Sources of Arsenic in Groundwater and its Health Significance - A Review

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ABSTRACT
Arsenic is present in earth’s crust and occurs in more than 200 natural minerals. Under favourable environmental conditions, arsenic enters into the groundwater. Groundwater has been the major source of arsenic exposure to human population around the world. The incidence of arsenic in drinking water, above the standard limit (0.05mg/L as per IS: 10500) has emerged as a major public health problem. Water constituting arsenic above 10µg/l is a major concern. Arsenic has reference dose or reference value of 3E-4 mg.kg⁻¹.d⁻¹ as an estimate of a daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime. Lesions manifest at exposure levels of about 0.002-0.02 mg As kg⁻¹.d⁻¹. The trivalent form of arsenic is considered to be 60 times more toxic than pentavalent form. This communication contemplates on presenting the sources of arsenic, and the influencing factors that facilitate arsenic to groundwater, health implications and present regulation on drinking water standards. From the review, it is clear that the consumption of arsenic contaminated water can cause a wide range of acute and chronic diseases in humans. The source of arsenic for groundwater is mainly geogenic in nature. Therefore, if the groundwater is selected as the source of water, routine monitoring for arsenic becomes a vital step before it is conveyed to the end users for drinking or irrigation or industrial purposes.

INTRODUCTION
Arsenic is a well known ubiquitous metalloid which is widely dispersed in the Earth’s crust. It has properties of a metal as well as a non-metal and occurs in the elemental state for a smaller extent (Nriagu 2002). It is recognized as a toxic and carcinogenic substance which is present within organic and inorganic compounds. High concentrations of arsenic occur in mineral complexes with metals and other elements. Arsenic exists in the average concentration of approximately 5mg/kg of soil (Garelick et al. 2008). In the aqueous environment, the +3 and +5 oxidation states are most prevalent, as the oxyanions arsenite (pH=9-11) and arsenate (pH=4-10) (Smedley & Kinniburgh 2002). Microbial actions on soil also generate arsine gases, which may eventually dissolve in water. Humans are commonly exposed to arsenic mostly through groundwater utilization and marginally through the food chain (Huq et al. 2006). People consuming water with arsenic concentration exceeding 10µg/L (according to WHO Guidelines) are of greater concern, in view of the fact that, it has the potential to cause a wide range of chronic and acute illness.

Arsenic contamination of groundwater has been identified in different parts of the world. Regardless of localized inputs of arsenic, from human activities, much of the contamination of groundwater with arsenic was shown to arise from geogenic sources and the affected groundwater was found in countries on nearly every continent or major land mass (Barringer & Reilly 2013).

Hence, this review mainly concentrates on the geogenic sources of arsenic into the groundwater. The anthropogenic sources are also been highlighted wherever it is necessary. The influencing factors which help in mobilizing the arsenic in the groundwater is provided as a basic information. The health significance and present drinking water regulations with oral slope factors are also enumerated.

SOURCES
Natural sources of arsenic are related to types of rocks with associated geological and geothermal activity. More than 200 minerals contain arsenic, which occur in crustal materials and among them the major contributors for groundwater contamination are Realgar (As₄S₄), Arsenopyrite (FeAsS), Anargite (Cu₃AsS₅), Arsenolite, and Orpiment. Other mineral are Loellingite, Safforlite, Niccolite, Rammelsbergite, Cobaltite, Enargite, Gersdorffite, Glaucochlor etc. Occurrence of some of the arsenic bearing crustal materials and their background concentrations are summarized in Tables 1 and 2. Anthropogenic activities also directly or indirectly aid in introducing arsenic to groundwater (Smedley & Kinniburgh 2002). Sources of As, that arise from human activities include mining and processing of ores and manufacturing using As-bearing sulfides. Activities like alteration of topog-
raphy and rigidity of soil, thereby facilitating for easy dissolution of soil constituents during natural formation of groundwater. Contamination can occur by natural runoff and subsequent seepage of arsenical compounds applied to the farm lands, atmospheric deposition, or improperly disposed chemicals.

