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'As' Contamination in Ground Water in Punjab Cities, Pakistan

Q. U. A. Fatima*, E. Rasheed, H. Akram, S. Niazi
Department of Chemistry, National University of Sciences and Technology (NUST), Islamabad, Pakistan
***Corresponding Author email**: quratulainfatema2005@gmail.com

Abstract
The presence of different heavy metals contaminates the groundwater of various parts of the world. Still, the primary contaminant is Arsenic (As), which results from both natural and anthropogenic sources, causing severe effects on human health and the ecosystem. Groundwater is a natural resource that millions of people use for diverse purposes, including agricultural, domestic, and mining purposes. It is naturally present in the Earth's crust, while anthropogenic activities contaminate the groundwater in various regions of the world. In this article, we reviewed the 'As' concentration in different cities of Punjab province of Pakistan, including Sahiwal, Lahore, Kasur, Multan, Chakwal, Rahim Yar Khan, Jhelum, and Muzaffargarh. Furthermore, this review highlights the sources, health outcomes, and remedies for 'As' contamination in the groundwater. The literature revealed that chronic exposure to As contamination is related to health issues, including cardiovascular disease, neurological disorders, carcinogenesis, and skin disorders. This article also overviews several technologies (Coagulation, absorption, Ion exchange, membrane filtration, Biological Oxidation), but technical and economic limitations obstruct their implementation.

Keywords: Groundwater pollution, 'As' sources, Health effects, Treatments

1. INTRODUCTION

Water plays a significant role in the biosphere, supporting all forms of life. Out of total earth water, 2.5% is freshwater, while 30% is groundwater [1]. Groundwater is the most important natural resource because it is the backbone of our ecosystem [2]. It is the largest unfrozen source of freshwater [3]. This vital natural resource supplies freshwater for drinking, as well as water used for industrial processes, power, energy production, and irrigation [4]. Groundwater is essential in maintaining lakes, rivers, and swamps, hence supporting the diverse ecosystem [5]. The requirement for groundwater has increased due to population growth, environmental challenges, agriculture, tourism, industrialization, and rising living standards [6]. Groundwater is closely linked with the five major world's surface water ecosystems and, together with the atmosphere and oceans, forms an integral part of the Earth's water cycle [3].

Additionally, as compared to sources of surface water, natural groundwater contains low levels of bacteria, suspended solids, and viruses, with only a small amount of dissolved mineral content. These characteristics of groundwater make it an ideal choice for human consumption. However, its association with the surface allows for the risk of contamination from human activities that affect its quality [7]. Groundwater contamination is a serious global challenge for ecosystem sustainability. Rapid industrialization, economic growth, and urbanization are the major contributors to the contamination of groundwater [8]. A national survey reported that in Pakistan, only 56% of households have access to clean drinking water. According to global parameters, 25.61% of Pakistan's population have access to safe drinking water, with 30% of urban residents and 23.5% of rural residents falling within this group. By 2025, two-thirds of the world's population is expected to reside in countries with severe water shortages [1].

Groundwater contamination, resulting from both human actions and natural processes, along with various social impacts, has become a significant environmental challenge worldwide [7]. Anthropogenic activities (such as farming, ecosystem degradation, deforestation, and over-extraction of groundwater) are the primary cause of drinking water contamination in the densely populated regions of Pakistan. As a result, government agencies have declared groundwater in cities like Karachi, Lahore, Sialkot, Faisalabad, Gujarat, Peshawar, and Kasur to be undrinkable [8]. A similar situation exists in Pakistan's capital, Islamabad, and its twin city, Rawalpindi, where water samples have been found to be contaminated with total coliforms and fecal coliforms at rates of 94% and 34%, respectively. Often, groundwater pollutants are colorless and odorless, making them difficult to detect [9].

