

Review

A Review on Detection Techniques, Health Hazards and Human Health Risk Assessment of Arsenic Pollution in Soil and Groundwater

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Abstract: One of the most significant elements in the environment is arsenic (As). It is a hazardous metalloid that causes contamination of soil and water supplies as a result of numerous anthropogenic and natural sources. This pollution has detrimental impacts on human health and the ecosystem, making it crucial to monitor and control. The release of As from minerals into the soil and groundwater depends on the kind of mineral, pH, and redox conditions. As is typically found in two forms, trivalent arsenic (As³⁺, arsenite) and pentavalent arsenic (As⁵⁺, arsenate), both of which are inorganic and extremely deadly. When it comes to toxicity, arsenite is more dangerous than arsenate. Many people have been affected by As poisoning, due to exposure to As through water and food. Nowadays, accurate, fast measurement of As in the field remains a technical challenge; however, the X-ray fluorescence method is considered the most reliable, cost effective and capable of measuring a wide spectrum of metals. Health risk assessment is a crucial parameter to estimate the health hazards of the As molecule. The risk assessment approach proposed by the USEPA is common and widely used, amongst others. On the numerous health risk assessment models/frameworks used to foresee the carcinogenic and non-carcinogenic health impacts brought on by As-contaminated water, little information is currently accessible. This discussion also emphasizes the need for more study on the risks to human health posed by specific As species (both organic and inorganic) found in As-contaminated water.

Keywords: arsenic; soil; groundwater; X-ray fluorescence; health risk assessment models



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1. Introduction

Arsenic (As) is the most hazardous material on the list, while being only the 20th most prevalent element in the Earth's crust [1]. Because of its extreme toxicity, it is a major source of concern in both terrestrial and aquatic settings. In aquifer systems, rock–water interactions are the primary source of As release and groundwater quality degradation. As is usually found in two states in natural water bodies: trivalent arsenic (As³⁺, Arsenite) and pentavalent arsenic (As⁵⁺, Arsenate), both of which are inorganic and very poisonous [2]. Arsenite is more poisonous than arsenate in terms of toxicity. The amount of As released from minerals into groundwater depends on the kind of mineral, pH, and redox conditions [3] as well as the presence of other ions that facilitate As desorption from secondary minerals [4]. Natural occurrences of elevated As levels in unconsolidated sediment aquifers have been documented [5]. Anomalies of As in groundwater can be increased or decreased as a result of human activity and climatic variability. Aquifer management or recharging the aquifer [6] with uncontaminated water can lead to a reduction in contamination. On the other hand, significant groundwater withdrawal [7] or surface contaminated water reaching the aquifer can pollute the water via As pollution [8].

On a regional level, it appears that two essential mechanisms are involved in the creation of high-As groundwater: first, a geochemical trigger releases As from the aquifer solid phase into the groundwater. In addition, the discharged As stays in the groundwater and cannot be removed by flushing. There are various geochemical causes that may be identified. Oxygen or other oxidizing agents are introduced into mining and mineralized areas, where they cause sulphide ores to oxidize [9]. This could occur after mining excavation, a shift in the hydrogeological regime, or a decline in the water table. The most significant catalyst in the majority of arsenic-affected aquifers appears to be the desorption or dissolution of As from oxide minerals, mainly iron oxides.

Groundwater in aquifers is particularly susceptible to water–rock interaction and As release because aquifers often have high solid:solutions ratios (3–20 kg/L). Additionally, compared to surface water, aquifers more frequently exhibit the physical and chemical conditions that favour the mobilization and transportation of As. Despite this, elevated As concentrations in groundwater are more of an anomaly than a pattern. In the majority of nations, background values in groundwater are frequently much lower than 10 µg/L [5]. Investigations across the globe have identified several large aquifers with serious groundwater As issues. Despite some apparent commonalities, the hydrogeological and geochemical conditions in these afflicted aquifers vary. Large alluvial and delta plains, as well as sedimentary inland basins, particularly those in arid and semi-arid regions, are at particular risk. Groundwater with a high As content is more likely to form and persist in aquifers that are geologically young (Quaternary).

Even though As can exist in the environment in a variety of oxidation states (−3, −1, 0, +3 and +5), natural waters primarily include arsenite (As(III)) or arsenate (As(V)), depending on the redox state of the environment. As can combine with carbonate ligands to generate aqueous complexes, and As(III) can combine with reduced sulfur to form thioarsenites, which may be significant in some groundwater [10]. Surface waters and even soil solutions rich in organic matter may include organic As species formed by microbiological methylation processes, but groundwater seldom contains a significant amount of these species [11].

As levels in groundwater can differ greatly (Table 1) in different geographical regions. Some major aquifers have natural concentrations above 50 µg/L in addition to volcanic and geothermal inputs, anthropogenic influences, and mining-influenced water [12,13]. Bangladesh, West Bengal, Chile, Argentina, China, Mexico, Vietnam, and various regions of Canada and the United States of America have all reported finding these aquifers [12,14,15]. Even while As concentrations above 50 µg/L are not unusual, they are not common. Complex factors, including bedrock type (though not usually), historical and current hydrogeology, and the geochemical environment, govern these elevated As levels. The most extensively researched region for naturally occurring high As groundwater is Bangladesh and West Bengal, where high As in alluvial and deltaic aquifers has had a considerable negative influence on human health. Here, As concentrations in shallow drinking-water wells are above 50 µg/L in more than 25% of all wells [12].

Table 1. Arsenic level in groundwater in different geographical locations [12].

Country	Range As (µg/L)
United Kingdom	<0.5–10
Bangladesh	<0.5–2500
India (West Bengal)	<0.5–3200
Germany (Northern Bavaria)	<10–150
USA (Coeur d’Alene, Idaho)	<1400
Chile (Antofagasta)	100–1000

The impacted aquifers originated in micaceous sands, silts, and clays of the Holocene period and are typically shallow (100–150 m deep). The West Bengal basement complex and upland Himalayan catchments are the most likely sources of the sediments. A layer of clay or silt covers the top of the aquifers, preventing oxygen from the atmosphere from

penetrating. This layer, combined with organic materials in the sediments, has created reducing conditions that encourage the mobilization of As. According to theory, the As is mostly produced by desorbing and reducing arsenate from quickly buried Fe oxides.

In Bangladesh, deeper aquifers often have lower As concentrations. The variations in the total As reservoir present in host sediments, the As oxidation state, and the As speciation in the sediments may be related to the variances between the two aquifers. Aquifer flooding and groundwater recharge in the Bengal basin are further important elements. Greater hydraulic driving factors throughout the Pleistocene helped groundwater flow for longer periods of time through older, deeper layers [12]. Older sediments are frequently oxidized and contain enough hydrated ferric oxides to sorbedly immobilize As. Table 2 lists the equilibrium constants for a few As species in aqueous solution.

Table 2. Aqueous speciation of arsenic [16].

Arsenic Acid	Acidity
$H_3AsO_4 = H_2AsO_4^- + H^+$	$pK_{a1} = 2.25$
$H_2AsO_4^- = HAsO_4^{2-} + H^+$	$pK_{a2} = 6.98$
$HAsO_4^{2-} = AsO_4^{3-} + H^+$	$pK_{a3} = 11.58$
Arsenous acid	
$H_3AsO_3 = H_2AsO_3^- + H^+$	$pK_{a1} = 9.24$
Monomethylarsonic acid	
$CH_3AsO(OH)_2 = CH_3As(OH)O_2^- + H^+$	$pK_{a1} = 4.19$
$CH_3As(OH)O_2^- = CH_3AsO_3^{2-} + H^+$	$pK_{a2} = 8.77$
Dimethylarsinic acid	
$CH_3AsO(OH) = (CH_3)_2AsO_2^- + H^+$	$pK_{a1} = 6.14$

As exhibits oxyanion-forming metalloids' normal geochemical behavior in the surficial environment, where it is mobile, not just at pH values typically observed in groundwaters (6.5–8.5), but also in both oxidizing and reducing environments. Although arsenic can exist in the environment in a variety of oxidation states, it primarily manifests as trivalent arsenite (As(III)) or pentavalent arsenate (As(V)) in natural groundwater. Except for in biological tissues where they may be dominant (for example, arsenobetaine [17], organic arsenic forms may be created by biological activity, primarily in surface waters). However, they are rarely quantitatively important. Arsenic typically exists in oxic conditions as an oxysalt or oxyanion. On the other hand, in anaerobic soils, it is frequently discovered in conjunction with sulfur. As a result, in uncontaminated aerobic sediments and soils, arsenate ($As^V O_4^{3-}$), while in contaminated sediments and soils, arsenite ($As^{III} O_3^{3-}$), is the dominant species [18,19]. As can also take on methylated forms, which are pH-sensitive and can develop in surface conditions. Both As(III) and As(V) can exist in a variety of stable aqueous and solid forms within the Eh and pH range that naturally occurs in soils. Redox disequilibrium causes both forms to frequently coexist in fluids and in small amounts in some minerals.