The incidence of arsenic in groundwater is attributed to several geochemical processes, including oxidation of arsenic bearing sulfides, desorption of arsenic from oxide and hydroxides, reductive dissolution of arsenic bearing oxides and hydroxides, release of arsenic from geothermal water, and evaporative concentration, as well as leaching of arsenic from sulfides by carbonate (Nickson et al. 2000).

The concentration of arsenic in groundwater is found in groundwater due to the strong influence of the water rock interactions along with favorable physical and geochemical conditions of aquifers for the mobilization and accumulation of arsenic in water. Aqueous forms of arsenic are taken up from As-bearing sulfides, arsenides, sulfosalts, oxides, oxyhydroxides, Fe-oxides, -hydroxides, -sulfates, Fe-, Ca-Fe- and other arsenates. The dissolution of arsenic mineral in groundwater was observed to be in the order of native-arsenics > arsenolite > orpiment > realgar > arsenopyrite > tennantite (Islam et al. 2013).

A major inorganic form of soluble arsenic in natural waters usually occurs as oxy anions of trivalent arsenic (arsenous acid, As(III), H$_3$AsO$_3$) or pentavalent arsenate (arsenic acid, As(V), H$_2$AsO$_4$). Minor forms of arsenic species found in water are mono-methyl-arsenic acid (CH$_3$AsO(OH)$_2$); mono-methyl-arsenous acid (CH$_3$AsO(OH)$_3$); di-methyl-arsenic acid [(CH$_3$)$_2$AsO(OH)]; di-methyl-arsenous acid [(CH$_3$)$_2$AsOH][(CH$_3$)$_2$AsO)]; tri-methyl-arsine [(CH$_3$)$_3$As] and tri-methyl-arsine oxide [(CH$_3$)$_3$AsO] (National Research Council 1999; Le 2002). Table 3 is the list of different forms of trivalent and pentavalent arsenic present in the environment.

Sea food, fish and algae are the richest organic sources of arsenic. Ratnaike (2003) reviews that arsenic intake is higher from solid foods than from liquids including drinking water. Organic and inorganic arsenic compounds may enter the plant food chain from agricultural products or from soil irrigated with arsenic contaminated water (Rossman 2007).

Mukherjee et al. (2006) reviewed the arsenic contamination in groundwater on a global scale. In the review, it is mentioned that the majority of the groundwater around the world, the arsenic source of contamination is mainly through geogenic sources (Afghanistan, Argentina, Bangladesh, Canada, Cambodia, Chile, China, Egypt, Finland, Ghana, Hungary, India, Iran, Japan, Mexico, Myanmar, Nepal, New Zealand, Pakistan, Romania Sri Lanka, Switzerland, USA and Vietnam). Table 4 provides the list of countries in which high level of arsenic concentration is found in groundwater.

### INFLUENCING FACTORS

Many factors control arsenic concentrations and transport in groundwater, which include: Redox potential (Eh), adsorption/desorption, precipitation/dissolution, Arsenic speciation, pH, metal sulfide and sulfate ion concentrations, iron concentrations, biological transformation, etc. Further, these factors may vary from aquifer to aquifer that depend upon the geological settings, geo-chemistry and geo-environmental conditions of an aquifer. Under anaerobic conditions, groundwater normally contains arsenite. Arsenic is particularly mobile at pH values typically found in groundwater (pH, 6.5-8.5) under both oxidizing and reducing conditions. Arsenite is readily oxidized to arsenate in aerobic water at pH values above 7.0. Conversely, arsenate can be reduced to arsenite at low pH values. Under oxidizing conditions, arsenite is dominant, as the H$_3$AsO$_3^-$ form at low pH (less than approximately 6.9), or as the HAsO$_4^{2-}$ form at the higher pH. Under reducing conditions, at pH approximately near to 9.2, the uncharged arsenic species H$_2$AsO$_3$ predominates. That is, the pentavalent species are predominant and stable in the oxygen rich aerobic environment, whereas the trivalent species are predominant in a moderately reducing environment. Redox potential (Eh), pH and DO are all important factors controlling As speciation and chemistry in the groundwater.

