

## Review Article

## Arsenic-Based Pollution Status in Pakistan

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## Abstract

Environmental pollution is on the rise in Pakistan, due to increased industrialization and urbanization which has resulted in consistent release of toxic effluents. These effluents render both soil and water unfit for crop production. About 80% people of urban area in Pakistan lack access to really clean and potable water due to discharge of hazardous industrial wastes, toxic synthetic organic chemicals, heavy metals, pesticides and municipal wastes. In Pakistan, area using the waste water for irrigation is 32,500 hectares. Pakistan is producing thousands of tons of vegetables but these vegetables are contaminated with chromium, cadmium, copper, lead, nickel, zinc, cobalt, magnesium, iron and arsenic because of untreated city effluent and usage of sewage water especially in big cities. In some areas of the Pakistan, the presence of arsenic in subsurface aquifers and drinking water systems is a potentially serious human health hazard. A majority of shallow subsurface aquifers and tube wells are contaminated with arsenic at levels which are above the recommended arsenic level of 10 ppb. Arsenic concentrations of soil samples are relatively higher in surface soils than in deep soils from the same location. The highest average arsenic content in the soils of the agricultural areas of Sindh (irrigated with Arsenic rich lake water) was found to be 46.2mg/kg followed by 35 mg/kg in surface soil collected from various regions of Punjab. The mean values of total arsenic in Manchar lake sediment were found in the range of 11.3-55.8. Human health effects were also observed in local of Pakistan, due to the consumption of arsenic contaminated surface and ground waters having As > 50  $\mu\text{g L}^{-1}$ .

## Introduction

Among metal and semi-metals, arsenic is of growing concern because of its high toxicity and widespread natural occurrence in the environment. Arsenic is the 20<sup>th</sup> most abundant element in the earth's crust makes about 5mg kg<sup>-1</sup> of the Earth's crust at an average concentration of 2mg kg<sup>-1</sup> in igneous and sedimentary rocks [1]. Arsenic is usually found in the atmosphere, soils, rocks, organisms and natural waters. The presence of arsenic in the environment is associated with human activities, and it is estimated that about 60% of the arsenic is present in the environment from anthropogenic sources [2]. Generally low levels of arsenic in soils and sediments has been reported, while elevated levels of arsenic were detected in these soils and sediments, which affected by human activities [3]. Arsenic concentration varied in the area, less than 1mg/kg to as high as 100,000mg/kg in the soil [4] and one in every 60 people living on earth in an area where 50ug/L or above arsenic in groundwater [5]. It is generally accepted that the inorganic species, arsenite [As<sup>3+</sup>] and arsenate [As<sup>5+</sup>], are the predominant species in most environments, where the organic ones could also be present [6]. The trivalent compounds (arsenites) are more toxic than the pentavalent compounds, i.e. arsenates [7,8]. Toxicity As<sup>3+</sup> is believed to be due to its binding to thiol groups of biologically active proteins, their acute toxicity being attributed to inhibition of metabolic enzymes.

It has been reported that As<sup>3+</sup> is 4 to 10 views more soluble in water than As<sup>5+</sup>. However, the trivalent methylated arsenic species found more toxic than inorganic arsenic because to create powerful DNA breakdown [8].

Long-term drinking water exposure causes skin, lung, bladder, cardiovascular disease and kidney cancer, and pigment changes, skin thickening (hyperkeratosis), neurological disorders, muscle weakness, loss of appetite and nausea [9-13]. As individuals are exposed to high arsenic content of water, the skin lesions induced [14].

Anthropogenic arsenic contamination of soils can result from mining, milling and smelting of copper, lead and zinc sulphide ores, hide tanning waste, dyes, chemical weapons, electroplating, gas, municipal sludge land, combustion of fossil fuels, arsenic additives to animal feed, coal fly ash and agricultural use of arsenic pesticides [15-23]. In the last decade has been reported the global input of arsenic to soils by human activities to around 52.000 to 112.000 tons per year [24]. Volcanic derived sediment, sulphide minerals and metal oxides are natural sources [25], while various industrial wastes, mining, sewage and pesticides are man-made sources of arsenic [26]. Arsenic compounds were used in the preparation of a variety of products. Arsenic used in glass production and wood preservation industry. The latter industry was, until the end of 20th century, the most active user of such compounds in the United States [27], but the industry voluntarily reduced the Chromated Copper Arsenate using (CCA) since 2003 has resulted in a limited availability of CCA-treated wood and products [28].