The current 10 µg/L WHO (World Health Organization) provisional guideline value for As in drinking water is implemented by European and USEPA laws. Although many nations still use the WHO pre-1993 guideline value of 50 µg/L as their national norm, this is partly owing to the challenges associated with evaluating low concentrations and partially due to compliance issues. As a result, the concentrations of 10 µg/L and 50 µg/L continue to be used as benchmarks for As testing and reporting.

The elemental speciation of As in soil indicates bioavailability, which is more significant than the overall concentration of As in the environment [20]. The most common chemical manifestations of As speciation are oxidation states and mineral phases [21]. Researchers claim that the metal speciation, not the total metal amount, indicates the biological component [22]. As can be present in soil in a variety of chemical forms, including (i) solid precipitates, (ii) adsorbed by organic or inorganic soil components, (iii) free ionic forms, (iv) structural components of primary and secondary minerals, and (v) exchangeable forms [23]. As contents in soils range from 5 to 15 mg/kg, with an average of 7.2 mg for global soils and 7.4 mg for American soils [12]. Higher amounts (average 13 mg/kg;

Table 3) can also be found in peats and bog soils; however, this is primarily due to an increased prevalence of sulphide mineral phases under the lower pressure.

Table 3. Concentration range of As in different types of soil [12].

Soil Type	Concentration Range (mg/kg)
Mixed soil	0.1 to 55
Peaty and bog soil	2 to 36
Peat	Up to 9
Acid sulphate soil	1.5 to 45
Soil near sulphide deposits	2 to 8000

Since it is released by sulfide oxidation, altered by different biogeochemical processes, and attenuated by adsorption and co-precipitation with Fe-minerals, clays, and organic matter, arsenic behaves like many other chalcophile elements. It has the ability to create a variety of secondary As minerals, such as native arsenic, arsenates, and, in a few rare instances, arsenites [24], as seen in the Namibian Tsumeb deposit. Surface soils' attenuation and As concentration can serve as an effective indicator of sulfide mineral occurrences [25]. For instance, concentrations in soils in the northern section of Nevada define zonal anomalies or "chalcophile corridors" surrounding significant bedrock gold resources.

Over 200 million people worldwide are at risk of environmental and public health issues due to groundwater contamination by arsenic [26]. In majority of the countries, drinking, cooking, bathing, and irrigating food crops with As-contaminated water all serve as routes for As to enter the food chain. Thus, a primary route for human As exposure is through the consumption of As-contaminated food and water. As has been linked to long-term skin lesions, neurotoxicity, diabetes, cardiovascular conditions, and a number of malignancies, including skin, liver, bladder, and kidney cancers. Health risk models can be used to assess the health risks associated with exposure from consuming As-contaminated water and food [27].

As(-III), As (0), As(III), and As(V) are the four valency states of arsenic, with oxidized As(III) and As(V) being the most common forms in nature. While arsenate, As(V) is typically the stable form and exists as arsenic acids in oxygenated settings, arsenite, As(III) is the dominating form under reducing conditions. With organic sulfur, nitrogen, and carbon, arsenic forms bonds. As(III) interacts with sulfur and sulfhydryl groups, such as cystine, organic dithiols, protein, and enzyme, but not with amine groups or organics that include reduced nitrogen components. As(V), in contrast, does not react with sulfhydryl groups but does with reduced nitrogen groups such as amines. With both the trivalent and pentavalent forms of carbon, organo-arsenicals are formed. As(V) is a form of As used in numerous industrial and commercial processes, including the production of glass, the refinement of copper, and the common form found in oxidizing soils. As(III) is anticipated to be the main As form found in waste sites, water-saturated soils, and soils containing substantial amounts of organic matter. Arsenic (III and V) hinders sorption and co-precipitation with solid-phase organics and inorganics by complexing with dissolved organic matter in the environment. Arsenic's mobility in soil and aquatic systems is therefore a major environmental problem. Numerous As detection techniques have currently been created, published on, and evaluated elsewhere. The majority of them achieve limits of detection below the 10 g/L WHO arsenic guideline threshold. However, a sizable portion of currently used techniques are only appropriate for lab settings. In these situations, analysis takes too much time and is unsuitable for frequent monitoring of numerous samples. Therefore, a quick portable sensor must be created, in light of these issues. Research on potential ways to meet this need has recently focused on the use of electrochemical methods. The World Health Organization states that there is an urgent need to produce reliable, delicate, and affordable field measurement equipment. This research reviews technologies that could be used to monitor and detect environmental As levels. We also reviewed the models for assessing human health risks.

2. Sources of Arsenic Contamination

Sources of As contamination in the lithosphere have been defined as geogenic sources of As contamination. It is made up of a variety of parent rocks and arsenic-containing minerals, such as carbonates, oxides, silicates, and sulphides [24]. As is abundant in sulphide-containing minerals such as arsenopyrite (FeAsS) and pyrite (FeS) [28]. Even arsenopyrite has been discovered in the environment to be a major arsenic-bearing mineral [29].

Broad-spectrum antibiotics, including tetracycline, oxytetracycline, and chlortetra-cycline antibiotics, are among the most commonly utilized. The majority of antibiotics used in the cattle and poultry industries are tetracyclines [30]. Tetracyclines were only partially absorbed by animals, leaving (30%–90%) of them in animal excrement [31]. Tetracycline antibiotics have accumulated in the soil as a result of the application of these waste items, such as swine dung, as soil supplements. Animal feces also contains harmful contaminants such as copper (Cu), As, and lead (Pb) in addition to antibiotics. Their application to the soil may cause antibiotic–heavy metal combined contamination. A recent soil assessment found that the long-term application of animal manures contaminated the soil As at concentrations ranging from (4 to 12) mg/kg, and accumulated tetracycline at (18 to 40) µg/kg in the topsoil [32].

Soils are recognized as the most important environmental element that acts as a sink for trace elements released by anthropogenic activities, and numerous research efforts in soil science have been conducted. Pesticides, such as herbicides, fungicides, insecticides, and other agrochemicals, are commonly employed in intensive agriculture to control weeds, insects, and diseases in a variety of crops. The amount of trace elements introduced into the soil vary according to the type of pesticide used [33]. Various As containing fertilizers have been used in agricultural lands for better harvests, which is ultimately responsible for As contamination in soil. Moreover, the release of waste generated during the manufacturing of pesticides and herbicides may pollute soil and water systems [34]. The range of As contents (mg/kg) in limestone fertilizers and pesticides, investigated fertilizers, and minerals are given in Tables 4–6, respectively. The effects of mining are likely the most frequently recognized source of As in the environment.

Table 4. Range of contents of As in agricultural limestone and pesticides [33].

Trace Element	Limestone (mg/kg)	Pesticides (%)
As	0.1–24.0	0.8–60

Table 5. Range (first line, minimum or unique value; second line, maximum value) of As contents (mg/kg) of investigated fertilizers [33].

Fertilizers	Principal Element	As (mg/kg)
Ammonium sulphate	N	4.2
		29.0
Ammonium nitrate	N	2.7
		119.7
Calcium nitrate	N	2.2
		10.1
Urea	N	5.6
		33.4
Calcium cyanamide	N	2.2
		2.4
Superphosphate	P	28.5
		321.5
Triple superphosphate	P	2.4
		8.0
Potassium sulphate	K	1.0
		50.0
Soil, usual range	–	<0.1
		1000.0

Table 6. Concentration of As in minerals [35].

Minerals	Concentrations (mg/kg)
Sulphide minerals	
Pyrite	100–120,000
Pyrrhotite	5–100
Marcasite	20–276,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5000
Oxide minerals	
Haematite	up to 29,000
Iron (III) oxyhydroxides	up to 76,000
Magnetite	2.7–41
Maghemite	up to 186,000
Carbonate minerals	
Calcite	1–8
Dolomite	<3
Siderite	<3
Silicate minerals	
Quartz	0.4–1.3
Feldspar	<0.1–2.1
Biotite	1.4
Amphibole	1.1–2.3
Olivine	0.08–0.17
Pyroxene	0.05–0.8
Sulphate minerals	
Gypsum/anhydrite	<1–6
Barite	<1–12

Burning of coal has a profound effect on contamination of As in the environment. Emission of As takes place in the environment by volatilization of As_4O_6 due to burning of coal, which condenses in the flue system and is ultimately transferred into water reservoirs [36]. Recent studies state that serious As anomalies in groundwater system occur not in areas influenced by metalliferous mineralization or geothermal activity, but in ordinary sedimentary aquifers. An important discovery of recent years has been that the sediments composing these aquifers do not tend to contain unusually high arsenic concentrations.

As contamination of groundwater varies based on different geographic location. Groundwater contamination is caused by a number of geological processes, including the erosion of sedimentary rocks rich in As, the weathering of minerals, and volcanic eruptions [37]. The As poisoning of groundwater is generally acknowledged to be caused by natural biogeochemical processes and natural geogenic sources, rather than by anthropogenic sources or activities (e.g., arsenic-enriched minerals and rocks) [38]. As contamination might be instigated due to human activity, including excessive groundwater withdrawal and pumping [39], the use of phosphate fertilizers, insecticides with added As, and irrigation water that has been contaminated with As or surface contaminated water reaching the aquifer [40]. Sources of As contamination in various countries in the world is given as follows (Table 7).