There are three major types of natural geological conditions giving rise to high levels of arsenic in groundwater (IARC Monograph 2004).

1. **Aquifers composed of rocks or sediments enriched with arsenic-containing minerals of geogenic origin, such as sulfide mineralization.**
2. **Aquifers containing sediments coated with iron oxy-hydroxide (FeOOH) phases enriched in arsenic through hydrological action, where arsenic is mobilized into the pore water by reducing conditions.**
3. **Aquifers enriched in arsenic through high rates of evaporation in arid areas, leading to increased mineral concentration in groundwater; the arsenic is mobile in such aquifers because of the high pH (> 8.5) caused by concentrations of alkali and alkali earth metals in the solution.**

The geo environmental conditions contributing for arsenic are alluvial sediments (Bangladesh, Vietnam, China, Spain, USA, Canada) with high phosphate and organics (India, Hungary and Romania), or lake sediments, high alkalinity (Mongolia and Argentina). Natural coastal zones and black shale (Taiwan, USA, Canada), loess, volcanic rock/
Table 1: Arsenic present in natural minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Occurrence</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native Arsenic</td>
<td>As</td>
<td>Hydrothermal Veins</td>
<td>Ko et al. 2012</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>FeAsS</td>
<td>Lode Gold, Cu Sulfide, Sn, the most abundant</td>
<td>Meunier et al. 2010</td>
</tr>
<tr>
<td>Cobaltite</td>
<td>CoAsS</td>
<td>Cu, Zn ores, high temperature deposits, metamorphic rocks</td>
<td>Kwong et al. 2007</td>
</tr>
<tr>
<td>Gersdorffite</td>
<td>NiAsS</td>
<td>high temperature deposits, metamorphic rocks</td>
<td>Senior et al. 2009</td>
</tr>
<tr>
<td>Enargite</td>
<td>Cu₃As₄</td>
<td>Hydrothermal Veins and Replacement</td>
<td>Lattanzi et al. 2008,</td>
</tr>
<tr>
<td>Niccolite</td>
<td>NiAs</td>
<td>hydrothermal modification of ultramafic rocks</td>
<td></td>
</tr>
<tr>
<td>Orpiment</td>
<td>As₂S₃</td>
<td>Vein deposits and norties</td>
<td>Anita 2011</td>
</tr>
<tr>
<td>Realgar</td>
<td>AsS</td>
<td>Vein deposits, Clay, Lime stone and Hot springs</td>
<td>Jin et al. 2000</td>
</tr>
<tr>
<td>Tennantite</td>
<td>(Cu,Fe)₂AsS</td>
<td>Hydrothermal Veins</td>
<td>Bruckard et al. 2010</td>
</tr>
<tr>
<td>Arsenolite</td>
<td>As₅O₃</td>
<td>Secondary mineral formed by oxidation of arsenopyrite</td>
<td>Islama et al. 2013</td>
</tr>
<tr>
<td>Claudetite</td>
<td>As₂O₃</td>
<td>Secondary mineral formed by oxidation of realgar, arsenopyrite</td>
<td>Pichler et al. 1999</td>
</tr>
<tr>
<td>Scorodite</td>
<td>FeAsO₂·2H₂O</td>
<td>Secondary Mineral</td>
<td>Kosloff et al. 2012</td>
</tr>
<tr>
<td>Annabergite</td>
<td>(Ni, Co)₄(AsO₄)·8H₂O</td>
<td>Secondary Mineral</td>
<td>Cook 2010</td>
</tr>
<tr>
<td>Hoernestite</td>
<td>Mg(AsO₄)·8H₂O</td>
<td>Secondary Mineral</td>
<td>Voigt 1999</td>
</tr>
<tr>
<td>Conichalcite</td>
<td>CaCu(AsO₄)(OH)</td>
<td>Secondary Mineral</td>
<td>Henderson 2008</td>
</tr>
<tr>
<td>Pharmacosiderite</td>
<td>Fe₃(AsO₄)₃(OH)·5H₂O</td>
<td>Oxidation product of arsenopyrite and other As minerals</td>
<td>Tutor et al. 2013</td>
</tr>
<tr>
<td>Kankite</td>
<td>Fe₃As₅O₈·3.5H₂O</td>
<td>-</td>
<td>Walker et al. 2009</td>
</tr>
<tr>
<td>Loellingerite</td>
<td>Fe₃(AsO₄)₃(OH)·5H₂O</td>
<td>Mesothermal vein deposits</td>
<td>Borba et al. 2000</td>
</tr>
<tr>
<td>Adamite</td>
<td>Zn₃(OH)(AsO₄)</td>
<td>Secondary Mineral</td>
<td>Armienta et al. 2000, 2005</td>
</tr>
<tr>
<td>Selgimannite</td>
<td>PbCuAsS</td>
<td>Hydrothermal vein</td>
<td>Mandal &amp; Suzuki 2002</td>
</tr>
<tr>
<td>Safflorite</td>
<td>(Co,Fe)As₂</td>
<td>Mesothermal vein, Hornfels</td>
<td>Senior &amp; Sloto 2006, Murcott 2012</td>
</tr>
<tr>
<td>Rammelsbergite</td>
<td>NiAs₂</td>
<td>Mesothermal vein</td>
<td>Nisagui et al. 2007</td>
</tr>
</tbody>
</table>