In Pakistan, groundwater contamination varies significantly across regions, with high levels of organic, inorganic, and microbial pollutants [10]. Common pollutants include pathogens (like bacteria, viruses, and protozoa) and chemical substances such as nitrate, sulfate, fluoride, and heavy metals [11]. Ecologically, mineral-laden groundwater can harm plant and aquatic life, destabilizing ecosystems. Mineral contamination in groundwater occurs when naturally occurring or human-induced mineral deposits leach into water supplies, leading to elevated concentrations of substances that can pose health and environmental risks [12]. Minerals like Arsenic (As), Fluoride (F), Iron (Fe), Manganese (Mn), and Lead (Pb) can enter groundwater from surrounding rocks or through human activities such as mining, agriculture, and industrial waste disposal. Contamination of groundwater through Arsenic (As) is among the most critical and serious environmental issues, particularly in developing countries, due to As's high toxicity and its potential to cause harmful health effects, even at low levels of exposure [12].

1.1. 'As' contamination in groundwater

'As' is a naturally occurring element and a well-known human carcinogen metalloid mainly found in the groundwater worldwide with atomic number 33 [12,13]. It ranks fourteenth in seawater, twentieth in abundance in the Earth's crust, and twelfth in the human body [13, 14]. It usually appears in three allotropic forms, including grey, black, and yellow. When heated, Arsenic quickly oxidizes to form Arsenic trioxide (As_2O_3) and emits a garlic-like odor [14]. It mainly exists in four oxidation states (-3, 0, +3 and +5) [12]. 'As' often referred to as the "king of poison", a highly toxic element ranked number 1 on the WHO's 2001 priority list of hazardous substances. Since 1993, 10μg/L of 'As' concentration was allowed in drinking water [12,14]. PCRWR and UNICEF reported that in several regions like in Punjab cities Rahim Yar Khan (21%), Multan (71%), and Shuja Abad (43%) and in Sindh, including Sehwan (44%) and Dadu (58%), the level of 'As' has exceeded from the limit recommended by World Health Organization (WHO) [11, 15]. Previous studies reported high levels of 'As' in Tarbela and Chashma, with readings as high as 750 mg/L. The latest studies indicate that in some areas, the 'As' level in groundwater wells has exceeded WHO safety limits by about 64% to 100%. It is estimated that 47 million people are exposed to 'As' in both Punjab and Sindh. According to the International Agency for Research on Cancer (IARC), it is a significant source of mutagen, carcinogen, and tetragen. Naturally, 'As' exists in two forms: trivalent As (III) and pentavalent As (V). Trivalent 'As' is more toxic than Pentavalent 'As' [7,14].

1.2. Sources of 'As'

'As' contamination in groundwater is caused by both natural and anthropogenic sources (Fig. 1), including industrialization, mining, and weathering processes, urbanization, volcanic eruption, and agricultural pesticides [16]. Natural sources of 'As' in water include the dissolution of the Earth's crust, runoff, volcanic activity, and leaching [12,13]. Anthropogenic sources, on the other hand, stem from various human activities, such as timber preservation, fossil fuel combustion, Lead and Copper smelting, leather preservation, waste burning, pesticide use, and the production of As-containing. Most people are exposed to 'As' through food and drinking water.

Chronic 'As' poisoning often results from consuming a diet grown with As-contaminated water, which has been used for irrigating crops, vegetables, and rice intended for human consumption [16].