Table 7. Sources of arsenic contamination in different countries in the world [41–55].

Country	Sources of As	References
Norway (Fichtelgebirge region)	Industrial sources	[41]
Lithuania (Raseiniai region)	Geogenic and agrogenic	[42]
Spain (Asturias region)	Mining activity	[43]
Sweden (Västerbotten district)	Mining activity	[44]
Finland (Tampere region)	Geogenic (bedrock)	[45,46]
France (Verdun)	Destruction of chemical ammunition	[45]
Germany (Freiberg)	Geogenic: bedrock Mining industry	[45]
Poland (Złoty Stok and Żeleźniak)	Gold mining, ore mining	[47]
Belgium (Reppel-Bocholt)	Industrial activity	[48]
Portugal (Freixeda)	Mining industry	[49]
Greece (Chalkidiki)	Geothermal activities	[50]
Canada (western Quebec)	Geogenic: Bedrock aquifers	[51]
Bolivia	Volcanic eruptions	[52]
Mexico	Volcanic sediments and mining	[53]
Bangladesh	Holocene alluvial sediments with high phosphate	[52]
India (West Bengal)	Alluvial/deltaic sediments with high phosphate	[53]
Japan (Fukuoka)	Volcanic sediments	[52]
Taiwan	Coastal zones, black shales	[53]
Australia (Perth, Western Australia)	Pyrite sediments	[54]
Burkina Faso (Western Africa)	Volcanic rocks	[55]

3. Mobilization of Arsenic

Mobility of As is mostly influenced by processes occurring at mineral surfaces, including precipitation, dissolution, adsorption, and desorption. These reactions are governed by geochemical variables such as pH, Eh, ionic composition, and mineral type [56]. As is effectively immobilized via sorption under neutral pH and oxic circumstances, or co-precipitates with metal oxides [13]. These processes involve surface complexation reactions and the creation of certain inner sphere complexes. The mobility of metal oxides is increased by dissolution at low pH and lowered redox potential. Sulfide mineral formation regulates As concentrations under highly reducing circumstances [57]. The sorption of As is enhanced by dissolved calcium, while competition for sorption sites reduces As sorption in the presence of anions such as phosphate and bicarbonate [58].

The mobility of As may also be influenced by dissolved organic matter, whose concentrations typically vary from 1 to 20 mg/L in fresh streams and can be greater in wetlands. Fulvic or humic acids effectively prevent As from adhering to iron oxides, alumina, quartz, or kaolinite by forming stable complexes with the mineral surface [59].

A geochemical trigger of some kind that releases As from the solid phase of the aquifer into the groundwater is the first of two main processes that appear to be involved in the creation of high-As groundwaters on a regional scale. Second, the released As is still present in the groundwater and should not be removed by flushing. Numerous geochemical causes may be present. Sulphide ores begin to oxidize in mining and mineralized areas when oxygen or other oxidizing factors are introduced. This may occur after a decrease in the water table, a modification of the hydrogeological regime, or mining excavation. The most significant catalyst for As desorption or dissolution from oxide minerals, notably iron

oxides, appears to be in the majority of arsenic-affected aquifers. Since adsorption reactions are surface reactions, this process' initial adaptation to environmental changes is likely to be relatively quick [5].

Because of the natural weathering and dissolution of its parent minerals, As is frequently found in relatively high amounts in sediments and groundwater. Microorganisms can also mediate a variety of processes, including oxidation-reduction and methylation, that regulate the As concentration in these materials. However, the movement of As between the various mineral forms, solid phases, and organic matter can be achieved by purely chemical mechanisms. One of the more significant mineral components of soils and sediments is iron(III) oxide, which can be found as intergrain cements, particle coatings with a complex and diverse composition, and discrete amorphous or crystalline phases. Fe(III) oxides are formed as secondary weathering products [60].

It is becoming more and more obvious that bacteria are crucial for the speciation and mobilization of As. According to [61] Lloyd and Oremland, 2006 [62] Oremland and Stolz, 2005, microorganisms can play a substantial role as catalysts in the reactions of arsenite oxidation, arsenate respiration, methylation, and volatilization. The microbial reactions serve as detoxification processes or sources of energy. Many chemoautotrophs use CO₂ as their only carbon source and oxygen, nitrate, or ferric iron as their terminal electron acceptors to oxidize As(III). Some heterotrophs can also use organic carbon to oxidize As(III) [63]. On the other hand, numerous prokaryotes, such as *Bacillus selenitireducens* and *Bacillus arsenicoselantis*, are able to respire As(V) or oxidize As(III) [64]. Additionally, other redox processes brought on by microbes might cause the release of As indirectly. As(V) is produced when, for instance, the dissimilatory Fe-reducing bacteria *Shewanella* alga lowers Fe(III) to Fe(II) in scorodite [65].

A significant step in the mobilization of As in a variety of subsurface environments appears to be the microbial oxidation of organic materials in combination with the reduction of Fe(III) to Fe(II). According to [66] Fredrickson et al., 1998, both organic matter and reduced inorganic species, such as Fe²⁺, Mn²⁺, S²⁻, or H₂, can act as reducing agents in microbial metabolism. The lacustrine sediments are said to be home to the two most extensively researched genera of Fe(III) reducers, *Geobacter* and *Shewanella* [67,68]. Anaerobic metal-reducing bacteria may be crucial in the mobilization of As in the groundwater; the penetration of labile dissolved organic carbon (DOC) into shallow aquifers by irrigation pumping may facilitate the considerable reduction of Fe oxyhydroxides, leading to higher As concentrations in groundwaters, according to [57] Harvey et al., 2002 and [69] Islam et al., 2004. The simultaneous mobilization of As and Fe(II) from aquifer sediments strongly suggests that their mobilization was caused by the reduction of Fe oxyhydroxides by the increased activity of indigenous bacteria present in the sediments; this phenomenon also sheds light on the mobilization mechanism of As in groundwater. Organic material from the surface that seeps into the shallow aquifer may encourage the activity of microbial communities, thereby leading to a reduction of Fe oxyhydroxides and As release.

As is primarily found in three phases in aquifers: silicate phases, organic matter and sulfide phases, and iron and manganese oxide phases. It is believed that a three-stage process led to the emergence of these phases [70]. According to British Geological Survey researchers, the high concentration of As in groundwater is caused by hydrogeochemical processes [12]. They hypothesized the possibility of two separate geochemical causes. First, under dry environments, rapid evaporation rates and mineral weathering may result in high pH levels (>8.5). At such pH levels, either As desorption from the binding mineral surfaces or a reduction in the amount of adsorption may occur. Second, under severely reducing conditions, iron and manganese oxides may dissolve and release As that has been adsorbed under pH values that are neutral or nearly neutral.

Generally, fertilizers contain phosphate, which competes with As for adsorption on the soil; as a result the As is displaced and enters the groundwater system. Increased irrigation

and fertilizer use has mobilized phosphate from fertilizers into shallow aquifers, causing As to mobilize via anion exchange onto the surfaces of reactive mineral surfaces [70].

As an alternative process for the genesis of high-As groundwater, a new theory is based on the displacement of As by dissolved bicarbonate. As is leached into groundwater by the carbonation of As sulphide in the presence of bicarbonate, which results from the weathering and dissolution of sedimentary carbonates. The physical characteristics of the sediments, such as the grain size of clay minerals, have a role to play in controlling the distribution and mobility of As, and other altered mineral such as scorodite may also contribute As into groundwater [71]. Due to the advent of reductive conditions during sediment burial and diagenesis, it is usually believed that microbial processes regulate As release by dissolving As-bearing Fe-oxides, with the presence and type of organic matter [72] and the presence of SO_4^{2-} also playing an important role. According to groundwater geochemical analyses, similar processes were proposed as the main cause of As release in Hungary [73]. Varsányi and Kovács' (2006) [74] investigations into the mineralogy and aqueous geochemistry of SE Hungary's sediments revealed a correlation between As and both extractable organic matter and Fe-oxides. However, they hypothesized that two processes—(i) dissolution of As-bearing Fe-minerals (as previously proposed) occurring in low pH (7.6) in areas of groundwater recharge and (ii) high concentrations of organic ligands promoting mobilization in areas of groundwater discharge with longer residence times—were responsible for As release [74]. According to a recent study in Eastern Croatia, the spatial distribution of As in groundwater is related to the geological, geomorphological, and hydrogeological development of the alluvial basin. Reductive dissolution of iron oxides, desorption of As from clay minerals and/or iron oxides, and competition for sorption sites with organic matter may be the main mechanisms regulating As mobilization [75].

4. Detection of Arsenic

Since human and environmental health are directly and closely intertwined, accurate and ongoing As monitoring of the environment is essential. The increasing demand on ecological systems, brought on by growing human population, rising urbanization, and rapid increasing of industrialization, has made environmental monitoring more crucial in recent years. In order to effectively monitor the environment, scientists must use a multidisciplinary approach [76], focusing on:

- Importance of monitoring groundwater quality.

- Monitoring of groundwater quality to help identify specific pollutants, a certain chemical, and the source of the pollution.

- Identifying trends, short and long-term, in water quality.

- Preventing and managing water contamination as a form of environmental planning.

