

Review

The Arsenic Biogeochemical Cycle: A Review

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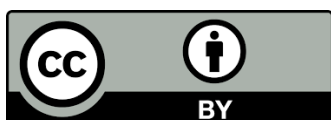
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Abstract

This paper reviews the arsenic in the environment. Arsenic contamination is currently one of the leading environmental problems worldwide. The arsenic (As) cycle is the subject of this article because As is an element with a significant impact on living beings and because of its interrelation with other biogeochemical cycles. The biogeochemical cycle of As is closed, so this trace element returns to sediments where it can be changed in its chemical state by micro-organisms present in soils. In addition, some minerals contribute to the sequestration and retention of As. This element interferes with other critical biogeochemical cycles such as sulfur, phosphorus, iron, manganese, and antimony. Another factor to consider is determining the content and interference of organic matter in the soil, as it forms very stable compounds with As. On the other hand, in aquatic environmental conditions, with a high concentration of organic matter and anaerobiosis, a reducing environment is created that facilitates the mobilization of As in the sediments.



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Keywords

Arsenic; biogeochemical cycles; impact environment; arsenic minerals; human health impact

1. Introduction

Biogeochemical cycles represent the exchange of energy and nutrients necessary to make life possible on Earth. They are closely related to the geological, hydrological, and biological processes that occur in the different compartments of the Earth's crust (atmosphere, hydrosphere, lithosphere, and biosphere). The primary biogeochemical cycles are Carbon (C), Nitrogen (N), Phosphorus (P), and sulfur (S). Alterations in biogeochemical cycles, mainly due to human activities such as agriculture, livestock, and mining, translate into changes in ecosystems' physical-chemical and biological properties. At a global level, there are many examples of imbalances in biogeochemical cycles, which cause significant environmental problems such as deforestation, soil erosion, desertification, contamination of large bodies of water, changes in the atmosphere that can modify the climate, produce rain acid or destroy ozone [1-7].

The arsenic (As) cycle is the object of study in this topic because it is an element that has a significant impact on living beings, is closely related to anthropogenic activities, and can interrelate with other biogeochemical cycles.

It is a metalloid widely distributed in the earth's crust [8-10] (about $5 \times 10^{-4}\%$), with atomic number 33, and is considered a trace element. In 2018, it became clear that As is probably the only element in the periodic table that has been the focus of controversy for centuries, constituting one of the most toxic elements on earth and presenting numerous impacts [11, 12] and can be considered a global environmental challenge [13].

Human exposure to arsenic through various sources has become a primary global concern. This is because arsenic has been shown to have an extremely toxic potential with severe consequences that pose a serious threat to the health, economic, and social well-being of people, especially in the less developed countries of the world [14]. It is estimated that about 107 countries worldwide are affected by As contamination in groundwater, and more than 500 million people worldwide are at risk of As exposure [15]. It is a Potentially Toxic Element (PTE) and is considered one of the most toxic and significant environmental elements [16]. Arsenic is carcinogenic, mutagenic, and teratogenic [17]. Its compounds have been listed as Group I carcinogens according to the U.S. Environmental Protection Agency (EPA) [18] and the International Agency for Research on Cancer [19]. Their toxicity, transfer mechanisms to different ecosystem components [20, 21], carcinogenic risk assessment, and related public health issues [22] have been extensively studied.

Inorganic arsenic is widely distributed in the environment. It appears in nature mainly in two oxidation states: As (III) and As (V), among which we can mention arsenic trioxide, As_2O_3 , sodium arsenite, NaAsO_2 , arsenic pentaoxide, As_2O_5 and lead or calcium arsenates, $\text{Pb}_3(\text{AsO}_4)_2$ - $\text{Ca}_3(\text{AsO}_4)_2$. It has been proven that As (III) is more toxic than As (V), and these are more toxic than metallic As. It is believed that the more significant toxicity of As (III) is due to its ability to be retained in the organism since it binds to sulfhydryl groups [23]. Arsenic (III) is usually associated with sulfide deposits, which are very abundant in pyritic belts [24]. It also forms organic compounds and can be methylated by bacteria and other living organisms in sediments and natural waters [25, 26].

The presence of organic species is usually negligible [17]. Elemental arsenic has several allotropic forms. More than 25 arsenic compounds have been identified in biological samples and in living organisms. As (III) undergoes various detoxification processes, such as oxidation to As (V) and biomethylation to MA and DMA, among other substances [23].

Identifying the numerous species of arsenic present in the ecosystem is very important.

Authors such as Zhang 2022 showed more than 300 As species [27].

The most important species defined by several researchers are resumed [28-31].

