

Arsenic Occurrence, Ecotoxicity and its Potential Remediation

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Abstract

Arsenic levels in water, sediments, and biota of the estuaries and coastal ecosystems have been well documented. Natural and anthropogenic activities such as industrial offshore oil spills and groundwater pollution have increased its levels in natural water systems. This brief review provides a clear view on arsenic occurrence, ecotoxicity and its potential remediation. Both humans and biota were affected from arsenic contamination. The development of substitute materials for arsenic applications in the agricultural and forestry industries and controls of arsenic emissions from the coal industry may be possible strategies to significantly decrease arsenic pollution sources and dissipation rates into the environment. At the same, to develop cost effective green remediation technology for cleaning As in water and soils is essential.

Keywords: Arsenic toxicity; Bioremediation

Introduction

Arsenic (As) is a naturally occurring metalloid that is widely distributed in water, soil, air and biota from natural and anthropogenic sources [1-4]. Exposure to arsenic usually occurs via the ingestion, inhalation and skin contact. Arsenic has been found in drinking water in several countries worldwide which caused a major public health issue. Cardiovascular, diabetes, and cancers are some of the general health effects that result from exposure to arsenic. There are three main groups of arsenic compounds: inorganic, organic and arsine gas [1]. These groups are based on its valence state: (1) Arsenides/arsine gas with -3 oxidation state, (2) Metalloid arsenic with 0 oxidation state, (3) Arsenite trivalent compound with +3 oxidation state, and Arsenate pentavalent with +5 oxidation state [1].

A better understanding of the chemistry of arsenic is needed to identify its toxic properties and its effects on humans and natural environment. Oxidation states affect many properties of arsenic such as soil adsorption, soil solubility and toxicity to animals. Trivalent arsenic was dominant in the reducing conditions in flooded soils while pentavalent arsenic at oxidizing conditions in drained soils. Inorganic forms of arsenic are highly toxic compared to organic arsenic [5]. Organic arsenic includes methylated metabolites in three forms- monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide. Inorganic forms of arsenic are trivalent arsenite and pentavalent arsenate [6]. Volcanic eruptions, soil erosion and anthropogenic activities are some examples that result in arsenic environmental pollution [3]. Arsenic may also be found in surface water, groundwater and drinking water in the United States [1]. This review provides a brief analysis of the occurrence, toxicity of arsenic, remediation and its implications on contaminated groundwater.

Sources of Arsenic and its Occurrence

Arsenic may be associated with sulphur, iron and oxygen to form a combination of different elements [7]. Arsenic is present in more than 200 mineral species and the most common is arsenopyrite. However, these minerals are relatively rare in the natural environment. Among the most common occurrences in ore zones are arsenian pyrite ($\text{Fe}(\text{SAs})_2$), arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), cobaltite (CoAsS) and niccolite (NiAs) [8]. Arsenopyrite is an iron arsenic sulfide (FeAsS). Minerals are naturally-occurring inorganic produced solids which form a definite crystal structure. Due to mining, arsenopyrite is exposed into

the atmosphere which leads to acid mine drainage. Acid mine drainage is currently a main pollutant of surface water. It is caused when water flows over or through sulfur-bearing materials forming solutions of net acidity. Acid mine drainage results in loss of aquatic life and restricts stream use for recreation, public drinking water and industrial water supplies.

Approximately one-third of the atmospheric flux of arsenic is of natural origin [9]. Volcanic eruption is one of the most important natural sources of arsenic. The presence of inorganic arsenic is found in groundwater used as drinking-water in many countries. It has been related to leaching from arsenic containing geological materials (rocks, minerals and mineraloids). These geochemical environments play a vital role in the distribution and transportation of arsenic. There are several factors that influence the fate of As in environments such as location, geology, and hydrology of aquifer materials. Anthropogenic sources include mining, processing, industrial wastes and application of pesticides as well as poultry wastes [2-4].

