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Occurrence, behaviour and speciation of arsenic in groundwater

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Reports on the occurrence of arsenic in groundwater resources and the associated health hazards due to human consumption have been made from various parts of India and the world during the past few years. Arsenic in groundwater is present in various species like H_3AsO_3 , H_2AsO_3 , $HAsO_3$, H_3AsO_4 , H_2AsO_4 , and $HAsO_4$. The toxicity of arsenic may vary from one species to another. The effects of Eh and pH on arsenic speciation have been studied. It has been shown that some correlations exist between arsenic verses pH and arsenic verses Eh. One of the toxic arsenic species, H_3AsO_3 , has been identified in groundwater in West Bengal, India.

GROUNDWATER, which is used for drinking or domestic purposes, must be free from contamination; but because of industrialization, urbanization and various other sources, it is being contaminated. About 2,20,000 inhabitants of India, particularly from West Bengal have symp-

toms of arsenic poisoning from groundwater¹. In India, arsenic is found in groundwater in West Bengal, Orissa and Andhra Pradesh. Arsenic-enriched groundwater is also found in other parts of world, e.g. Bangladesh, USA (Arizona) and Korea². Processes of arsenic mobilization from its source to groundwater are mainly either natural or anthropogenic. In general it depends on hydro-chemical characteristics of groundwater aquifers, presence of oxidized/reduced mineral phases and arsenic-rich solid

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phases^{3,4}. Arsenic-rich aquifers are often characterized by elevated concentrations of dissolved iron, moderate bicarbonate, specific pH range, nitrogen and phosphates mostly in reducing condition and acidity (low pH), iron and sulphates in the toxic horizon. Sequential chemical leaching exhibits that arsenic in groundwater in Bangladesh is present in three phases: (i) Fe and Mn oxides, (ii) organic matter and (iii) sulphide and silicate phases. Arsenic in groundwater aquifers is present in various species like H_3AsO_3 , H_2AsO_3 , HAsO_3 , H_3AsO_4 , H_2AsO_4 , and HAsO_4 . All the arsenic species are not toxic. Therefore, to examine the intensity of arsenic contamination in groundwater, it is necessary to know more about the arsenic species. However, for de-arsenification processes, arsenic speciation is equally important. For the study of physico-chemical behaviour of arsenic in groundwater, technical inputs from various countries have been examined, and more emphasis was given to Arizona (USA), Korea, Bangladesh and West Bengal. The purpose of this article is to identify the chemical species in which arsenic is present in groundwater and the effect of Eh and pH on arsenic solubility in groundwater.

Occurrence

The occurrence of arsenic is mainly due to two reasons: natural and anthropogenic. Arsenic is widely distributed

in nature and principally occurs in the form of inorganic or organic compounds. Inorganic compounds consist of arsenite, the most toxic form and arsenate the less toxic form⁵. The main ores of Arsenic are arsenopyrite, arpi-ment, realgar and arsenopaldenite. It is present in nature as iron arsenate, iron sulphate and in calcareous soil as calcareous arsenolite. In flood deposits, it is found as arsenite. The main anthropogenic sources are industrial waste, phosphate, fertilizers, coal, oil, cement, mine tailing, smelting, ore processing, metal extraction, metal purification, chemicals, glass, leather, textiles, alkali, petroleum refineries, acid mines, alloys, pigments, insecticides, herbicides and catalysts.

The main stages of arsenic are As^{5+} , As^{3+} , and As^{3-} . It can form hydrides (AsH_3), acids (H_3AsO_3 , H_2AsO_3 , HAsO_3 , H_3AsO_4 , H_2AsO_4 , HAsO_4) and also halides (gas- AsF_4 , solid AsBr_3 , AsI_3)⁶. It can also form arseno betaing arseno, chlorine and nanomethyl arsenate. Arsenic can also form bands with organic sulphur, nitrogen and carbon. Arsenic (III) and (IV) can also be formed by dissolving organic mater in natural environment. This can prevent sorption and co-precipitation with the solid phase organics and inorganics⁷.

The most commonly found arsenic compounds in groundwater are trivalent arsenite or pentavalent arsenate. Organic forms of arsenic compounds occur primarily in seafood obtained from several marine organisms that ex-