- Compliance with international standards set by international organizations such as the WHO.

- Importance of monitoring of soil.

In order to record compositional and temporal changes, environmental monitoring of soils includes systematically identifying the inorganic and organic constituents in certain soil types. This entails proving the existence of contaminants and their levels of concentration.

To ensure soil viability, early detection of changes and their effects on soil quality are essential. Soil monitoring enables the creation and implementation of policy initiatives that ensure soil preservation [77]. To enable the creation of evidence-based policies that promote sustainable soil management, it is vital to keep track of changes in the range of distinct soil types that are prevalent in a given location. Additionally, the European Union's statistical office conducts an EU-wide monitoring effort in addition to national soil monitoring networks (SMN) [78].

With a view to precisely analyze As in an environmental sample to parts per billion (ppb) values, which are specified here as mg/kg for solids and $\mu\text{g/L}$ for water, fixed laboratory techniques are necessary. Pretreatment of the environmental sample, either with acidic extraction or acidic oxidation digestion, is required prior to detection of As in the

sample, allowing As in the sample to be transformed into As acid solution [79], which is analyzed by using acceptable analytical methods which are given as follows,

- a. Atomic fluorescence spectroscopy (AFS)
- b. Graphite furnace atomic absorption (GFAA)
- c. Hydride generation atomic absorption spectroscopy (HGAAS)
- d. Inductively coupled plasma–atomic emission spectrometry (ICP-AES)
- e. Inductively coupled plasma–mass spectrometry (ICP-MS).

These analytical laboratory instruments, on the other hand, are huge, costly to use and maintain, and require fully equipped laboratories. Field assays, on the other hand, may be appropriate for sample screening or site surveys because they are reasonably affordable and can yield a wide variety of screening findings in a short period of time.

High-performance liquid chromatography (HPLC), ion chromatography (IC), gas chromatography (GC), capillary electrophoresis (CE), and capillary electrophoresis coupled with a high-sensitivity detector have all been used to develop a number of highly sensitive methods for the determination of As in liquid samples. These methods include atomic fluorescence spectrometry (AFS) and graphite furnace atomic absorption spectrometry (GF-AAS). The electrochemical approach, which has a number of benefits including speed, good selectivity, and sensitivity, is also among the analytical methods that are advised [80]. This method, however, also has drawbacks, including weak repeatability and significant interference [81,82]. High-purity reagents are needed for extremely sensitive techniques as HPLC-HG-AFS, GC-MS, CE, and IC-ICP-MS, which also consume a lot of reagents and have highly pretreatment-dependent outcomes [83]. Due to the expensive nature of the equipment, these approaches might not be accessible in all laboratories. As a result, the second pretreatment may be beneficial for the typical laboratory.

For primary analysis of soils, usually wet-chemical methods such as atomic absorption spectrometry (AAS), atomic emission spectrometry (ICP-AES or DCP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) are widely used. These analytical methods require sample digestion or extraction of the analyte elements and the sampling steps are laborious and poses risks of contamination, whereas, X-ray fluorescence (XRF) is a reliable, cost-effective method for the detection of a wide range of elements in soil. Nowadays, portable (hand-held) XRF instruments have been commonly used for in-situ detection of heavy metal ions in soils. Despite the lower sensitivities, the ability to assess a range of metals is undoubtedly a strength. Significant sampling versatility is also provided by the capability of sampling both solid and liquid samples.

Gas chromatography (GC) is a rapid, sensitive, and accurate technique for the determination of trace elements. Pyrolysis and GC have been combined, to provide the procedures for determining As that Chiavari, G. and Ferreira have proposed [84,85]. The method offered by Ferreira involves first extracting the organic As from the soil sample, followed by pyrolysis, and then GC-MS analysis. In contrast, Chiavari's method uses pyrolytic product directly into GC-MS for determination, which can only be applied for qualitative determination for some inorganic As. The method provided by Ferreira is that the organic As was extracted from the soil sample, and then the extract was pyrolyzed and determined by GC-MS; however, these methods are not suitable for the determination of total As in soil.

Technically speaking, measuring As quickly and accurately in the field is still difficult. Different technological advancements in various instruments have had differing degrees of success. However, the main objective of creating field assays that accurately and consistently assess As has not been accomplished. Technologies that have shown promise are shown in Table 8, along with remarks. For instance, the XRF techniques may measure a number of elements in addition to As. Another notable feature of XRF is its capacity to analyze aqueous (groundwater) and solid samples simultaneously in the field. When paired with separation techniques and spectrometers, colorimetric methods provide consistent sensitivities and the potential to measure As speciation. Despite the restrictions on whether arsenate can be directly metabolized, ASV (anodic stripping voltammetry)

appears to be highly promising. As in samples is measured using a variety of techniques in various nations throughout the world (Table 9).

Table 8. Different detection methods of arsenic [86–95].

Methods	Detection Limit (µg/L)	Comments	References
Colorimetric Assays	1 ppb	Simple and relatively inexpensive. However, limited to arsenite and arsenate, some promise for speciation. Not able to detect any of the organic arsenates that may be found in groundwater. Moreover, generates poisonous arsine gas that poses a hazard to the operator.	[86]
XRF hand held devices	60 ppm	X-ray fluorescence is a promising technology for detecting As directly in the soil sample without requiring aqueous soil extractions. It can also measure a wide spectrum of metals in addition to As in samples.	[87]
ASV	0.05–0.5 ppb	High sensitivity and experienced operators required. Interference from other environmental metals a concern.	[88,89]
SERS	Not determined	Arsenic applications may be interesting.	[90]
Bio-assay	10 ppb	Uses bacteria and plants for arsenic detection. Mainly a semi-quantitative assay for arsenate and arsenite in water. There are uncertainties about true measurements as opposed to determining bioavailable arsenic.	[91]
Electrophoreses Techniques	2 ppm to 0.25 ppb	Some possibilities for a compact sensor unit. One of the few techniques that has directly measured organo-arsenic compounds.	[92,93]
LIBS	400 ppm	Poor sensitivity.	[94]
TTPIXE	Not determined	Very fast, reliable, multi-elemental character and good precision.	[95]
Polarography	10 ppb	Inadequate detection limits, the usage of hazardous mercury, and the availability of better electrochemistry techniques	[90]
NAA	0.001–0.02 ppb	High sensitivity, possible spectral interferences	[90]
ICP-MS	(0.002–0.06) ppb	Accurate and lower detection limits compared to ICP-AES	[90]
ICP-AES	0.7 ppb	High sensitivity, but expensive equipment and trained workers are required	[90]

Colorimetric tests require test kits, which had low performance in field experiments; this created a significant incentive to improve the performance of colorimetric field kit technologies during the Bangladesh crisis. In one study, investigators changed the reducing agent with a view to transform arsenate and arsenite into arsine gas from powdered zinc metal to sodium borohydride, because zinc metal displayed slow reactivity and had the potential of being contaminated with As. These assays are unable to determine any of the organic arsenates that may be found in groundwater. Lastly, these assays are not benign; they produce toxic arsine gas that may cause adverse effect to the operator. In addition, the test strips constitute mercury solid wastes. While colorimetric assays are quick and economical, reliability and sensitivity are still major concerns. However, work is still being carried out to increase detection sensitivity. Utilizing separation technologies to concentrate and purify the samples is a method for enhancing the sensitivity and selectivity of an experiment. One such advancement is the concentration of the arsenate or arsenomolybdate anion using a solid-state fibrous anion exchanger.

There are now a number of field-estimating approaches available in addition to traditional chemical analysis. Testing methods for estimating As presence is becoming important due to the increasing menace of As poisoning in the aquatic environment. The colorimetry method is the most popular field-testing approach. This technique involves oxidizing organic As to produce arsine gas, which reacts with a white mercuric bromide strip to change its color to yellow or brown depending on the amount of As present. Currently,

groundwater As levels are estimated using field kits made in Germany, the UK, and the USA (Table 10).

Table 9. Arsenic detection methods used by different countries [34,42,43,45,46,48,50,95–97].

Country	Sample Types	Methods	References
Finland	Soil, bedrock wells, dug wells, clay.	Portable X-ray fluorescence(XRF); Inductively coupled plasma atomic emission spectrometry (ICP-MS/AES). Thick target PIXE (TTPIXE)	[46,95]
Sweden	Groundwater, sediments around the Adak mine.	Varian Vista Pro Ax inductively coupled plasma–optical emission spectrometer (ICP-OES).	[34]
Lithuania	Wells water	Atomic absorption spectrometry (AAS)	[42]
Latvia	Snow	Inductively Coupled Plasma Mass Spectrometer “ICP-MS, Agilent 8900” ICP-QQQ.	[96]
Poland	Water sources of Podwiśniówka and Wiśniówka Duża acid pit lakes.	ICP-QMS; model ELAN DRC II, Perkin Elmer	[97]
Greece	Groundwater	Flame atomic absorption	[50]
Germany	Bedrock and Soil	XRF or by ICP-OES	[45]
Belgium	Soil	Inductively coupled plasma mass spectrometry (ICP-MS -HP 4500 series)	[48]
Spain	Sediments	Inductively coupled emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS; Bureau Veritas, Vancouver, BC, Canada)	[43]
France	Soil	ICP-MS (NF EN ISO 17294-2(A))	[45]

Table 10. Arsenic field-testing kits used in many countries (UNICEF Supply Catalogue, Copenhagen) [98].