Han et al. [2] reported that after 25 years of continuous application of poultry waste, As in the amended soil had a mean of 8.4 mg kg^{-1} compared to 2.68 mg kg^{-1} for a non-amended soil. Arsenic in the amended soil was mainly in the residual fraction (72% of total), which is generally considered the least bioavailable fraction. However, arsenic in poultry waste samples was primarily water soluble ($5.3\text{-}25.1 \text{ mg kg}^{-1}$), representing 36-75% of the total As.

Arsenate vs. Arsenite

The chemical forms and oxidation states of arsenic are more significant in regards to its toxicity. Many factors such as physical state, gas, solution, exposure and the rate of absorption into cells affect the

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Received May 30, 2016; Accepted June 01, 2016; Published June 05, 2016

Citation: Alexander TC, Gullede E, Han F (2016) Arsenic Occurrence, Ecotoxicity and its Potential Remediation. J Bioremed Biodeg 7: e174. doi:10.4172/2155-6199.1000e174

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level of toxicity. Methylation has known to be a principal detoxification pathway. Recent studies revealed that methylated metabolites may be partly responsible for the adverse effects associated with arsenic exposure [10]. Desesso et al. [11] stated that arsenate and arsenite interfered with the cellular production of energy, but act via different mechanisms. Arsenate structural similarity to phosphate allows it to replace for phosphate in energy-producing reactions within the cell known as adenosine triphosphate (ATP). In addition, arsenate may exert its toxic effects indirectly, via reductive metabolism to arsenite. The key to the toxicity of arsenite is its electrophilic nature in which the arsenite binds to electron-rich sulfhydryl groups on proteins. Arsenic may attack on the cell's energy production system which adversely affected cellular health and survival [11].

Arsenic and Marine Organisms

Arsenic has the tendency to bioaccumulate within animal tissue. Among marine animals, arsenic was found to be accumulative to levels of from 0.005 to 0.3 mg kg⁻¹ in shellfish [12]. Some shellfish may contain over 100 µg g⁻¹ of arsenic. The average arsenic content in freshwater fish was of 0.54 µg g⁻¹ on the basis of total wet weight, but some values reached as high as 77.0 µg g⁻¹ in the liver oil of freshwater bass. The arsenic content of urine varied normally from 5 to 40 µg per day (total As). Higher organic arsenic compounds such as arsenobetaine and arsenocholine were found in marine organisms. They are resistant to chemical degradation. In general, it was found that organic arsenicals were more rapidly excreted than inorganic forms and pentavalent arsenicals were cleared faster than trivalent [10].

Marine organisms such as oysters have the ability to concentrate high amounts of arsenic in their tissues [13]. The ubiquitous element arsenobetaine in marine animals have been studied for many years [14]. Arsenic concentration of each tissues ranged from 22.1 to 45.7 µg g⁻¹ of dry tissues in the pearl free oysters and from 27.4 to 50.4 µg g⁻¹ of dry tissue in the pearl-containing pearl oysters. Kantano et al. [13] found that the major arsenic accumulated in each tissue part was identified as arsenobetaine which is non-toxic form of arsenic.

Organic arsenic compounds such as arsenobetaine, arsenocholine, tetramethylarsonium salts, arsenosugars and arsenic-containing lipids are mainly found in marine organisms although some of these compounds have also been found in terrestrial species [15].

Arsenic Transport and Toxicity

Arsenic is a ubiquitous element that is widely distributed in the environment [16]. The release of As in the environment is a result of a variety of natural and anthropogenic sources. Natural emissions such as volcanic eruption, soil erosion, and forest fires release concentrations into the environment. The dispersal of As through means of anthropogenic activity such as combustion of fossil fuels and applications of insecticides, herbicides, fungicides, algicides, and wood preservatives are highly toxic to the environment [3,6,17]. As has the ability to be persistent in the top layer of soil, bioaccumulate in plants and animals and transport through various media [1,3]. The route of toxicity and the mechanism of uptake varied among media.