- In groundwater, the predominant species are oxidizing conditions [As (V) species (H_2AsO_4 , HAsO_4^{2-} , AsO_4^{3-}), reducing requirements ($\text{HAS}_3\text{O}^{3-}$)].
- In lake and river water As (V).
- The tissue of living organisms As (III) or As (V) is predominant in reduced conditions.
- Marine organisms: arsenobetaine and arsenosugars.
- Microbial: methylations reactions. Arsenic oxyanion: monomethyl arsenic acid (MMAA), dimethylarsinic acid (DMAA), dimethylarsine (DMA), and trimethylarsinic acid (TMAA).
- The uptake of soluble arsenic by the roots of plants: $\text{H}_n\text{AsO}_4^{n-3}$, $\text{H}_n\text{AsO}_3^{n-3}$.

The top ten pollutants and potential impacts on human life (as proposed by Pure Earth/Blacksmith Institute) assigns number two to Mining and mineral processing, with a DALY (Disability-Adjusted Life Years) values of 450,000-2,600,000 for Pb, As, Cd, Hg and hexavalent chromium (Cr(VI)) respectively. A high DALY value implies higher damage [3, 20, 32, 33].

The objective of this work was to review the arsenic biogeochemical cycle to investigate:

- Ways in which the biogeochemical cycles of arsenic and other elements interact with one another.
- I am studying arsenic in the different compartments of the ecosystem.
- It was knowing the importance of mineralogical composition on the mobility of arsenic in soil.
- She is researching the influence of past mining activities and the supergene alteration affecting the sediments and soils involved.
- I am analyzing the interference of Arsenic with other Biogeochemical Cycles such as sulfur, phosphorus, iron-manganese, antimony, and organic matter.

The most important questions or areas of interest in which the study hopes to shed light are knowing the problems and toxicity of arsenic and its behavior in the different compartments of the ecosystem (especially in soil, water, transfer to biota, and public health). Knowledge of the biogeochemistry of arsenic is essential to provide solutions for remediation projects in contaminated areas by heavy metals and trace elements such as arsenic. It is also of great interest for contaminated soil remediation projects through phytoremediation processes since it is vital to know the plants' suitability before carrying out these projects. Knowing how arsenic is found in the environment also provides solutions for a human health risk analysis project when a population is near a site with arsenic contamination.

2. Materials and Methods

The methodology used to do the literature review was following the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) standards, consulting a large number of related publications. The Science Citation Index Expanded (SCI-E), Web of Science® (WOS) was

used to obtain the scientific information for the present study. A summary of the literature consulted, classified by categories, is shown in Figure 1.

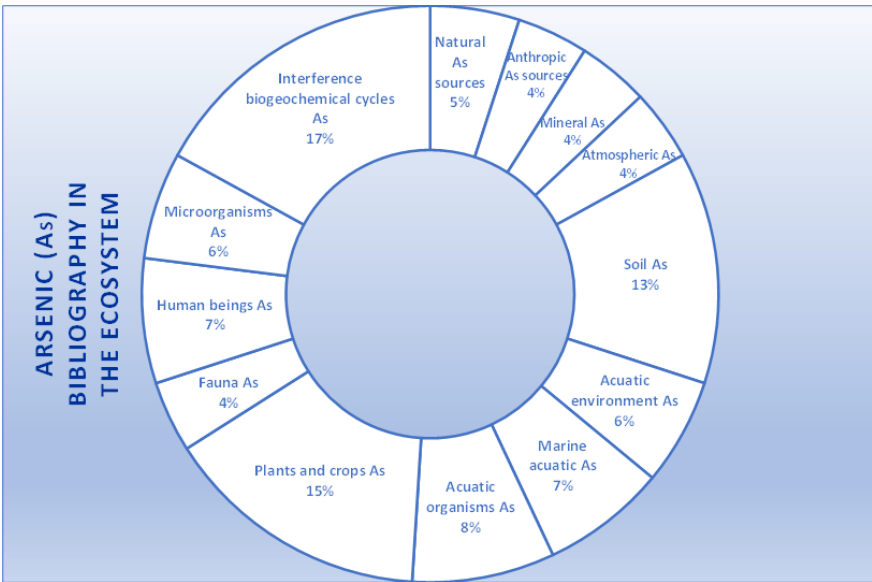


Figure 1 Summary of the literature consulted (1969-2023).

The samples were observed with an Olympus SZX 16 stereo microscope (Figures 3-7). The samples were analyzed with a JEOL-6100 scanning JEOL-6100 scanning microscope equipped with Oxford Instrument's INCA X-ray scattering microanalysis system for a detailed study.