Testing Kit	Country	Comments
Arsenic Testing Kit (0005500)	Germany	Does not let the sulphide interference be removed
Arsenic Testing Kit (0005510)	USA	There is no way to eliminate the sulphide interference.
Arsenic Test Kit, highly sensitive (0005520)	Germany	To counteract the impact of sulphide interference, an oxidizing agent is provided.
EZ Arsenic Test Kit (0005521)	USA	An option to eliminate the sulphide interference
Visual Arsenic Detection Kit (0005522)	UK	Removes any hydrogen sulfide and extra arsine gas.
Digital Arsenator (0005523)	UK	Removes hydrogen sulfide and arsine gas.

The earliest electrochemical approach for determining trace inorganic metals is polarography (or linear sweep voltammetry at the hanging mercury drop electrode (HMDE)) [99]. However, polarography has limited limits of detection because of strong capacitive currents. The selectivity advantages of differential pulse polarography (DPP) are combined with lower capacitive currents and enhanced detection limits. Due to its great sensitivity for a variety of elements, such as arsenic, which does not readily amalgamate with mercury, as well as the availability of low-cost commercial instruments, DPP was widely used for routine analysis of trace metals.

Microfabricated arrays are now being used more frequently in electro-analysis. A well-defined and reproducible geometry, the use of different materials for a working electrode, and finally the affordability of chips has encouraged study in the filed analysis field. With the

help of a compact battery-powered device and a microfabricated gold ultra-microelectrode array (Au-UMEA), Feeney et al., 2000 [88] were able to quickly analyze the presence of arsenic in groundwater on-site. The homogeneous ultra-microelectrode shape, sensitivity, cost-effectiveness, and suitability for application in the field of portable or in-situ equipment are only a few advantages that these arrays have [91]. Low noise levels, signal amplification while maintaining UME behavior, background current rejection, and potential integration into field portable instrumentation are just a few of the analytical benefits of using UMEAs. Microfabricated arrays have been used successfully for field measurements.

Target nuclides in the sample are activated during NAA (neutron activation analysis) to produce radioactive nuclides, which typically decay by emitting beta particles and gamma rays with a distinct half-life. The NAA high-resolution gamma-ray spectrometer finds produced gamma rays. One of the most delicate analytical methods, NAA is frequently utilized as a reference technique for new procedures. However, it has not been widely used to detect arsenic in water, presumably because seawater has a high salt concentration that results in spectrum interferences [100]. Utilizing $\text{Pb}(\text{NO})_3$ and TiCl_3 as the carrier and reducing agent may help solve this issue.

Electrochemical techniques for As detection have shown promise for detecting As in the field. ASV (anodic stripping voltammetry) is regarded as one of the most effective procedures for liquid samples, such as groundwater. Solid samples must be digested or extracted before being tested using this procedure. The Environmental Protection Agency (EPA) has already approved analytical method SW-846-7063 for ASV, which can measure free (i.e., not adsorbed or bonded to any other species in solution) As in the range of 0.1 to 300 g/L [101]. Commercially available versions of the laboratory equipment for this procedure can be easily transported and utilized in the field, while not being built expressly for it. In terms of sensitivity and accuracy, the technique performed as expected in the lab; however, when As samples were spiked with other metals at concentrations twenty and forty times that of the analyte, the sensitivity for As detection significantly dropped.

In many nations, including the Nordic nations, wood preservation facilities that use inorganic impregnation chemicals like chromium (Cr), copper (Cu) and arsenic (As)- (CCA) are among the most frequent sources of soil contamination when it comes to heavy metals. A thick target particle-induced X-ray emission (TTPIXE) technique was used to analyze As in the soil samples; soil samples taken from an area where a wood preservation plant was active were studied [95]. TTPIXE is a very fast and reliable method for monitoring trace elements in soil. Other advantages are include being multi-elemental, and excellent accuracy. Sample pre-treatment is needed in this method. PIXE is now a well-established analytical method, especially evaluated for the determination of Cr, Cu and As, and widely described in the literature by Johansson and Rajander [95,102].

Bio-assay is a technique using bacteria for As detection. All cell-based organisms have complex As detoxification mechanisms that involve a wide range of proteins that chemically change, transport, and expel As from the cell [103]. The presence of As regulates the biological production and activation of these proteins, frequently through unique genetic processes (the identity of which varies depending on the organism, the kind of detoxifying mechanism, and the analyte). The activation of genes that encode As resistance proteins is dependent on the reversible binding of a regulatory protein to a deoxyribonucleic acid (DNA) regulation sequence linked with that gene in one common mechanism. When the regulator binds to the analyte, it can turn on the gene, causing it to produce the proteins needed to activate the As detoxification system. It is feasible to create a microbe that produces a visual signal, usually fluorescing bright yellow, when it comes into contact with As compounds, using molecular biology techniques. For the biosorption of hazardous substances, a variety of microorganisms including algae, fungus, yeast, and bacteria have been utilized. For instance, *Chlorella vulgaris* can oxidize As(III) to As and change inorganic arsenic compounds (V). The arsenite-oxidizing bacteria that have so far been isolated can either use arsenite oxidation as a source of energy, or it has been suggested that they do it as part of a detoxifying process. Exergonic growth that uses arsenite as an electron donor

produces a significant quantity of free energy. While marine algae convert arsenate into non-volatile methylated As molecules as methylarsionic acid and dimethylarsinic acid in seawater, other microbes can reduce arsenate to arsenite or even arsine (AsH_3). This finding, however, has not yet been used in a useful way to create an analytical system for arsenic speciation or a biosensor for As(III).

With a single laser pulse, the laser-induced breakdown spectroscopy (LIBS), method can qualitatively and quantitatively evaluate the elemental composition of aerosols, liquids, gases, and solids in real time. In order to create a small laser-induced breakdown, also known as a laser spark, a powerful, pulsed laser beam is directed onto the intended sample. A little portion of the sample matter is vaporized, atomized, and electrically excited by the ensuing high-temperature plasma. These atoms' electrons accumulate energy, and as the plasma cools and the electrons return to their initial state, they produce light at distinctive wavelengths (i.e., ground state). Since the approach vaporizes the sample arsenic, speciation is not achievable, and since the detection limit is so low (400 ppm), much research is required to raise the detection limits [104]. Arsenic analysis cannot successfully be performed using LIBS due to the As detection limits. The strength of the emission line(s) for a certain metal, plasma temperature, soil moisture, grain size, as well as detector signal to noise, all affect the detection limits for LIBS.

By determining the wavelength and intensity of the laser light scattering, Raman spectroscopy may identify and quantify the concentration of molecules. A molecule is adsorbed onto a metal surface (often silver), and the molecule reflects laser light. The vibrational spectrum of a target molecule affects how much the dispersed light's wavelength changes. Although minimum detection limits have not been established, arsenite and arsenate in solution have known Raman spectra. However, a sensor for the detection of perchlorate, chromate, dichromate, and cyanide anions has been created that uses cationic coated silver particles as substrates [105]. The coating draws the anions to the SERS (surface enhanced Raman spectroscopy) substrate where they are recognized and measured by their distinctive Raman scattering. To 60 ppb, the chromate anions were detectable by the researchers [101]. If SERS technology exhibits comparable sensitivity and selectivity for detecting arsenic chemicals in environmental field research, it can be developed into a potential portable field detection system. Recent developments in laser and microfabrication have made it possible to miniaturize this technology, making SERS technology a genuine contender with the potential to achieve selectivity for arsenic.

A micro-cantilever used in AFM (atomic force microscopy) has a "detector film" coating that interacts with the targeted species. Surface stress, a rise in temperature, or an increase in mass are just a few of the changes that can result from the adsorption of a target analyte onto the film. The micro-cantilever deforms as a result of each of these surface modifications (bending). Cesium and chromate have both been detected using this approach [106,107]. These sensors all displayed great selectivity, ppb detection limits, and excellent sensitivity. It could be possible to create a covering that can bind arsenic only. For numerous sensing applications, arrays of micro-cantilevers have been created.

The most popular technique for extracting total As from soils and sediments entails wet-ashing the sample with a mixture of acids, which can be done in microwave-digestion ovens [107]. Arsenic in solid phases can also be determined using a SSE (selective sequential extraction) [108]. The widely used aquifer system in Bangladesh has successfully used SSE to identify the source of As [109]. As in soils may be rapidly, automatically, and sensitively fractionated using flow injection (FI) on-line sequential extraction in combination with a detection technique. When compared to conventional batch-mode sequential extraction, the method has a number of benefits, such as improved accuracy, reduced sample/reagent consumption, and reduced risk of contamination and analyte loss [110].