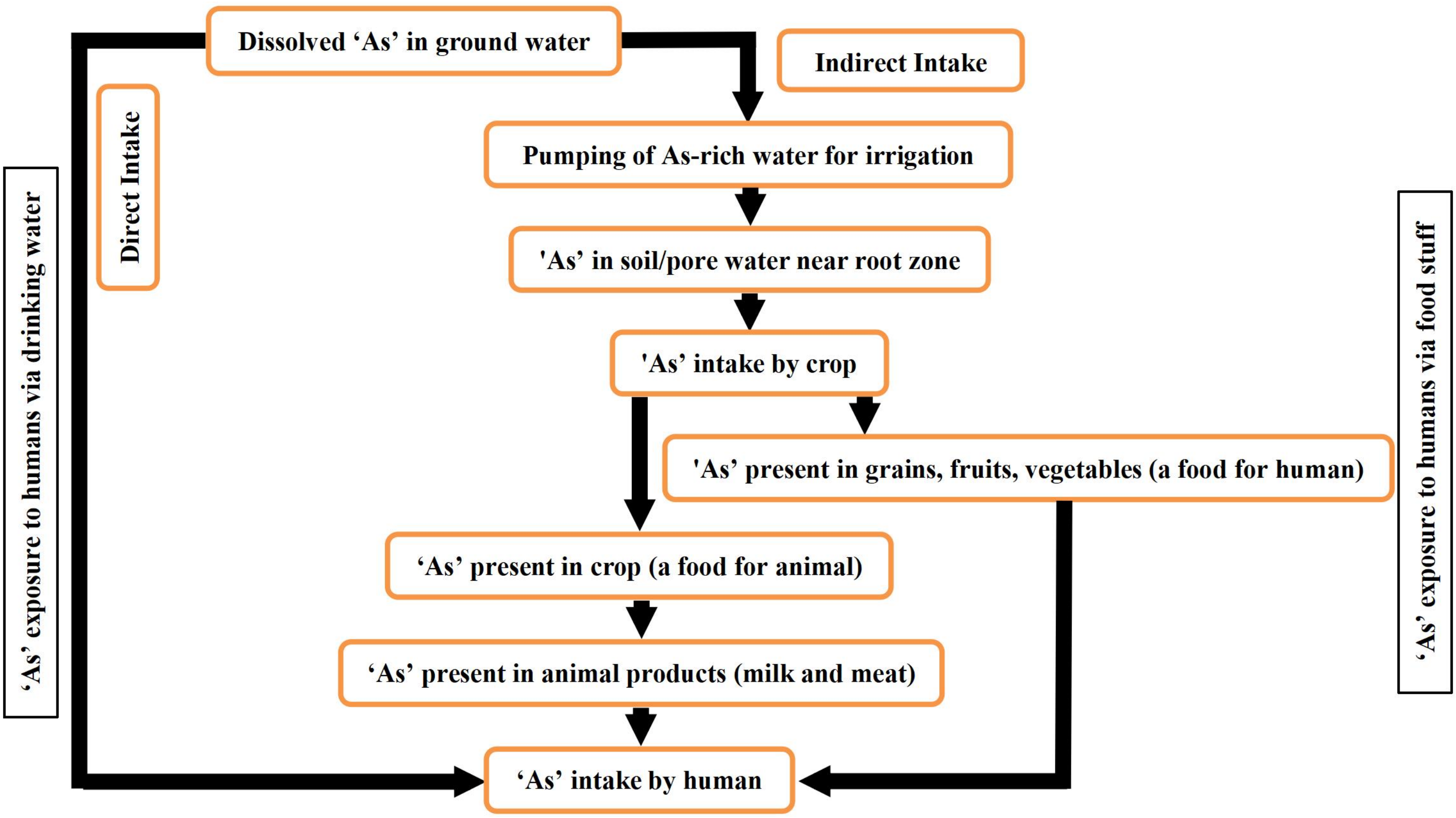

Figure 1: Flow Chart of Arsenic (As) intake by human beings

1.3. 'As' Concentration Level

The Table provides information on the population and 'As' concentrations at two levels (10 μg/L and 50 μg/L) across various cities. It also highlights both natural and human-made (anthropogenic) sources of 'As' in groundwater, such as air pollution, coal burning, agricultural activities, industrial waste, and coal mining. Additionally, the Table illustrates how 'As' concentrations in groundwater vary between different cities. Lahore and Kasur are affected by anthropogenic sources, while natural sources impact Chakwal. Graphical data shows that the concentration of 'As' at 50µg/L is maximum in Sahiwal and minimum in Chakwal, as shown in Table.