3. Results

Arsenic is a metalloid in the biosphere, lithosphere, and hydrosphere and has a complex dynamic biogeochemistry. Figure 2 shows a schematic of the biogeochemical cycle of As. It can be seen that both the As found naturally in sediments and minerals, as well as that generated by anthropogenic actions, can reach the atmosphere and then be deposited in soils and waters of the earth’s crust and pass to different compartments among which aquatic organisms, plants, fauna, and humans stand out. As previously mentioned, the As cycle is closed, and this trace element returns to sediments, where it can be transformed by microorganisms present in soils [34].

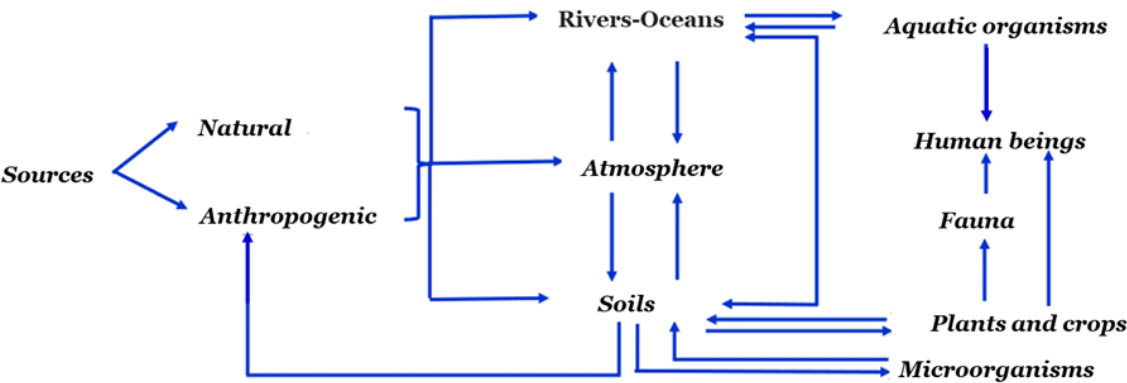


Figure 2 Diagram of the arsenic biogeochemical cycle.

3.1 Arsenic Sources

Familiar natural sources of arsenic can include fossil fuels, hydrothermal reservoirs, sedimentary rocks, and volcanic rocks, especially their weathering products. Some anthropogenic activities leading to increased arsenic concentrations in the environment include using fossil fuels, mining and smelting non-ferrous metals, preserving wood, and pesticide production and application.

The arsenic cycle is based on these arsenic sources (natural and/or anthropogenic), is regulated by different environmental factors, and comprises other oxidation states and chemical speciation.

It can be seen in Figure 2 that the sources of As in the environment are both geogenic and anthropogenic [35]. It is difficult to distinguish between the two, as anthropogenic activities that release arsenic into the environment originate from materials with geogenic As. Living organisms act as bioaccumulators and transfer this element to different environmental compartments until the cycle is closed. Both soil and marine sediments are essential reservoirs.

3.1.1 Natural Sources

Arsenic is found in several natural reservoirs such as oceans, rocks, atmosphere, biota, and soil, but more than 99% of As is found in rocks and more than 300 minerals [36, 37]. As of July 2023, there are 750 known minerals for which arsenic is a critical component (According to the International Mineralogical Association). These include elemental arsenic, arsenates, sulfides, oxides, mixed-anion, and arsenites, arsenides, arsenates [19]. As it appears as a significant constituent in a large number of minerals, approximately arsenic compounds consist of 60% arsenates, 20% sulfides and sulfosalts, 10% oxides, and the rest arsenite, arsenides, native arsenic and/or metal alloys [38]. Three origin types can be differentiated for arsenic minerals: hydrothermal, sedimentary, and metamorphic (Table 1).

Table 1 Most frequent arsenic minerals. Adapted from [27].

Mineral	Composition	Occurrence
native As	As	Hydrothermal veins
niccolite	NiAs	Phylons and norites
rejalgar	AsS	Seams, often associated with oropiment, clays and carbonates in “hot springs”
oropimente	As ₂ S ₃	Hydrothermal veins, “hot springs”. Also as a product of sublimation of volcanic emanations.
cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
arsenopyrite	FeAsS	It is the most abundant As mineral. Very frequent in seams
tennantite	(Cu, Fe) ₁₂ As ₄ S ₁₃	Hydrothermal veins
enargite	Cu ₃ AsS ₄	Hydrothermal veins
arsenolite	As ₂ O ₃	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other arsenic minerals

claudetite	As_2O_3	Secondary ore formed by oxidation of arsenopyrite, native arsenic and other arsenic minerals
escorodite	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	Secondary mineral
annabergite	$(\text{Ni, Co})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	Secondary mineral
hoernesite	$\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	Secondary ore, in slag
hematolite	$(\text{Mn, Mg})_4\text{Al}(\text{AsO}_4)(\text{OH})_8$	Ore in fissures of metamorphic rocks
conicalcite	$\text{CaCu}(\text{AsO}_4)(\text{OH})$	Secondary mineral