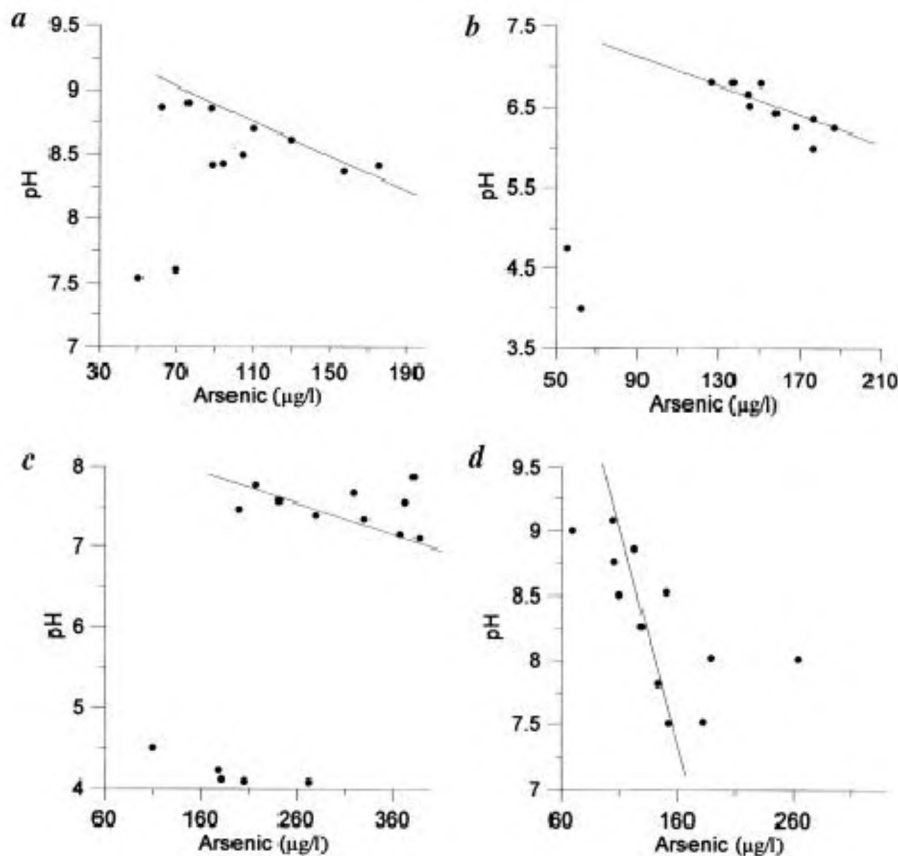


Figure 1. pH vs arsenic levels. *a*, Arizona; *b*, Korea; *c*, Bangladesh and *d*, India.

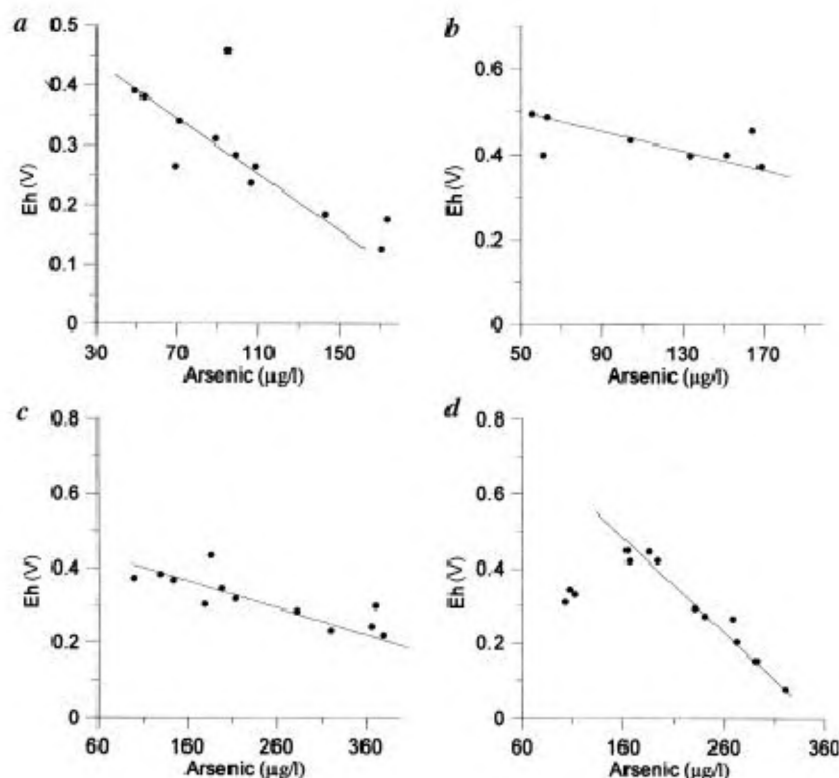


Figure 2. Eh vs arsenic levels. *a*, Arizona; *b*, Korea; *c*, Bangladesh and *d*, India.

tract arsenic from water and methylate the same to an organic compound. The maximum permissible limit of arsenic in drinking water is 50 µg/l, defined by World Health Organization. The hydrogen ion concentration (pH), redox potential (Eh) and arsenic content used in this study have been taken from published data^{8–13}.