sediments (Mexico and Chile) thermal spring (Greece, Argentina, USA, Canada), mineralized sandstones (Germany) and closed basin lakes (USA, Canada and Chile) are the different environmental conditions contributing for arsenic to groundwater (Nordstrom 2002).

**HEALTH COMPLICATIONS**

Water containing arsenic concentrations more than 0.05 mg/L (according to drinking water specifications, Bureau of Indian Standards 10500: 2012), is of major concern when it is used for consumption or cooking purposes (Ground Water Association 2007). The ingested arsenic is transmitted through the blood stream and may get concentrated within the internal organs, skin, hair and nails (Barr et al. 2005). Soluble trivalent arsenic compounds, approximately 95% of the ingested dose is absorbed from the gastrointestinal (GI) tract and are eliminated from the body through urination. The trivalent form, As III is considered to be 60 times more toxic than pentavalent form As V (Ratnaike 2003, Yousef et al. 2008). In vivo, both forms of arsenic have similar effects, i.e., the absorbed arsenate is mostly reduced to arsenite in the body (i.e. liver). Methylation of inorganic arsenic in liver executed by the enzyme methyl transferase in the presence of adenosylmethionine (methyl donor) and glutathione (GSH, essential co-factor), results in the formation of organic arsenics end metabolites mono-methyl-arsinous and di-methyl-arsinous (Mandal & Suzuki 2002).

Exposure to high levels of arsenic can cause short term or acute symptoms, as well as long-term or chronic health effects. Nausea, vomiting, and diarrhea are very common symptoms in humans following oral exposure to inorganic arsenicals, both after acute high-dose exposure and after repeated exposure to low doses; these effects are likely due to a direct irritation of the gastrointestinal mucosa. Acute, high-dose exposure can lead to encephalopathy, with clinical signs such as confusion, hallucinations, impaired memory, and cerebral infarction (Chin 2008), while long-term exposure to lower levels can lead to the development of peripheral neuropathy characterized by a numbness in the hands and feet that may progress to a painful “pins and needles” sensation. Typical dermal effects include melanosis and keratosis (Jyoti et al. 2012). The long term effect is hyper keratinization of the skin (especially on the palms and soles), formation of multiple hyper keratinized corns or warts, and hyper pigmentation of the skin with interspersed spots of hypo pigmentation. Lesions typically begin to manifest at exposure levels of about 0.002-0.02 mg As/kg/day but may appear at even lower levels. At these exposure levels, peripheral vascular effects are also commonly noted, including cyanosis, gangrene and black foot disease (Chin et al. 2007).
vascular effects of oral exposure to inorganic arsenic include increased incidences of high blood pressure-hypertension (Islam et al. 2012), Ischemic heart disease (heart attack) and other circulatory problems (Fen et al. 2012).