Naturally occurring As is found in minerals, in the earth’s crust and rocks contain about 2 to 3 μgg^{-1} (a range of 0.1 to hundreds of μgg^{-1} is stated). Sedimentary rocks generally have high As levels (0.5-455 μgg^{-1}), while the content in igneous rocks is (0.06-113 μgg^{-1}). Sands and sandstones tend to have the lowest concentration of As. Besides this, most of the As is bound to pyrite. The two predominant natural sources of As in the atmosphere are low-temperature volatilization (about 26,000 tons per year) and volcanic activity (about 17,000 tons per year) [39, 40].

The most crucial primary As minerals are arsenopyrite (FeAsS), enargite (Cu_3AsS_4), tenantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), rejalgar (AsS) and oropimente (As_2S_3) [41]. Enargite (Cu_3AsS_4) and arsenopyrite (FeAsS) are the sulfide minerals with the highest As content. Oxidation of these two minerals represents the primary source of As in Acid Mine Drainage (AMD) [10]. Examples of arsenates are shown in Figures 3-7. They are minerals of secondary origin that contain oxygen in their structure.

Figure 3 corresponds to the mineral conicalcite found in the oxidation zone of arsenic-rich copper deposits.



Figure 3 Conicalcite $\text{CaCu}(\text{AsO}_4)(\text{OH})$.

Figure 4 corresponds to the mineral duftite, which usually appears associated with malachite, as shown in the photograph. It originates from weathering of lead and copper ores with arsenic.



Figure 4 Duftite-malachite $\text{PbCu}(\text{AsO}_4)(\text{OH})$.

Figure 5 corresponds to the mineral erythrite. It is a hydrated cobalt arsenate. It appears in the alteration zone of cobalt-bearing sulfide deposits, forming very characteristic cobalt crusts or flowers on them.



Figure 5 Erythrite $\text{Co}_3(\text{AsO}_4) \cdot 8\text{H}_2\text{O}$.

Figure 6 corresponds to the mineral mimetite occurring in the oxidation zone of lead-arsenic deposits.



Figure 6 Mimetite $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$.

Figure 7 corresponds to the mineral green parnaute associated with azurite, found in oxidized copper in hydrothermal deposits.

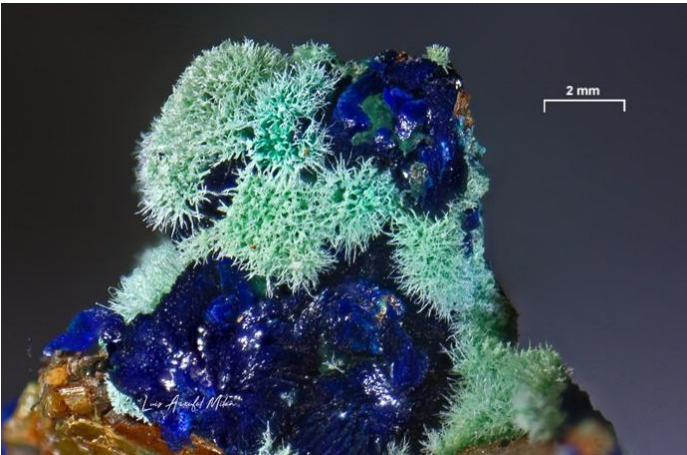


Figure 7 Parnaute $\text{Cu}_9(\text{AsO}_4)_2(\text{SO}_4)(\text{OH})_{10} \cdot 7\text{H}_2\text{O}$ -azurite.

Although not a significant component, arsenic is also found in varying concentrations as part of a large number of minerals, both primary and secondary. The highest concentrations of arsenic occur in sulfides such as pyrite, arsenopyrite, chalcopyrite, galena, and marcasite (Table 2), where arsenic is found to replace sulfur in the structure. In these minerals, the arsenic content can exceed 10% by weight of the mineral. Other minerals where arsenic can be found in appreciable concentrations are oxides and oxyhydroxides (Table 2), especially those of iron and, to a lesser extent, those of manganese and aluminum, mineral phases where it can be part of the structure or adsorbed on the surface [42-44].