5. Health Hazards

As can enter the body through different exposure pathways such as ingestion, inhalation, or skin adsorption. Ingestion is the most common way to consume As. Long-term

exposure to As contamination results in lethal effects to human health. Drinking As-contaminated water is the most typical route to take As, through ingestion, and can lead to acute and chronic poisoning. Acute As poisoning has no distinct symptoms. Weariness, colitis, loss of reflexes, weight loss, weakness, anorexia, gastritis, hair loss, and anorexia are a few of the non-specific symptoms of chronic poisoning [111]. Meanwhile, experimental data suggests that prolonged As poisoning contributes to the development of illnesses including cardiovascular disease (CVD), hyperkeratosis, disturbances of the nervous and peripheral vascular systems, gastrointestinal symptoms (lack of appetite, vomiting, diarrhoea, etc.), hyperpigmentation, circulatory disorders, hepatic and kidney disorders and hyperpigmentation [112]. In addition to causing arsenicosis, exposure to As harms other human bodily systems. Table 11, exhibits a list of negative health consequences due to As exposure. The first noticeable indications of low As levels in drinking water are atypical black–brown skin pigmentation, known as melanosis, and keratosis, or hardness of the palms and soles. Individuals will experience skin depigmentation, if they continuously take As, which looks like raindrops (white-spots) and is known as leukomelanosis in medical terms. As poisoning is difficult to diagnose since it can harm internal organs without creating any evident exterior signs. Increased As concentrations in hair, nails, urine, and blood can indicate human exposure to arsenic before outward symptoms appear [113].

Table 11. Adverse health effects as a result of exposure to arsenic [52].

Human Body Systems	Adverse Health Effect
Cardiovascular system	Stroke, hypertension, peripheral vascular disease, Raynaud’s syndrome, cardiac arrhythmia, coronary heart disease, peripheral arterial disease, cardiomyopathy
Hepatic system	Hepatic fibrosis, hepatic necrosis, cirrhosis, hepatoportal sclerosis, non-cirrhotic portal fibrosis, angiosarcoma, gastrointestinal lesion, hepatomegaly, liver cancer.
Nervous system	Muscle cramps, Peripheral neuropathy, polyneuropathy, EEG abnormalities, numbness, spontaneous pain, hallucinations, disorientation, hearing loss, cognitive disorders, encephalopathy and agitation in extreme cases.
Renal system	Kidney cancer chronic kidney disease, acute tubular necrosis, glomerular damage, acute renal failure.
Respiratory system	Chronic cough, shortness of breath, bronchiectasis, chronic obstructive pulmonary disease, lung cancer.
Reproductive system	Infertility, prostate cancer, low sperm quality, premature delivery, spontaneous abortion, and stillbirth.
Endocrine system	Diabetes mellitus, hyperthyroidism, pancreatic cancer.

Individuals, population groupings, and geographic places appear to have different symptoms and indicators caused by As. As a result, there is no common definition of As poisoning. This makes determining the health effects of As more difficult. Similarly, there is no way to distinguish between internal tumors caused by As and cancers caused by other reasons. In 1993, the World Health Organization (WHO) reduced the As in drinking water guideline value from 50 µg/L to a provisional value of 10 µg/L. This restriction has been established by most Western countries in their current drinking water regulations. However, due to a lack of adequate testing facilities, many impacted countries continue to use the 50 µg/L standard [114].

Apart from water, other potential sources of exposure of As to human are food, soil and air. As, on the other hand, can be found in seemingly innocuous sites such as playground equipment, boat docks, patio decks, gazebos, sidewalks, fences, and picnic tables. The source of As found in these structures is chromate copper arsenate, a wood preservative and pesticide that has been used for more than 60 years to protect wood from fungi, dry rot, mould and termites. It has been discovered that children are susceptible to As poisoning from this source.

Exposure to inorganic As disrupts the activity of enzymes, several significant anions and cations, cell transcriptional activities, and has negative impacts on health. Regardless of whether the As is in its As(III) or As(V) state, 70%–90% of the As in drinking water is absorbed in the human digestive system. After consumption, inorganic As is quickly absorbed from the digestive system and transported by blood to numerous body organs. Glutathione quickly converted arsenate that was absorbed through the gastrointestinal system (after entering the cell) to arsenite (GSH). Similar to As(III), As(V) exposure occurs in chronically exposed populations. The type of tissue and the species of As play a role in the affinity of As deposition in tissues. Analysis of the subjects who drank arsenic-contaminated water for a longer period of time revealed higher quantities of As in their hair, nails, scales, urine, and liver tissue [115]. While elevated levels of As in hair and nails (which include proteins containing cysteine) indicate chronic exposure, elevated levels of As in blood and urine indicate recent As exposure [116,117]. The order of the propensity for As species deposition in all keratin-rich tissues is As(III) > As(V) > monomethylarsonic acid (MMA) > dimethylarsenic acid (DMA). In comparison to inorganic As, the methylated forms of arsenic, MMA(V) and DMA(V), are thought to be less toxic to tissues and more easily eliminated by urine. Although the majority of the As from the body is eliminated by urine, minor amounts of As are also eliminated through bile, hair, nails, skin, and breast milk [116]. Normal values of As in different body parts are as follows (Table 12) and health complications induced by different As species is given in Table 13.

Table 12. Normal arsenic values in different parts of human body [118].

Human Body Parts	Reference Value of As
Hair	0.08–0.25 mg/kg
Nail	0.43–1.08 mg/kg
Urine	0.5–0.05 mg/L
Blood	0.001–0.004 mg/L

Table 13. Health complications induced by different As species [7,119–137].

As Species	Effect on Human Health	References
Inorganic As (As ^{III} & As ^V)	Cancer	[119,120]
	Inorganic arsenicals do not cause any significant renal injury in humans.	[121]
	Immunotoxicity	[122]
	Mitochondrial dysfunction	[123]
	High sugar level. (Hyperglycemia)	[7]
	Diabetics	[124]
	Oxidative stress	[125]
	Abnormal function of male reproductive system	[126]
	Induction of genetic alteration/mutation	[127]
	Heart disease	[128]
	Mutation of gene	[129]
	High blood pressure	[130]
	Arsenite (As ^{III})	Cancer
Liver diseases		[132]
Metabolic diseases e.g., fatty liver.		[133]
As trioxide (As ₂ O ₃)	Breast Cancer	[134]
Organic As	Vomiting, abdominal pain, hyperactive bowel and diarrhoea.	[135]
	No hepatic effects of organic arsenicals on humans have been reported yet.	[136]
	No neurological symptoms or brain lesions were observed during experiments.	[137]

As exposure has negative impacts on children's health and development in addition to adult health. In other words, especially in the case of prenatal As poisoning, children are more vulnerable than adults [138]. Numerous epidemiological research showed that exposure to As has a slightly higher risk of delayed fetal growth, and increased fetal and neonatal mortality, because arsenic easily crosses the placenta. Rahman and his coworkers' population-based cohort analysis showed that exposure to As raises the probability of a child dying [139]. A prospective birth cohort research in Bangladesh found that exposure to As during pregnancy may have a negative impact on the early development of the immune system [140]. Another epidemiological investigation revealed that toddlers between the ages of two and three who had high blood As levels also had lower intellectual functioning [141]. According to a case-control study by [142] George et al., 2015, exposure to low to moderate levels of As may increase the risk of pneumonia in children under the age of five. Urinary As concentrations have also been associated to a higher risk of pneumonia [142]. Rahman and colleagues demonstrated a strong correlation between prenatal arsenic exposure and excess mortality in children aged one to five years from drowning, which may be mediated by cognitive impairment [143]. Consequences on human health of several sorts caused by As exposure worldwide have been illustrated in Table 14.

Table 14. Health implications originating from As exposure in different countries [144–152].

Country	Study Type	Health Effects	References
United States	Case-control	Prominent transverse white lines in the fingernails and toenails called Mee's lines	[144]
United States	Cross-sectional	Restrictive or obstructive lungs diseases, and bronchitis	[145]
Australia	Cross-sectional	Diarrhea and stomach issues	[146]
Bangladesh	Prospective cohort	Increased frequency of miscarriages	[147]
India	Cross-sectional population survey	Hyperkeratosis, hyperpigmentation and skin tumours	[148]
India	Cohort	Peripheral neuropathy	[149]
Pakistan	Cross section survey	Respiratory tract disease	[150]
Taiwan	Case-control	Bladder cancer	[151]
Chile	Cross-sectional	Skin lesions	[152]

Arsenic toxicity's underlying molecular mechanisms have been the subject of extensive basic research, but the exact mechanisms are still unknown. Arsenic toxicity varies depending on its chemical species, dose, length of exposure, type of cell and tissue, and metabolism. The evidence from the literature review shows that arsenic toxicity mechanisms include oxidative stress, excessive production of reactive oxygen species (ROS), changes in some signaling pathways and gene expressions, damage to the structure and function of proteins, particularly SH-proteins, mitochondrial dysfunction, disruption in the antioxidant defense system, changes in the secretion of some important hormones, and damage to the structure of cellular macromolecules/cofactors. The body's antioxidant defense mechanisms are essential for limiting the potential harm brought on by excessive ROS formation because ROS is continuously produced throughout normal aerobic metabolism. By impeding antioxidants that remove free radicals from cells, As increases the generation of ROS. Arsenic exposure causes excessive ROS generation, which interferes with signaling pathways important in cellular metabolic processes such as cell growth, proliferation, differentiation, and DNA repair [153].