Neurobehavioral alterations are observed more in arsenic exposed children, as they tend to drink more water per unit of body weight than adults. Chronic exposure of humans to inorganic arsenic in the drinking water has been associated with an excess incidence of miscarriages, stillbirths (Richard et al. 2006, Abul et al. 2005), preterm births, and infants with low birth weights. Animal data suggest that arsenic may cause changes to reproductive organs of both sexes, including decreased organ weight and increased inflammation of reproductive tissues, although these changes may be secondary effects. However, these changes do not result in a significant impact on reproductive ability. Long-term (years to decades) exposure to even relatively low concentrations of arsenic in drinking water can increase the risk of developing cancers in skin, lung (pulmonary), kidney and bladder (Guo et al. 2001, Ismail et al. 2008, Mazumder 2008, Claudia et al. 1998, Ferreccio et al. 2013). Some of the diseases aggravated by consuming arsenic contaminated water are furnished in the Table 5.

Arsenic is also suspected to contribute immunological, neurological, and endocrine diseases, but as with the above symptoms, the epidemiological study of diseases caused by arsenic poisoning is only in its infancy. Gandhi & Rakesh (2013) concluded that exposure of arsenic in gestational stage causes developmental and behavioral toxicity. Further, it is a potent carcinogen and toxicant, which easily passes the placenta. Studies have also shown the possibility of causing DNA damage due to oral exposure to arsenic (Feng et al. 2001, Yolanda et al. 2012).

REGULATIONS OR GUIDELINES

The limits for certain contaminant or pollutant are set for safe consumption of the water by different regulatory bodies across the world. Generally, WHO guidelines are followed to set the standard limits. Table 6 provides the information on limits set by Indian Standards (IS10500:2012), World Health Organization (WHO), United States Environment Protection Agency (USEPA), Central Public Health and Environmental Engineering Organization (CPHEEO) and Indian Council of Medical Research (ICMR).
Table 4: Arsenic contamination in different parts of the world.

<table>
<thead>
<tr>
<th>Continent</th>
<th>Country</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australasia &amp; Oceania</td>
<td>Australia, New Zealand,</td>
<td>Appleyard et al. 2006</td>
</tr>
<tr>
<td>Africa</td>
<td>Egypt, Ghana,</td>
<td>Nariman et al. 2011</td>
</tr>
</tbody>
</table>

Table 5: Effect of arsenic exposure on human health.

<table>
<thead>
<tr>
<th>System</th>
<th>Health Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardiovascular</td>
<td>Acrocyanosis and Raynaud’s Phenomenon, Heart attack, cardiac arrhythmias, thickening of blood vessels, loss of circulation leading to gangrene of extremities, hypertension, (Barringer &amp; Reilly 2013)</td>
</tr>
<tr>
<td>Dermal</td>
<td>Hyperpigmentation, basal cell carcinoma and squamous cell carcinoma, abnormal skin thickening, Symmetric hypereratos of palms and soles (palmoplantar), melanosis or depigmentation, Bowen’s disease, facial edema, Desquamation</td>
</tr>
<tr>
<td>Gastrointestinal</td>
<td>Esophagitis, Colitis, anorexia, weight loss, Heartburn, nausea, abdominal pain, Liver Cancer (Robert &amp; Anna 2008)</td>
</tr>
<tr>
<td>Hematological</td>
<td>Anemia, low white-blood-cell count (leucopenia), Megalobastosis</td>
</tr>
<tr>
<td>Neurological</td>
<td>Brain malfunction, hallucinations, memory loss, seizures, coma, peripheral neuropathy, hearing loss, encephalopathy</td>
</tr>
<tr>
<td>Pulmonary, Respiratory</td>
<td>Chronic cough, restrictive lung disease, cancer, Lung Cancer, Laryngitis, tracheal bronchitis, rhinitis, pharyngitis, shortness of breath, perforation of nasal Septum (Abul &amp; Mahfuzar 2002)</td>
</tr>
<tr>
<td>Renal</td>
<td>Hematuria, proteinuria, shock, dehydration, cortical necrosis, cancer of kidneys and bladder, Nephrosis and Nephritis (Yu et al. 2009)</td>
</tr>
<tr>
<td>Reproductive</td>
<td>Spontaneous abortions, still-births, congenital malformations of fetus, low birth weight, prostate cancer (Yang et al. 2008, Rahman et al. 2013)</td>
</tr>
<tr>
<td>Endocrine System, Metabolic</td>
<td>Diabetes mellitus and goiter</td>
</tr>
<tr>
<td>Ophthalmic</td>
<td>Lens Opacity</td>
</tr>
<tr>
<td>Hepatic</td>
<td>Cirrhosis, hepatomegaly, portal hypertension, fatty degeneration,</td>
</tr>
<tr>
<td>Hematological</td>
<td>Bone marrow hypoplasia, aplastic anemia, leucopenia, thrombocytopenia, impaired folate metabolism, karyorrhexis</td>
</tr>
</tbody>
</table>