Table 2 Arsenic concentration in some of the most common minerals [42-44].

<i>Mineral</i>	<i>As concentration (ppm)</i>	<i>Reference</i>
Sulphides:		
pyrite	100-77,000	[42]
pyrrhotite	5-100	[39]
galena	5-10,000	[42]
sphalerite	5-17,000	[42]
chalcopyrite	10-5,000	[42]
Oxides:		
hematite	Up to 160	[42]
Fe oxides	Up to 2,000	[43]
Fe (III) oxyhydroxide	Up to 76,000	[44]
magnetite	2.7-41	[42]
Silicates:		
quartz	0.4-1.3	[42]
feldspar	<0.1-2.1	[42]
biotite	1.4	[42]
amphibole	1.1-2.3	[42]

olivine	0.08-0.17	[42]
pyroxene	0.05-0.8	[42]
Carbonates:		
calcite	1-8	[42]
dolomite	<3	[42]
siderite	<3	[42]
Sulphates:		
gypsum/anhydrite	<1-6	[42]
barite	<1-12	[42]
jarosite	34-1,000	[42]
Phosphates		
apatite	<1-1,000	[42, 43]

As(V) adsorption on iron oxyhydroxides is the most effective mechanism for arsenic retention in the solid phase. Phosphates are another group of minerals with relatively high arsenic contents, such as apatite (Table 2). Arsenic can substitute for Si(IV), Al(III), Fe(III), and Ti(IV) in many mineral structures, thus being found in many rock-forming minerals, although in deficient concentrations. For example, most silicates contain about 1 ppm or less, and carbonates (calcite, dolomite, and siderite) typically have less than 10 ppm [43]. Under highly reducing conditions, As co-precipitates with iron sulfides as arsenopyrite (FeAsS) or as arsenic sulfides (AsS, As₂S₃). Furthermore, these sulfides are easily oxidized under aerobic conditions, giving off As to the environment.

3.1.2 Anthropogenic Sources

Regarding anthropogenic activities, it should be noted that some industrial processes, such as smelting non-ferrous elements, especially copper, lead and zinc, or coal-fired power plants contribute to As in air, water, and soil. Another essential source is the supergene alteration of arsenic-rich minerals during mining processes [26]. Other sources are agriculture, forestry, urban waste, and animal husbandry, as well as the formulation of numerous pesticides, fungicides, and biocides [44-47].

3.2 Atmospheric Arsenic

The element can reach the atmosphere from emissions (natural and anthropogenic) and aerosols, being found as volatile As and As in particulate matter (soils, sediments). The primary natural sources of As emissions correspond to volcanic activity [48, 49]. Human activity contributes to 75% of the As present in the atmosphere [50]. Available information on species present in aerosols is scarce. However, it is known to be generally low, except at specific points where emissions occur from smelting activities, fuel oil combustions, or other industrial activities [51]. In general, As(V) is the main arsenic species in aerosols, and the As(III) content is much lower [49]. The U.S. OSHA states that the permissible exposure level (PEL) for As is 10 mg m⁻³ air. The action level is 5 mg m⁻³ air [52, 53]. Typical background levels for arsenic in rural, urban, and industrial areas are 0.2-1.5, 0.5-3, and <50 mg m⁻³ air respectively [54]. Inorganic As(III) and As(V) may be present in PM and associated with particulate matter of varying rank 0.2-2.0 mm [55-57].

The range of As concentration in particulate matter in ng/m^3 is higher than 100 for Taiwan, China, India, and Korea, with average values in the USA and lower values in Spain and Canada [58].

3.3 Arsenic in Soil

The dynamics of arsenic in soil, i.e., its mobility and bioavailability, are influenced by several factors [59]:

- 1) The chemical species of As. The order of toxicity of arsenic compounds would be as follows: monomethylarsonous acid (MMA(III)) > dimethylarsinous acid (DMA (III)) > arsenic trioxide (As III) > arsenic pentoxide (As V) > monomethylarsonate (MMAV) > dimethylarsinic acid (DMAV) [60].
- 2) pH. Arsenic tends to be more available at very alkaline pH [47]. In general, As(V) adsorption decreases with increasing pH, contrary to As(III) adsorption, which increases with increases in pH [59].
- 3) Redox potential. In oxidizing environments with high oxygen concentrations, As (V) predominates, while As(III) is the most abundant form in reducing environments [61].
- 4) Soil texture. The sand and silt fractions show a relatively low adsorption capacity due to the joint surface area and the predominance of quartz, while clay is the main adsorbent [62].
- 5) Adsorption on carbonates. Calcium carbonate is found in soils at neutral pH or higher; therefore, the reaction with arsenate occurs in this pH range [62].
- 6) Other mineral phases. Secondary Fe minerals, such as goethite, jarosite, and schwertmannite, contribute to the sequestration and retention of As, favoring a natural attenuation process in soils [37, 63].