Different ROS, including superoxide, hydrogen peroxide, hydroxyl, and peroxy radicals, are formed in the cells under both healthy and pathological or stressful conditions [154]. Oxidative damage to DNA, proteins, and lipids occurs when the antioxidant system is unable to keep up with the pace of ROS generation. Numerous harmful effects on human

health, including as cancer, aging, neurological disorders, Alzheimer's and Parkinson's diseases, as well as cardiovascular diseases, have been linked to oxidative DNA damage.

One-carbon metabolism is greatly influenced by a number of micronutrients, including folate, vitamin B12, pyridoxal phosphate, riboflavin, choline, and betaine. However, folate has a significant impact on the methylation of As, urine excretion, and blood As concentrations. The effects of other micronutrients involved in 1-carbon metabolism, including vitamin B12, pyridoxal phosphate, riboflavin, choline, and betaine, are less well understood [155]. Determining the impact of nutritional modulation of 1-carbon metabolism, which may offer a further strategy for lessening the burden of disease brought on by long-term As exposure, thus requires further fundamental studies.

The formation of methylated metabolites through this process, however, lessened exposure to arsenic by speeding up the rate of clearance, leading to the long-held belief that methylation of inorganic arsenic was a detoxifying process. It has recently been determined that 1-carbon metabolism, a crucial metabolic system, controls the supply of methyl groups for the methylation of arsenic, which in turn impacts the methylation and removal of arsenic [156].

6. Human Health Risk Assessment Models/Frameworks

It is not a reliable and thorough method to evaluate the danger of As to human health by comparing the amount of As in water to the allowed limit. The risk to an individual human from intake of As-contaminated water and food depends upon many factors, such as rate of intake, exposure time, conversion factor, exposure duration, exposure frequency, body weight and type of population [157]. Additionally, the acceptable limit of arsenic in drinking water is only for total As, although As is primarily present in groundwater as inorganic species, therefore this limit does not distinguish between the toxicity of inorganic and organic arsenic species in water. The carcinogenic and non-carcinogenic risk to humans is calculated using USEPA formulae. Compared to other health risk assessment models/frameworks, USEPA models are considered to be more reliable, hence these models must be explored further to determine carcinogenic and non-carcinogenic risk caused by individual As species in groundwater and soil.

The two main ways that humans are exposed to As, which can cause health risks, are water and food [158]. Health risk assessment is an effective way to determine the risk posed to human health. Generally, humans are exposed to the pollution via three different pathways including: ingestion, dermal contact, and inhalation. For non-carcinogenic, the chronic daily dose (CDD) (mg/kg/day) of potentially toxic metals received three exposure pathways; ingestion, dermal contact, and inhalation can be estimated using Equations (1)–(3).

$$CDD_{ing} = \frac{c \times R_{ing} \times CF \times ED \times EF}{BW \times AT} \quad (1)$$

$$CDD_{inh} = \frac{c \times R_{inh} \times EF \times ED}{PEF \times BW \times AT} \quad (2)$$

$$CDD_{derm} = \frac{c \times SA \times SAF \times DAF \times ED \times EF \times CF}{BW \times AT} \quad (3)$$

where c is the concentration of heavy metals (mg/kg); CDD_{ing} is daily exposure amount of metals through ingestion (mg/kg/day), CDD_{inh} is daily exposure amount of metals through inhalation (mg/kg/day), and CDD_{derm} is daily exposure amount of metals through dermal contact (mg/kg/day) [159]. All the exposure factors used to estimate the intake values and risk are also listed in Table 15 and different models used for human health risk assessment are presented in Table 16.

Table 15. Exposure parameters for health risk assessment [160].

Parameter	Definition
R_{ing}	Ingestion rate of soil
ED	Exposure duration
EF	Exposure frequency
CF	Conversion factor
BW	Body weight (average)
AT	Average time
SA	Skin surface area (exposed)
SAF	Skin adherence factor
DAF	Dermal adsorption factor
R_{inh}	Inhalation rate of soil
PEF	Particle emission factor

Table 16. Different models used for human health risk assessment [161].

Models/Frameworks	Country	Sources	
Summary relative risk estimate (SRRE).	Taiwan (South-west)	Water	Total As
Mantel–Cox method	Taiwan (North-eastern Coast).	Water	Total As
Generalized estimating equation (GEE) models	Bangladesh	Water	Total As
Biologically-based dose–response (BBDR) model	USA	Comparative genomic data from individuals with known exposure from drinking water	Inorganic As
USEPA one-hit model (1989)	West Bengal, India	Water	Total As
USEPA risk assessment approach	USA, Pakistan, Vietnam, Turkey, Thailand, India and Mongolia	Water/Soil	Total As
Cox’s Proportional Hazards Regression Models	Taiwan (North-eastern Coast)	Water	Total As
Cumulative arsenic exposure index (CAI)	Bangladesh	Water	Total As
Death and disability adjusted life years (DALYs). Monte Carlo modelling	Bangladesh	Water	Inorganic As
NRC multistage Weibull model	Taiwan vs. Chakdha block, West Bengal	Water	Inorganic As

6.1. Non-Carcinogenic Risk Assessment

After the calculation of CDD, the three exposure pathways are calculated; the hazard quotient (HQ) is typically used to describe the non-carcinogenic risk, which is calculated by dividing the daily dose by a particular reference dose (RfD) (according to the USEPA, the values of RfD for each element are different), as in following Equation (4). If the

HQ < 1, there is no adverse health effects; whereas, an HQ > 1 means there are likely adverse health effects [159]; and the hazard index (HI) is the sum of HQ and indicates the total risk of non-carcinogenic elements for a single element [160], calculated by Equation (5):

$$HQ = \frac{CDD}{Rfd} \quad (4)$$

$$HI = \sum HQ \quad (5)$$

According to the USEPA 1989, if the value of HI is smaller than 1, it represents “no significant risk” of non-carcinogenic effects exists, whereas, when HI values are higher than 1, it is considered there is a possibility of non-carcinogenic effects occurring [159].

6.2. Carcinogenic Risk Assessment

The carcinogenic risk represents the chances of developing cancerous diseases in a whole lifetime due to exposure to carcinogenic hazards [162]. Carcinogenic health risks can be calculated for an individual heavy metal over a lifetime, by following Equations (6) and (7) [163]:

$$CR = CDD \times SF \quad (6)$$

$$TCR = \sum CR \quad (7)$$

where CR is the carcinogenic risk; TCR is the total carcinogenic risk; SF is the slope factor (mg/kg/day). CR and TCR values less than 1×10^{-6} are regarded as negligible, whereas a CR and TCR exceed the 1×10^{-4} is likely to be harmful to human health.

Different parameters, such as speciation and bioavailability of As, are critical in determining the risk to human health. Because different species have different levels of toxicity and bioavailability in water [164]. Analysis of As species, that are ingested through water, food, or soil, metabolized in the liver, bladder, and kidneys, accumulated in the hair and nails, and then eliminated in the urine or feces, is crucial. As far as we are aware, just a few research studies have been completed to assess the speciated As contents in people. Additionally, there is little information available on the health concerns associated with exposure to individual As species, such as As(III), MMA(III), DMA(III), or As(V), MMA(V), DMA(V), from a variety of sources, including groundwater [165]. Therefore, research on As speciation in groundwater, plants, and diverse human body parts such as hair, nails, blood, and urine is necessary in order to evaluate the health hazards posed by various As species.

7. Discussion

Table 8 provides a summary of the state of science and technology for colorimetric assays at the moment. All of these tests can only identify inorganic As, and depending on the assay used, all As species need to be transformed to arsenate or arsenite. Combining separation methods with polyoxomolybdate chemistry results in a promising As detection test in terms of sensitivity, repeatability, and accuracy in the future (Table 17).

Electrode fragility is a frequent complaint made against electrochemical technologies (such as ASV) in the industry. A gold microelectrode array survived 30 days in one research, however. This experiment is a solid starting point for the development of this technology for both distant long-term sensors and rugged field devices. However, before this objective can be accomplished, considerable additional instrument development, including an independent field-testing program, will be needed in the future (Table 17).

The site characterization and analysis penetrometer system (SCAPS), which combines conventional cone penetrometer technology with XRF technology to quickly outline the subsurface distribution of pollutants, was created by the SERDP (strategic environmental research and development program) [166]. Although the apparatus can measure As in a lab setting, it has not been tried in an outdoor setting. Lead contamination permeates every site examined for the experiments, causing XRF arsenic values to be inaccurate. The possibility exists for XRF in conjunction with a cone penetrometer to measure As under circumstances

where interference from lead would not be an issue, given that XRF has demonstrated great sensitivity and value for direct measurement of As in other field applications. Research efforts are ongoing for the development of a portable XRF device for groundwater analysis for future use.

Table 17. Efforts for the development of detection methods of As for future research [88,89,105,106,167–170].