**REFERENCE DOSE OR ORAL SLOPE FACTOR**

Reference dose or reference concentration is defined as an estimate of a daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime. RfD or RfC is based on No Observed Adverse Effect Level (NOAEL) or Lowest Observable Adverse Effect Level (LOAEL), combined with appropriate uncertainty factors to account for interspecies variability in sensitivity, interspecies extrapolation, extrapolation from LOAELs to NOAELs and extrapolation from sub-chronic to chronic data. Oral cancer Slope Factor is a measure of the incremental lifetime risk of cancer by oral intake of the chemical. Arsenic has RfD value 3E-4 mg.kg⁻¹.d⁻¹. RfD: Reference Dose is computed by multiplying the consumption rate and divide by the mass of a reference person.

CONCLUSION

An attempt is made to recapitulate on the arsenic sources in groundwater and associated health complications. Arsenic in trivalent form is considered to be more toxic than...
pentavalent form. According to the present review, it is evident that major source of arsenic in groundwater is geogenic in nature. Alluvial deposits, volcanic sediments and geo thermal water are the main arsenic source of groundwater. Several factors are responsible for concentration and transport of arsenic in groundwater. Arsenic can cause wide range of chronic and acute illness when consumed in varying concentration. Consuming water constituting arsenic above 10µg/L is a major concern. Hence, the source water has to be analyzed for arsenic and all possible actions must be recommended to remediate as first priority and also, if feasible, alternative sources are to be identified for supplying safe drinking water. Further, treatment methods have to be proposed and the mitigation measures have to be considered as location specific and it cannot be generalized for other regions. Educating the people on potential threat of consuming arsenic contaminated water is also an important step for overcoming arsenic exposure problems through drinking water. When the arsenic contaminated water is used for irrigation purpose the accumulation factor has to be considered as major parameter in order to avoid the unfavorable concentration reaching the consumer through food products.

REFERENCES


Table 6: Drinking water standards.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>IS10500:2012</th>
<th>WHO</th>
<th>USEPA</th>
<th>CPHEEO</th>
<th>ICMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.05</td>
<td>0.05</td>
<td>0.01</td>
<td>0.05</td>
</tr>
</tbody>
</table>

(1) Desirable, (2) Permissible, (3) Guideline Value, (4) Maximum Contaminant Level Goal (MCLG) - The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals, (5) Maximum Contaminant Level (MCL) - The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards, (6) Acceptable, (7) Cause for Rejection.


Rossman, T. 2007. Arsenic, Environmental and Occupational Medicine, 4th ed. Hagerstown, MD: Lippincott Williams & Wilkins, 1006-1017.


Arsenic contamination in surface drainage and groundwater in part of the Southern Asia tin belt, Nakhon Si Thammarat Province, Southern Thailand. Environ. Geol., 27: 16.