Arsenic soil content can be geogenic, inherited from the parent rock, or incorporated from the atmosphere, biota, and waters. The natural level of As in soils depends on the type of rock. The normal range is 1 to 40 mg/kg; generally, the stories in uncontaminated soils rarely exceed 10 mg/kg [39]. No European legislation sets reference values for As and other metals in grounds, although member countries have regulations. An example is the Finnish threshold and guideline values for metals in soils [64], which recommends that the total As concentration in agricultural soils should not exceed 20 mg kg^{-1} . USEPA, the Netherlands, Canada, etc., estimate cleanup values based on risk analysis according to soil use [65].

Samples with concentrations above the threshold value in the Land Use and Land Cover Survey (LUCAS) in European regions are generally low, with only 0.8% showing values above the upper guideline value, affecting southern and Mediterranean areas.

This fact urges a thorough investigation of the arsenic problem, especially in France, Italy, and Spain. The sporadic distribution of samples with elevated concentrations indicates that arsenic contamination may be a continent-wide problem, but only in a small percentage for agricultural areas [66].

In the case of paddy fields, due to the redox conditions that occur, As is highly mobile, and the transfer to the plant is very high. Therefore, As levels in these soils should be checked as As contents higher than 0,15 mg/Kg in rice can harm health [34, 67, 68].

Mining operations and ore activities represent the primary anthropogenic sources of local input of As in soil [69]. When the origin of PTE in soil comes from the parent rock, volcanic activities, or mineral leaching, it is considered a geogenic high level. Generally, these contaminants present low

mobility and do not exceed toxicity thresholds [69-72]. Mining areas are so complex that it is sometimes difficult to differentiate anthropogenic contamination from geogenic anomalies [73].

This can be studied in different parts of the world, in other mining areas, and under different environmental conditions. The behavior of As can change depending on the area's topography, lithology and climatic conditions, and the type of mining being carried out. The dispersion and contamination of As produced is different in each case, but there are recurring patterns. Considering an example of these processes in a Mediterranean climate and with non-active mining is interesting. In the Region of Murcia, located in southeastern Spain, the proposed Generic Reference Level (GRL) is 7.84 mg kg^{-1} [61]. The exclusion zones include the Sierra Minera de Cartagena-La Unión and their areas of influence (Portmán and Gorguel beach, among others). In these areas, concentrations exceed 300 mg kg^{-1} as shown in Figure 8, reaching 5000 mg kg^{-1} in some cases (coinciding with accumulations of mining waste, ponds, dumps, etc.) [74].

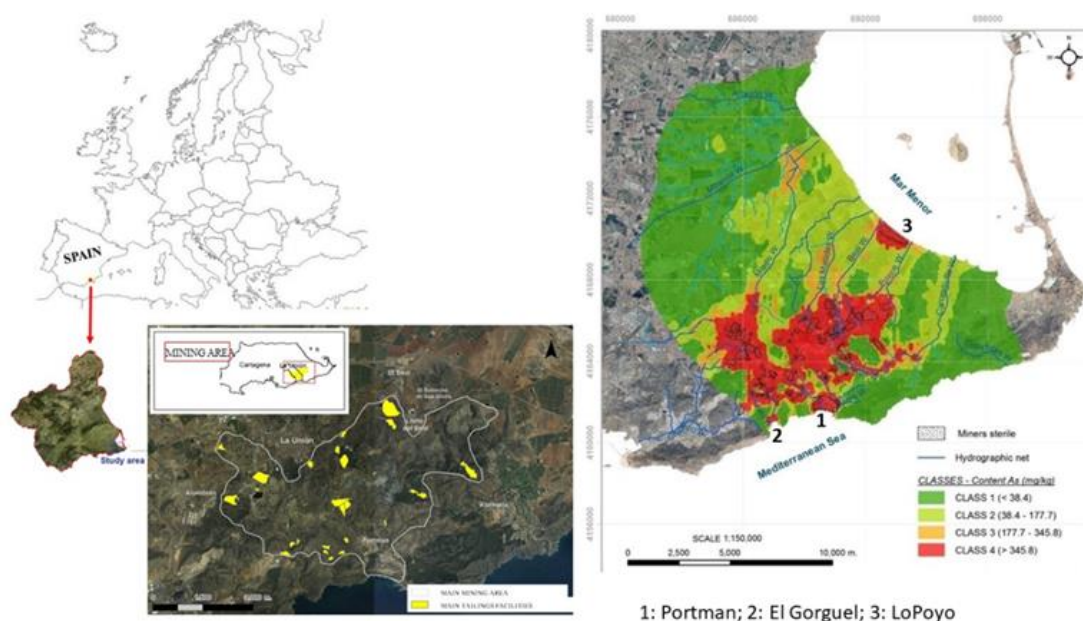


Figure 8 Map of arsenic zoning in Sierra Minera Cartagena-La Unión and adjacent areas [74].