Table. 1: 'As' contamination in several cities of Punjab

	City	*Population (2023)*	*Sources Anthropogenic and Natural*	*Major cations and anions composition*	*At 10µg/L (minimum percentage %)*	*At 50µg/L (maximum percentage %)*	*Reference*
1.	***Lahore***	13 million	Coal burning, air pollutant	Na^+, SO_4^{-2}, HCO_3^{-1}, F^{-1} and high pH	65	5	[15,35]
2.	***Kasur***	405,000	Agricultural activities, industrial waste and at high pH desorption process	Na^+, SO_4^{-2}, HCO_3^{-1}, F^{-1} and high pH	44	5	[15,33]
3.	***Multan***	5.36 million	Reductive dissolution of Iron hydroxides natural source	pH neutral to alkaline, Na^+, Ca^{+2}, HCO_3^{-1}, SO_4^{-2}, Cl^{-1} and PO_4^{-3}	61	3	[15, 31]
4.	***Chakwal***	1,734,854	Coal mining activities and geothermal source	pH neutral	99	0	[15,32]
5.	***Rahim Yar Khan***	5,564,703	Reductive dissolution of Iron hydroxides natural source	pH neutral, PO_4^{-3} and Fe^{+2}	81	3	[15,38]
6.	***Jhelum***	1,382,308	Coal mining activities and geothermal source	pH neutral	85	2	[15,32]
7.	***Muzaffargarh***	3,528,567	Iron hydroxides natural sour	Ca^{+2}, HCO_3^{-1}, SO_4^{-2}, Cl^- and PO_4^{-3}	80	6	[15,31]
8.	***Sahiwal***	2,881,811	agricultural activities, industrial waste and at high pH desorption process	Na^+, SO_4^{-2}, HCO_3^{-1}, F^{-1} and high pH	11	15	[15,33]

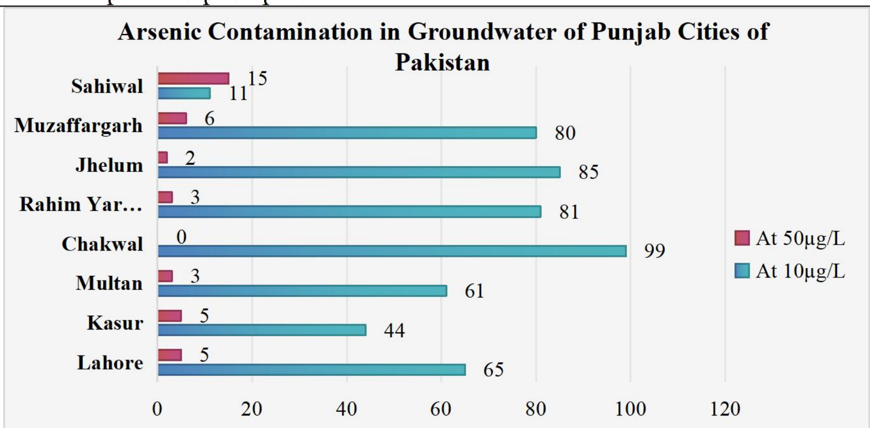

Figure 2 : 'As' Contamination in Groundwater of Punjab Cities of Pakistan

The 'As' contamination in groundwater of different Punjab cities of Pakistan e.g. Muzaffargarh, Jhelum, Rahim Yar Khan, Chakwal, Multan, Sahiwal, Kasur and Lahore at two standard concentrations of 'As' i.e. at 10µg/L which is minimum percentage level and a safe zone at 50µg/L which is maximum percentage level and a moderate zone (Fig. 2) shows that the highest 'As' contamination below the 10µg/L was found in district ***Chakwal*** (99%) followed by district ***Jhelum*** (85%), ***Rahim Yar Khan*** (81%), ***Muzaffargarh*** (80%), ***Lahore*** (65%), ***Multan*** (61%), ***Kasur*** (44%) and ***Sahiwal*** (11%). WHO guideline value for 'As' in drinking water (**10 µg/L**), which was safe and it also showed that the comparison of data with the limit at **50µg/L** shows that districts ***Chakwal*** (0%), ***Jhelum*** (2%), ***Multan*** and ***Rahim Yar Khan*** (3%), ***Kasur*** and ***Lahore*** (5%), ***Muzaffargarh*** (6%) and ***Sahiwal*** (15%) have considerable exceedance than Pakistan's standard for 'As' in drinking water.

2. Health effects.

The International Agency for Research on Cancer (IARC) has classified 'As' as a human carcinogen element since 1980. Numerous researchers have emphasized the significant health risks posed by 'As' in drinking water [17]. According to the 2012 report, 'As' can cause considerable health effects even at low levels of exposure. It is the primary source of cancer if the person intakes 'As' at a low level [22].

