and normally insoluble in water. Over and above this, high arsenic anomaly has suddenly appeared in recent times, as no report of arsenic contamination of groundwater can be traced earlier than the late seventies. In the present condition of emergence of greater area with As pollution, the relation between chemistry of arsenic and high arsenic anomaly in groundwater is an interesting subject of study.

CONCLUSION

(i) Part of the arsenic contamination in a vast area of the Ganges and Brahmaputra basin (West Bengal, North-eastern states, Bihar, Jharkhand and Uttar Pradesh) is possibly mainly geological.

(ii) The immediate source material for groundwater is likely to be ferric arsenate (with or without ferric arsenite) derived from an alteration product of the mineral arsenopyrite that was geologically transported to the Bengal delta and Assam valley.

(iii) Contamination takes place by chemical and biological processes that lead to the formation of arsenic acids from buried arsenate. The plausible chemical process is hydrolysis of arsenate.

(iv) Supply of excess oxygen during withdrawal of groundwater from tubewells appears to be responsible for hydrolysis.

(v) There is a need for integrated research to understand sources, release mechanisms, mobilization of As in aquifers and the chemistry of arsenic and high arsenic anomaly in groundwater of the Ganges and Brahmaputra river basin.

(vi) Thus, large number of people is unwillingly consuming arsenic contaminated water and is at grave health risk as no alternative sources are available. This strongly advocates necessity to take certain initiative to mitigate the problem and to spread the awareness of the problem among the affected population. However, the positive side of the research is that nearly half of the population of other nine blocks are safe and consuming arsenic free water.

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