The map in Figure 8 shows another area that deserves special attention: the LoPoyo wetland. This area is located within the open spaces and islands of the Mar Menor with the category of Natural Park, Site of Community Importance (SCI), and Special Protection Areas for Birds (SPAB). At the same time, it houses a mining tailings pond at the mouths of the Beal and Ponce wadis. As levels in this area can exceed 340 mg kg^{-1} , its bioavailability can be considered high.

3.4 Water Arsenic

The EPA (Environmental Protection Agency) established 1975 that the maximum concentration limit for As in drinking water should be $50 \text{ } \mu\text{g L}^{-1}$. In 2000, the EPA proposed a new value for drinking water of $5 \text{ } \mu\text{g L}^{-1}$ and $10 \text{ } \mu\text{g L}^{-1}$ in 2001, to protect consumers from long-term and chronic exposure effects. All these precisions illustrate well the recent evolution of As toxicology and the impossibility of drawing definitive conclusions [75].

The presence of the element in water is currently one of the significant environmental problems worldwide. About 200 million people living in 70 countries are at risk of having arsenic in their drinking water [75, 76]. The most affected regions are South America and South Africa [15]. In Bangladesh, for example, concentrations above $150 \mu\text{gL}^{-1}$ have been found [77] and higher than $2500 \mu\text{gL}^{-1}$ or $7800 \mu\text{gL}^{-1}$ in Argentina. In seawater and marine sediments, total As concentrations are $1\text{-}2 \mu\text{gL}^{-1}$ and $3,000\text{-}15,000 \mu\text{gL}^{-1}$, respectively [39].

In water bodies, the element comes mainly from the soil and atmosphere. The concentration of As in freshwater varies depending on the source, amount available, and local geochemical environment [40].

The redox potential and pH are the most critical factors controlling As speciation in aqueous systems [78]. Figure 9 shows a summary of the As cycle in aqueous systems, and it can be seen how arsenate generally predominates under oxidizing conditions, As(V) species (H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}), is prevalent in aerobic surface waters, while arsenite (HAsO_3^-) predominates when conditions become sufficiently reducing, it is commonplace in anaerobic groundwater [9].

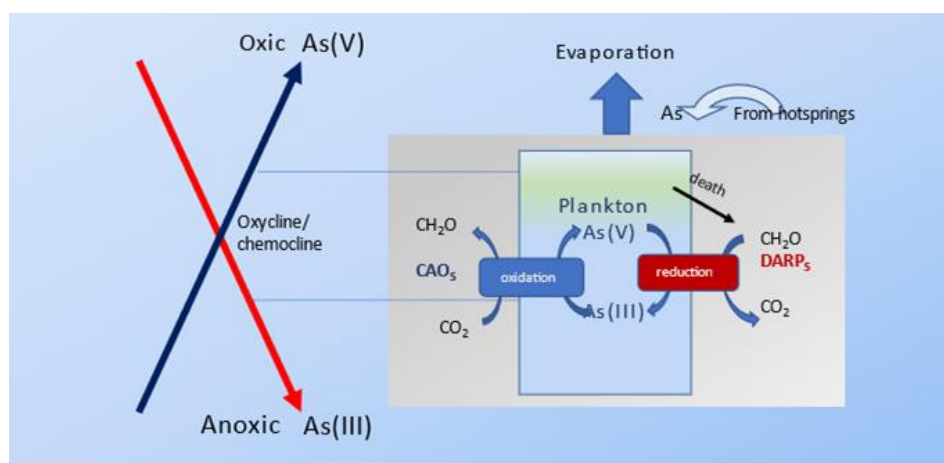


Figure 9 Arsenic release mechanisms under different redox conditions. Figure adapted from [9].

3.5 Arsenic in Marine Environments

The mean value for arsenic in seawater is around $2 \mu\text{g/L}$ [40] and a residence time of 39,000 years [79]. In seawater, As is present in soluble form as oxyanions. In oxidizing conditions, it predominates as arsenate (As(V) [76].