2.1. Respiratory System

Continuous intake of inorganic substances causes respiratory disorders such as coughing, shortness of breath, and chest sounds [20]. 'As' exposure can have profound effects on the human respiratory system. Inhalation of arsenic-contaminated air, particularly in industrial areas or through the burning of arsenic-rich materials or drinking, can lead to irritation of the airways, coughing, and shortness of breath. Long-term exposure may increase the risk of chronic respiratory conditions such as bronchitis and lung cancer. Arsenic can also weaken the immune response in the lungs, making individuals more vulnerable to respiratory infections. Consumption of Arsenic trioxide can cause significant health diseases like tracheobronchial, alveolar hemorrhage, submucosal hemorrhage and pulmonary edema [21].

2.2. Pulmonary System

Inorganic 'As' also affects the pulmonary system including coughing, chest sound, and breathing difficulty [20]. Various studies have shown that the intake of 'As' also affects the lungs and causes lung cancer. The survey was conducted in Taiwan, which reported that most of the people who consumed the inorganic Arsenic trioxide from the drinking water over 50 years were diagnosed with lung cancer [19].

2.3. Cardiovascular System

Studies have shown that 'As' increases the risk of hypertension and cardiovascular disease [20]. Long-term 'As' exposure has been associated with ischemic heart disease, myocardial injury, cardiac arrhythmias, and cardiomyopathy[30]. 'As' has also been shown to affect thrombocytes, enhancing agglutination in the presence of thrombin, which contributes to cardiovascular diseases [19]. Early-life exposure (under 20 years) to 'As' significantly increases the risk of cardiovascular conditions, such as hypertension, carotid atherosclerosis, and ischemic heart disease. Children exposed to average 'As' levels of 0.6 ppm have a higher risk of heart-related conditions [21]. Even low-level exposure can result in vascular damage.

2.4. Gastrointestinal System

Acute or subacute exposure to 'As' can cause gastrointestinal problems. However, gastrointestinal hemorrhage due to portal hypertension is rare, occurring in only 3 out of 156 cases studied. 'As' exposure can negatively affect the gastrointestinal (GI) system. Ingesting arsenic-contaminated water or food may lead to symptoms such as nausea, vomiting, abdominal pain, and diarrhea. High or prolonged exposure can damage the lining of the stomach and intestines, impairing nutrient absorption and leading to dehydration or malnutrition. In severe cases, it can cause gastrointestinal bleeding and long-term digestive issues. Gross splenomegaly is typically absent [20]

2.5. Renal System

In humans, kidneys play a primary role in 'As' excretion and are relatively less sensitive to their toxic effects compared to other organ systems. Targeted damage occurs in the capillaries, tubules, and glomeruli, leading to conditions like proteinuria and urinary casts. Severe 'As' poisoning can cause oliguria or, in extreme cases, renal failure, which may require [20,21].

2.6. Neurological Effects

Inorganic 'As' exposure, particularly through inhalation, can cause severe neurological effects [23]. Chronic exposure to 'As' in drinking water (100–1,000 µg/L) can result in peripheral neuropathy[20]. Acute exposure (1 ppb/day) may lead to encephalopathy, with symptoms like lethargy, headaches, hallucinations, coma, and restlessness. Repeated exposure can result in sensorimotor polyneuropathy resembling Landry-Guillain-Barré syndrome. Additional symptoms of encephalopathy include memory loss, distractibility, frequent urination, and persistent headaches [21].

2.7. Skin Cancer

Groundwater contamination with 'As' is a significant cause of skin disorders. A strong association between 'As' exposure and skin cancer has been observed. A literature search revealed that arsenite may contribute to the progression of UV-induced skin cancers. This effect is thought to involve mechanisms such as alterations in DNA methylation and impairments in DNA repair processes [19]. It was suggested that the reduced health burden of skin lesions might be attributed to lower concentrations of 'As' in the groundwater [18]. Early symptoms include pigmentation changes like dark brown and raindrop-shaped lesions, which can progress to Asal keratosis. Chronic exposure increases the risk of skin cancers, including squamous cell carcinoma (SCC), basal cell carcinoma (BCC), and Bowen's disease (in situ carcinoma). The person who is continuously exposed to 'As' has a high chances of skin cancer [18].