The high As contaminated (>50 mg L<sup>-1</sup>) Groundwater has been reported in various parts of the world [29-33]. In Pakistan, researchers and agencies (Pakistan Council for Research in Water Resources 'PCRWR' and UNICEF) were reported the level of As > 100  $\mu\text{g L}^{-1}$  in the groundwater [31,34,35]. Irrigation by using the

arsenic contaminated water can lead to the soil pollution and arsenic deposition in to the crops, the human consumed later and thus exposed to arsenic [36].

## Arsenic Contamination in Pakistan

During the 1990s, naturally occurring arsenic was found to be widespread in groundwater in the USA, Argentina, Taiwan, China, Hungary, Vietnam, and the Gangetic plain [33]. The World Health Organizations (WHO) current provisional guideline for arsenic in drinking water is 10ug/L, but all developing countries concerned with contaminated groundwater are still struggling hold with the recent WHO-guideline value of 50ug/L [37]. Arsenic is in the air of suburban, urban and industrial area available primarily as inorganic particulate (a variable mixture of AsIII and AsV, with the pentavalent form predominating) [38].

## Arsenic in Water

Mining has increased arsenic concentrations in Warsak Canal [39]. Large concentrations of arsenic, such as 0.942, 0.40, 0, 38, 0.643 and 0.475mg L<sup>-1</sup> were noted in Hattar industrial areas. The concentrations of arsenic exceeded from 10ug/l in 58% of the samples, reaching up to 906ug/L in forty nine groundwater samples analyzed from Muzaffargarh district of Punjab and Central Pakistan. In the rural areas concentrations stay below 25ug/L, because arsenic in the oxic shallow groundwater and in recharging water, sorbet to aquifer sediments. But In some urban areas shallow groundwater is found to contain elevated levels of arsenic [40]. In some areas of Pakistan, the presence of arsenic in underground aquifers and drinking water systems is a potentially serious health hazard. A majority of shallow subsurface aquifers and tube wells are contaminated with arsenic at levels that above the recommended arsenic level of 10ppb [41].

## Arsenic in Soil

Arsenic concentrations of soil samples are relatively higher than in the deep soils from the same place in surface soils. The highest average As content in the soils of agricultural areas of Sindh (irrigated with arsenic -rich lake water) was found that 46.2mg/kg [42], followed by 35mg/kg in the surface soil collected from different regions of Punjab [43]. The author suggested that the contribution of air pollutants derived from coal burning and the use of fertilizers for high levels of arsenic in the topsoil [43]. In some parts of Sindh province total arsenic levels in sediments and soils irrigated with lake water was higher than the threshold effect level , as indicated by interim sediment quality assessment values [44] and US EPA [45]. The averages of total arsenic in Manchar lake sediments were found in the range of 11.3 to 55.8mg/kg [42].

## Arsenic in Air

Methylated arsenic is believed that a minor component atmospheric arsenic [38]. Pakistan Environmental Protection Agency reported arsenic between the range 230-2230ng/m<sup>3</sup> in ambient air particles from district Lahore [45], which is much higher than that reported in the other parts of the world For example, 91-512ng/m<sup>3</sup> in Calcutta, India [46], 25ng/m<sup>3</sup> in Wuhan City, China [47], from 1.2 to 44 ng/m<sup>3</sup> in Los Angeles, USA [48].