Arsenic may be transported to the soil by means of wind, runoff, or leachate. Arsenic's residence in soil is usually deposited in the top soil surface but is not transported to far depths of the soil because of the partitioning of arsenic and oxidizing conditions of some soils [1]. Once arsenic is deposited in the soil, the compound is characterized as immobile. Arsenic is more mobile in saturated soils. The parameters that usually govern absorption are: pH, organic matter content, iron

oxide content, aluminum oxide and cation exchange capacity [18]. The presence of arsenic in the soil could be detrimental to plant life. The contamination of soils with arsenic obstructs plant growth [19]. Sheppard et al. [20] found that the average toxicity threshold was 40 mg/kg for crop plants. This phytotoxicity threshold varies among plant species. Plants in highly polluted soils or naturally high arsenic rates usually take up low concentrations in the plant tissues [21].

Arsenic is mainly disseminated across a variety of water bodies. The transportation of As in the water systems are largely influenced by anthropogenic activity such as direct dumping of chemicals or runoff from industries into water bodies. Arsenic tends to translocate from water bodies to sediment, biofilms, and aquatic life. The bioaccumulation of As in aquatic life does not appear to biomagnify among trophic levels [22]. The concentration of arsenic in aquatic organisms is largely found in algae and bottom feeders. Bottom feeders are readily exposed to arsenic and heavy metals because of the accumulation of these elements in the benthic sediment.

The presence of arsenic in drinkable water systems has caused problems in animals and humans. Natural occurring arsenic in groundwater possesses a serious health problem in India, Vietnam, Taiwan, Mexico, Argentina, Chile, Hungary, Romania, and parts of United States [23].

Potential Remediation

Bioremediation is a natural process that involves bacteria, fungi, and plants to change pollutants as these organisms carry out their normal life functions. Metabolic processes of these organisms are able to use chemical contaminants as an energy source. These processes make pollutants less toxic products. Bioremediation is a cost-effective method used to remediate heavy metals and metalloids through biological systems [24]. Ferns are the hyper arsenic accumulator plants that absorb arsenic from contaminated soil [25,26]. It has the ability to accumulate about 200 times concentration of arsenic higher than the concentrations measured in non-contaminated soils. The growth of fern plants was better candidate in the arsenic contaminated soil compared to non-contaminated soil.

Alternative potential remediation strategies for metal/metalloid contaminated soils include *in situ* biological remediation. *In situ* elemental inactivation is a technique used where additive is mixed with contaminated soil. Stabilization of trace elements in soil can be reached by soil additives that absorb, bind or coprecipitate the contaminating elements [4,27]. The main purpose of *in situ* remediation is to reduce trace element mobility by affecting leaching potential and bioavailability. Clays and aluminum, iron and manganese oxides and hydroxide have been added into arsenic-contaminated soil to reduce labile arsenic [28]. Iron oxide can be used to remediate arsenic through absorption. Iron oxides added to garden soils have shown decreases in water extractable As concentrations, together with lower accumulation levels in plant tissues [28].

Han et al. [3] reported the global industrial-age cumulative anthropogenic arsenic production and its potential accumulation and risks in the environment. In 2000, the world cumulative industrial age anthropogenic arsenic production was 4.53 million tonnes. The worldwide coal and petroleum industries accounted for 46% of global annual gross arsenic production, and the overall contribution to industrial-age gross arsenic production was 27% in 2000. Global industrial-age anthropogenic As sources (as As cumulative production) follow the order: As mining production > As generated from coal > As generated

from petroleum. The potential industrial-age anthropogenic arsenic input in world arable surface in 2000 was 2.18 mg arsenic kg⁻¹, which is 1.2 times those in the lithosphere. The development of substitute materials for arsenic applications in the agricultural and forestry industries and controls of arsenic emissions from the coal industry may be possible strategies to significantly decrease arsenic pollution sources and dissipation rates into the environment. At the same, to develop cost effective green remediation technology for cleaning As in water and soils is essential.

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Citation: Alexander TC, Gullede E, Han F (2016) Arsenic Occurrence, Ecotoxicity and its Potential Remediation. *J Bioremed Biodeg* 7: e174. doi:10.4172/2155-6199.1000e174

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