3. Treatments

In recent years, many techniques have been used to remove the 'As' from the environment. The method which was used to remove 'As' includes [24]

- Precipitation Processes
- Adsorption processes
- Ion Exchange Processes (anion exchange being the most common)
- Membrane Filtration Processes
- Biological Oxidation

Techniques such as coagulation, adsorption, and anion exchange are widely employed at the domestic level and are effective in removing 'As' from contaminated drinking water. In experimental stages, the, techniques like bio-oxidation have been used to treat polluted 'As' water [21]. These methods are effective but costly and less efficient [24].

3.1. Precipitation Process

In the precipitation method, ferric arsenate, arsenic sulfide, or calcium arsenate is used to remove 'As' [25]. This process involves a combination of filtration and coagulation to eliminate arsenic from contaminated water. Metals such as Al^{3+} and Fe^{3+} are commonly used in co-precipitation to treat polluted water. In water, 'As' reacts with specific chemicals to form low-solubility metal arsenates, such as calcium arsenate. These solid compounds are typically removed through sedimentation and filtration. [26]. In the coagulation process, 'As' is removed using aluminum, iron, and lime salts. 'As' (III) is converted to As (V) by using oxidizing agents like oxygen, hypochlorite, and permanganate because 'As' (V) is easily removed compared to As (III). This method is costly, requires skilled operators, and is only applicable on a large scale [21].

3.2. Adsorption Process

In this process, Activated alumina is used to treat As-contaminated water because it has a strong affinity for 'As' and binds it to its surface. When alumina is reached at maximum capacity, it can be regenerated using a neutralization process that involves caustic soda and sulfuric acid. The efficiency of alumina decreased by 20-30% after two to three regenerations, but this method is still efficient because it is less costly. As (V) is easily removed compared to As (III) by using Chlorine and other oxidizing agents for better results [27].

3.3. Ion Exchange Process

In this process, the ions adsorbed on a solid surface are replaced with dissolved ions [26]. It is used at domestic level [21]. Polymeric ion exchangers show a strong affinity for As(V) because it has a negative charge, while As (III) is neutral and requires peroxidation. The ion exchange process depends upon several factors like 'As' concentration, resin type, water PH, and competing anions (e.g., Cl^{-1}, CO_3^{-2}, SO_4^{-2}) that influence the process [28].

3.4. Membrane Filtration Process

In this process, ultrafiltration (UF), Microfiltration (MF), nanofiltration (NF), and reverse osmosis (RO) are used to treat 'As' contaminated water. These methods are based on pressure differences across membranes to separate contaminants. While MF and UF do not keep 'As' ions due to their size, NF and RO membranes effectively remove 'As' due to their small pore sizes relative to 'As' ionic radius. NF membranes combine Donnan, steric, dielectric, and transport effects for 'As' removal [28-32].

3.5. Biological Oxidation Process

Biological oxidation is a natural process used to treat arsenic-contaminated water by using specific microorganisms that can oxidize arsenite (As^{3+}) to arsenate (As^{5+}). Arsenate is less toxic and more easily removed from water through adsorption or precipitation. These bacteria use arsenic as part of their metabolic process, often in the presence of oxygen. This eco-friendly method is gaining attention as a cost-effective and sustainable solution for arsenic removal, especially in rural and low-resource areas. Microorganisms like *Geospirillum arsenophilus*, *Bacillus*, and *Geospirillum barnesi* can oxidize 'As' during their respiratory processes, using As(V) as a terminal electron acceptor. Chemical Oxidation (e.g., using Chlorine or potassium permanganate) is effective, but it produces harmful by-products like trihalomethanes. Biological oxidation is a cost-effective and eco-friendly process that can remove 95% of 'As' from groundwater under optimal conditions [21,29-38]

Although these processes are effective, they require further optimization to address the limitations of cost and efficiency for broader applications.

4. CONCLUSION

'As' Contamination in groundwater in Punjab cities is a serious public health and environmental issue. Its rise is due to rapid industrialization, urbanization, and inadequate water management practices. The health risks related to 'As' exposure range from cancer to cardiovascular diseases and neurological disorders, highlighting the importance of tackling this issue. Treatments require a combination of precautionary measures, including rules on industrial discharges, public awareness campaigns, and the development of renewable agricultural practices. Moreover, adopting highly efficient and cost-effective technologies is essential to ensure access to safe drinking water. A unified approach involving government agencies, community participants, and research institutions is crucial to reducing the contamination of groundwater and protecting future generations.

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