## Arsenic in Food (Vegetable, Grain, Fishes)

Toxic ions can remain in soil or leach through soil and can

contaminate groundwater, along with the soil and eventually enter the food chain and cause a danger to the health of animals and plants. Human exposure to these metals through ingestion of contaminated food or drinking water intake can lead to accumulation in humans, animals and plants [39]. Basic foodstuffs (crops of cereals and vegetables) are considered as a major pathway for entry of metals and metalloids in the food chain [42,49]. It is because of cultivated (land of irrigated land and irrigation water) and fertilizing media (fertilizers, pesticides and herbicides). Translocation of arsenic and other toxic components by plants are depend on the bioavailable arsenic instead of total content in soil [50,51].

Several studies on the linear relationship between arsenic content of vegetation and soil concentrations of both total and soluble species show that plants get the arsenic passively with the water flow. The plants can accumulate extremely large amounts of arsenic, according to the source of pollution and the location. It was observed that the use of arsenic rich irrigation water and land affected plant height, crop yields, and the development of root growth [51,52]. In Southeast Sindh greater accumulation of arsenic found in spinach , coriander and mint leaves in the range of 0.90-1.20mg/kg, while the lower arsenic uptake was observed in the onion, carrot , potato and in the range of 0.048 to 0 .256mg/kg [42]. The daily intake of arsenic from food stuffs in arsenic affected (irrigated with pond water) and unaffected (irrigated with water from the channel) region was found to be 343.5 and 144.7g/day in adults, respectively [42]. This daily dietary intake of total arsenic composite food by adults is higher than in other countries, 59.2g (adult males) and 34.1g (adult females) in Canada [53]. Irrigation with arsenic-laden groundwater in Asia also causes bioaccumulation of arsenic [54]. To assess the possible risk to the health of people consuming crops irrigated with arsenic contaminated water, information on the transfer of land arsenic for plants is needed to minimize the accumulation of arsenic in plants, consumed directly by humans, farm animals and wildlife [55].

## Effects of Arsenic

In plants, arsenic accumulates according to tolerance [36], especially in the root system, to various degrees in aerial parts, depending on the translocation [56]. The potential metal tolerance of different species vary considerably between different species and between different genotypes of the same species [57]. Several studies showed that low concentrations of arsenic stimulate plant growth, but excessive arsenic did damage to the plants. After entering the plant, arsenic can disrupt plant metabolism such as phosphorylation is decouple in mitochondria by arsenate and activities of the enzyme can be excised by arsenite, when reacted with sulfhydryl proteins [58]. The intake of arsenic by plants can compete with other nutrients in the soil such as phosphorus by phosphate transport systems [59]. On the other hand, the phosphate may directly affect the arsenic content of the soil for enhancing arsenic phytoavailability [58]. Seed germination and plant growth of wheat were stimulated at low and inhibited at high (5 to 20mg/kg soil) arsenic level [51]. Fitz and Wenzel [60] found that there was no evidence that arsenic is essential to plants, but the growth of plants is stimulated when applied at low concentrations. In recent studies, it was suggested that arsenic is absorbed as a arsenate and some parts converted to arsenite by an enzyme called arsenate reductase. Arsenite stored in the vacuole and further detoxified. Most arsenate transferred to leaf cells where

it is converted back to arsenite (in cytosol), and stored/detoxified in vacuole. Even majority of researchers have suggested that the form of arsenite transferred from roots to shoots [41]. The easily is easily taken up by plant roots, in most cases as arsenate (AsV), the dominant form of arsenic in aerobic environments [55]. Being an analog of phosphate, AsV and phosphate share the same intake tract. Special transporters have been identified that are thought to mediate much of the observed AsV influx and these include the *A. thaliana* Pht1; 1 and 1;4 high and medium affinity phosphate uptake systems. However, the affinity of the various transporters for phosphate AsV higher in hyperaccumulator *Pteris vittata* compared to non-accumulator plant species [61,62].

## Conclusion

i) The rise in arsenic pollution in the past decade is mainly increasing industrialization and urbanization in Pakistan.

ii) Due to increase industrialization arsenic is now ubiquitous to the environment (Air, water, soil) thus posing a serious threat to ecosystem.

iii) Proper remediation strategies must be adopted to minimize the risk to ecosystem.

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