Effect of pH and Eh on arsenic speciation

The influence Eh and pH on arsenic speciation and its solubility has been reported¹⁴. Alteration in the oxidation state of arsenic is usually influenced by Eh and pH. The most suitable pH for arsenic dissolution is low acidic (pH < 2.0), but it can be dissolved in other pH ranges (2–11) also, under suitable chemical and physical conditions. Arsenious acid usually forms at low pH under mildly reduced conditions and it is easily replaced by H₂O₃ when pH increases¹⁵. HAsO₃ is usually formed at very high alkaline pH (>12–0)¹⁶. For examining the influence of arsenic on pH in groundwater chemical data are studied, where arsenic is reported to be more than the permissible limit in groundwater (i.e. India, Bangladesh, USA and Korea). On grouping the arsenic levels/chemical data, arsenic vs pH (Figure 1) shows more or less a linear correlation. There are various types of redox reactions which consume organic matter in groundwater, like aerobic degradation, denitrification, ferric iron reduction and sulphate reduction. On the basis of available data from

arsenic-rich areas of different countries, a graph is plotted between arsenic and Eh values (Figure 2). A linear correlation exists between arsenic levels and Eh. Eh and pH are the most important chemical factors controlling the arsenic speciation. Under oxidizing conditions, H₂AsO₄[−] is dominant at low pH (less than about 6.9), while at higher pH, HAsO₄^{2−} becomes dominant (H₂AsO₄) and AsO₄^{3−} may be present in extremely acidic and alkaline conditions. A pH < 9.2, has shown uncharged arsenic species and the probability of H₃AsO₃ being dominant. In the presence of extremely high concentrations of reduced sulphur, dissolved As-sulphide species are found to be more regular. Reducing acidic conditions are more favourable for precipitation of orpiment (As₂S₃), regular (AsS) or other sulphides minerals containing co-precipitated arsenic. Therefore high arsenic waters are not expected wherever there is a high concentration of free sulphides¹⁷. The Eh vs pH phase diagrams (Figure 3) indicate the stability fields and boundary lines of the different arsenic species. Therefore, the existence of H₃AsO₃ within a reducing environment and in mixed pH conditions in the context of arsenic-rich groundwater of West Bengal is more prominent. However, the situation is different in Bangladesh (Figure 3c) where H₃AsO₃ (species) was found in oxidizing as well as in reducing conditions. The oxidizing potential with mildly acidic to alkaline behaviour of groundwater in arsenic-rich areas of Arizona and Korea (Figure 3a and b).

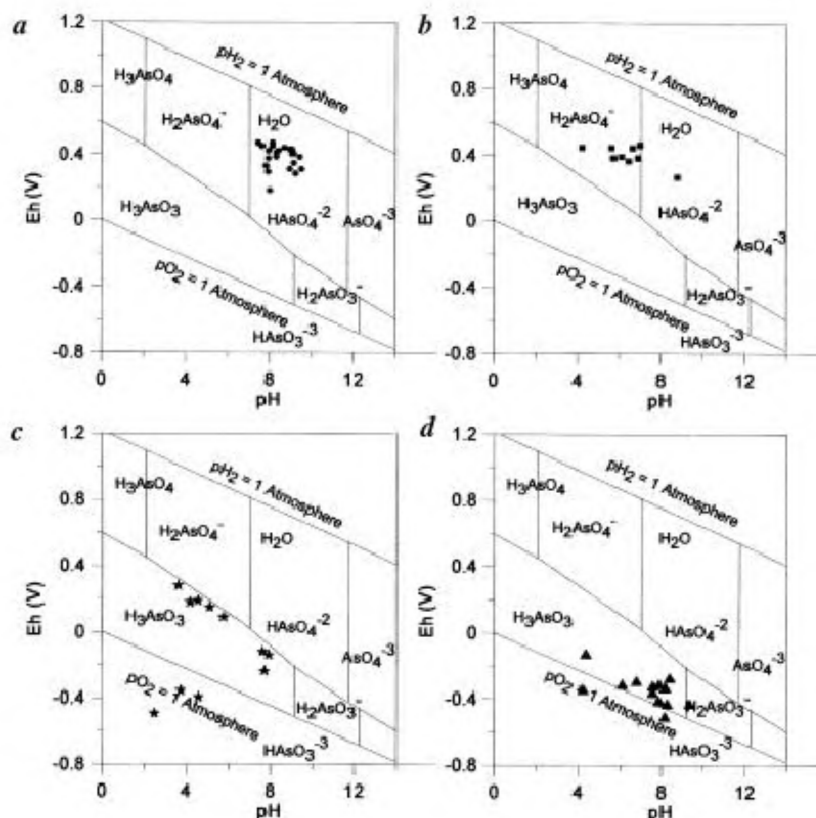


Figure 3. Effect of Eh and pH on arsenic speciation. *a*, Arizona; *b*, Korea; *c*, Bangladesh; *d*, India.

Conclusion

- Arsenic represents a new and poorly understood threat in various part of the world.
- Arsenic solubility in groundwater has shown some correlation between arsenic vs Eh and arsenic vs pH.
- Arsenic species in groundwater have been identified as H_3AsO_3 in West Bengal. In Bangladesh, H_3AsO_3 is more prominent. HAsO_4^- and H_2AsO_4^- are prominent in Arizona and Korea respectively.

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