Method	Detection Limit	Comments	Reference
Colorimetric assay (Molybdoarsenate chemistry coupled with separation technology)	1–15 ppb	Less toxic, cheaper, readily accessible equipment is needed. Arsenic speciation was made possible by the separation technologies. Separation protocols eliminate potential irritants.	[167,168]
ASV (Newly-designed field equipment)	0.05–0.5 ppb	Possibilities for arsenic speciation with high sensitivity. It is unclear whether this method can identify As species besides oxyacids.	[88,89]
Portable XRF device for groundwater analysis	50 ppb	Arsenic speciation might be possible with pre-concentrating samples onto the solid matrix.	[169,170]
Micro-cantilever-based sensors (not applied to As detection yet)	Not determined	Has not been used for As, but its exceptional selectivity and sensitivity for many other systems is intriguing.	[106]
Surface enhanced Raman (not applied to As detection yet)	Not determined	It has not been used with arsenic, although its exceptional chromate and other anions selectivity and sensitivity make it hopeful.	[105]

In this review, the most common analytical techniques for identifying As have been discussed. It was demonstrated that there are numerous analytical methods available for identifying the different types of As species in water samples. Additionally, other approach combinations that address a wide range of needs have been outlined. In particular, ICP-MS applications offer precise and repeatable results in a lab setting, as opposed to commercially accessible colorimetric tests, which deliver quick but perhaps inaccurate results when used on-site. Thus, it is evident that a quick and precise sensor is required. Arsenic detection could benefit greatly from the use of microcantilever-based sensors. Arsenic has not, however, been detected using a cantilever-based sensor. Despite the similar potential of SERS-based field analytical systems, neither of these technologies has been used for As detection in the field or the lab (Table 17). For XRF, the capacity to assess a range of metals is undoubtedly a strength, despite the lower sensitivities. Additionally, a great deal of sampling versatility is provided by the capability to sample both solid and liquid samples. Since electrochemical techniques have so far demonstrated their ability to produce correct results under controlled laboratory circumstances, they have the potential to be further developed into a portable, inexpensive analytical device that can meet the needs of a quick and precise sensor. A lack of competence for field measurements of organo-arsenic compounds is suggested by the literature review for this paper. Despite being considered to be less acutely hazardous than inorganic As, these substances nonetheless make up a sizable portion of the total environmental As and should not be disregarded in analyses of environmental As. Arsenic sulfur species require similar measures as well.

There were numerous worries regarding the expanding use of health risk assessment (HRA) in the areas of clinical health care, health promotion, and health education, towards the start of the 1980s. The most common and significant issues related to (a) the reliability of the underlying epidemiological data on which estimates of personal health risk were based; (b) the limitations of the statistical methods available for estimating risk, including the difficulties in combining different risk factors into a composite personal health risk score and the methods for adjusting for competing risks, as well as the health effects of lifestyle and sociodemographic characteristics; (c) how HRA questionnaires handle missing

data, as the replacement of “average values” could significantly reduce the validity of results provided to an individual; (d) the relative value of general health scores that did not infer probabilities of specific health problems vs. disease-specific risk estimates; and (e) whether the outcomes were likely to be misrepresented to employees as equivalent to a periodic clinical examination by a physician. Most of these issues have been argued by epidemiologists, biostatisticians, HRA creators, medical professionals, and HRA users, but less frequently explored through systematic study. The frequency and severity of uncertainties are influenced by a variety of factors, such as parameters, models, and inadequate data [171]. The ambiguity underlines the implications and restrictions of assessment conclusions in HHRA, as well as the range and possibility of risk results for assessors, decision-makers, and the public [172]. The risk assessment models may not be specific enough to accurately compare and differentiate between levels of risk which are considered as common limitations. The major flaws in the risk assessment matrix approach include poor resolution, unclear inputs and outputs, inefficient resource allocation based on inaccurate risk calculation, and outright mistakes in giving higher rankings to objectively lower hazards. Fundamentally, the USEPA reaffirmed that scientific uncertainties are inevitable in the process of risk assessment and should be identified, along with their impact on assessment. The USEPA produced a variety of tools, databases, and guidelines to enable management of risk from exposure to toxins based on quantitative measurements of uncertainty.

It is not a valid and thorough method to evaluate the As risk to human health by comparing the As concentration in water with the acceptable limit. Water intake, exposure time, exposure length, exposure frequency, body weight, and population type are just a few of the variables that can affect a person’s risk of consuming As-contaminated water [157,173]. Additionally, the allowed limit of arsenic in drinking water is only for total arsenic; however, since arsenic is mostly prevalent in groundwater as an inorganic species, this limit does not account for the differences in As toxicity between inorganic and organic species. Models/frameworks for estimating health risks to humans from exposure to As contaminated water are crucial first stages in the creation of management and remediation plans to safeguard people from poisoning. A range of risk assessment models or methods that have been utilized to evaluate the risk of As in water on human health are summarized previously. The USEPA health risk assessment model equations appear to be the most complete and promising technique for assessing the health risks of ingesting As from As-contaminated water among various models/frameworks. Since different As species have variable levels of toxicity and bioavailability in water, speciation and bioavailability of As are critical considerations in the assessment of human health risk.

Health risk assessment models can offer an essential link between environmental media and human receptors as well as a crucial ecological index. Several researches have been carried out to measure the heavy metal contents in samples in order to evaluate the current health risk [174]. Additionally, scientists have looked into the quantitative relationship between environmental media and pollution sources. Utilizing receptor, geo-statistical, and geochemical models, it is possible to determine the contributions of various sources to the enriched trace metals [175]. When the output of the source alters due to natural degradation and time accumulation, the regional health risk will increase or decrease. Quantifying the danger levels associated with future changes in metal concentrations is crucial. Actually, a small number of scientists are working on a lengthy investigation of heavy metal contamination in water and soil, mostly using long-term field sampling, tree ring surveys, and space–time Bayes analysis and prediction. Some studies are either incomplete theoretical derivations of statistical methods or lack comprehensive predictions of future dangers. Numerous related studies’ findings have revealed decreased levels of health dangers, and finally, a few efficient improvement strategies have been proposed. Furthermore, it has not been reported that any methodologies or models are now available that are centered on the temporal dynamics of pollution sources (disappearance or sustained growth of sources). To evaluate future metals contents, components are needed, including background values,

contribution level, and pollution source strength trends. Quantized source apportionment techniques, such as principle component analysis combining multiple linear regression (PCA-MLR) and positive matrix factorization (PMF), can be used to determine the percentage of heavy metals in soil input from sources [176,177]. A link between source strength and contribution rate is seen in certain relevant investigations. Obtaining the quantitative relationship between source intensity and economic development and further determining the accumulation rate of As is a practical way to forecast future heavy metal such as As and the risks it poses to human health.

Groundwater contains arsenic in a variety of chemical forms, including inorganic (As(III), As(V)), and organic forms. Humans' direct ingestion of drinking water or eating edible crops that have been irrigated with water contaminated with As are the main causes of As exposure. People, especially children and women, who live in less developed, low-income communities without access to safe drinking water and appropriate food, have a considerably higher risk of being exposed to As. Prior studies have mainly concentrated on how much exposure there is as a whole to As with water; there is a study gap that has to be filled in the future on the role of specific As species. Relatively little information is now available on this topic. In order to better protect our environment against As, new hybrid technologies and secure disposal methods for As-loaded wastes should be introduced.

8. Conclusions

One of the deadliest elements, arsenic comes from anthropogenic and geological sources and affects millions of people who depend on groundwater for drinking water. The creation of dependable and straightforward technologies for evaluating arsenic in the field or laboratory is urgently needed. There are numerous analytical methods available to identify different As species. Accurate and repeatable results are produced by lab-based equipment such as ICP-MS and graphite furnace AAS applications. AFM and SERS are examples of newer technology that is still in the early stages of research and could experience problems with cost and high-throughput. Arsenic in biological materials and environmental samples can be measured using X-ray fluorescence. The benefit of this approach is that sample digestion or separation are not necessary. XRF spectroscopy is more precise, reliable and able to detect wide spectrum of metals in addition to As in solid media, compared to other analytical methods. On the other hand, inductively coupled plasma–optical emission spectrometer (ICP-OES) is widely used technique to measure As in liquid media.

As-related symptoms and indications seem to vary amongst people, population groups, and geographical locations. As a result, As poisoning lacks a standard definition. The illness brought on by As is not well understood globally. This makes it more difficult to evaluate the impact of arsenic on health. Additionally, there is no way to distinguish internal cancer cases brought on by arsenic from cancers brought on by other reasons.

No available data regarding hepatic effects of organic arsenicals on humans have been reported yet.

In previously conducted researches, the effects of As in the presence of other contaminants and iron have not been completely examined, which is one of the major gaps in arsenic-related research. As a result, determining whether the presence of additional pollutants exacerbates arsenicosis symptoms is crucial. In light of new scientific findings, it is vital to alter As mitigation strategies and plans for cleaner water sources, as well as guidelines for targeting aquifers.

Groundwater contains As in a variety of chemical forms, including inorganic (As(III), As(V)), and organic forms of mono-methylarsonic acid and di-methylarsinic acid (MMA, DMA). The USEPA health risk assessment model must be further investigated in order to evaluate the carcinogenic and non-carcinogenic risk caused by individual As species in groundwater, since they are thought to be more reliable than other health risk assessment models/frameworks.

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