In seawater marine sediments the concentrations of total As are in the range $3\text{-}15 \mu\text{g g}^{-1}$ [39] and may be to organic matter that controls its speciation, toxicity and effects on biota [80]. Marine sediments are considered metal sinks and represent a fundamental role in the storage and distribution of arsenic [45, 81]. Authors such as Liu [45] consider that further studies on the distribution of this element in estuarine and coastal sediments are necessary to understand its dynamics.

The management of dredged material projects in harbors, which are necessary to maintain navigability and port safety conditions, is regulated in the OSPAR Guidelines for the Management of Dredged Material at Sea and its replacement in waters of the maritime-terrestrial public domain [82]. Chapter V establishes the criteria for the classification of dredged materials and the levels of

action defined according to their concentrations of contaminants. Regarding arsenic, it creates the following category: [As] = 35 (mg/kg). Action Level A. This material can have numerous productive uses, such as the regeneration and creation of beaches, the revival of contaminated soils, or uses in agriculture. [As] = 70 (mg/kg). Action Level B. These materials may be discharged into the sea only in non-restricted areas. [As] = 280 (mg/kg). Action Level C. These materials may be relocated in the waters of the public maritime-terrestrial domain through a containment technique in surfaced enclosures, port landfills, or underwater containment in unrestricted areas. [As] up to 1000 (mg/kg). Non-Hazardous Sediment.

These materials will require a study on productive use alternatives to dumping at sea. [As] > 1000 (mg/kg). Material that cannot be considered non-hazardous sediment. Category R materials may be relocated in the maritime-terrestrial public domain by prior application of a treatment technique that allows their classification as category A, B, or C.

Other options for marine sediment management are based on ecological and health risks, as As is considered a List of one bioaccumulative element (Primary Bioaccumulative Contaminants of Concern) with a bioaccumulation rate of 507 mg/Kg dry wt [83].

3.6 Arsenic in the Biota

Several investigations show that arsenic is not a necessary element for living beings. No known organism has specific absorption systems for this element. The uptake pathways for As are through transporters of minerals, nutrients, phosphate, and glucose... and it is produced accidentally. To understand the BIO part of the biogeochemical As cycle and its effects on living organisms, knowledge of As (V) uptake and physiology is essential [84].

A recently published study is very relevant to understanding the behavior of As in plants, so that in the species *Pteris vittate*, As (V) is reduced in the roots and sequestered in the leaves [85]. In humans and almost all mammalian species, inorganic As undergoes methylation processes and is excreted [86].

3.6.1 Aquatic Organisms

Arsenic reaching aquatic organisms comes mainly from water and soil's contribution to water. The concentration of As in the marine environment has increased in recent years, mainly due to anthropogenic actions [87]. This fact has attracted much attention in research, given the potential risk to human health through fish consumption [88]. Marine organisms are capable of bioaccumulating As up to concentrations of 1-100 mg kg⁻¹ [89]. Total As concentrations are higher in marine fish (1-10 g g⁻¹) than in freshwater fish (<1 g g⁻¹) [90]. The maximum allowable limit for the human diet is 0.03 mg kg⁻¹ for fish and 0.1 mg kg⁻¹ in shellfish [91].

Several studies show that arsenobetaine (AsB) is the main As species in marine fish tissues, typically accounting for more than 90% of total As [90, 92, 93].

The primary source of AsB accumulation in marine fish could be biotransformation rather than trophic transfer [90], accumulating in more significant proportion in muscle versus other organs in the marine grouper *Epinephelus fuscoguttatus* [92], with the efficiency of dietary assimilation of AsB being higher than that of different forms of arsenic [94]. This species is the result of blocking the element by the fish and seafood metabolism and show no toxicity to mammals because it is not metabolized and is excreted intact by humans [95, 96].

Teleost fish are often used as models for studies on endocrine disruption [97, 98]. At present, the toxicity of As on the immune system of fish has not been sufficiently studied. However, it is known that it accumulates in the retina, liver, and kidneys and causes an increase in the hepatosomatic index and histopathological alterations in the liver [99]. In other research carried out by the authors [100, 101], it was shown that As accumulates in the muscle (edible part) of gilthead seabream (*Sparus aurata*) specimens exposed for 30 days to a 5 μM of concentration of As_2O_3 . However, even in such reared conditions, the attention of As in these exposed fish was below the established legal limits.

Figure 10 shows representative histological images of European seabass (*Dicentrarchus labrax*) livers stained with hematoxylin-eosin from unexposed (A) or exposed to 5 μM As_2O_3 during 2 days (B) and ten days (C). Apoptotic and necrotic symptoms of cell death were observed [102].

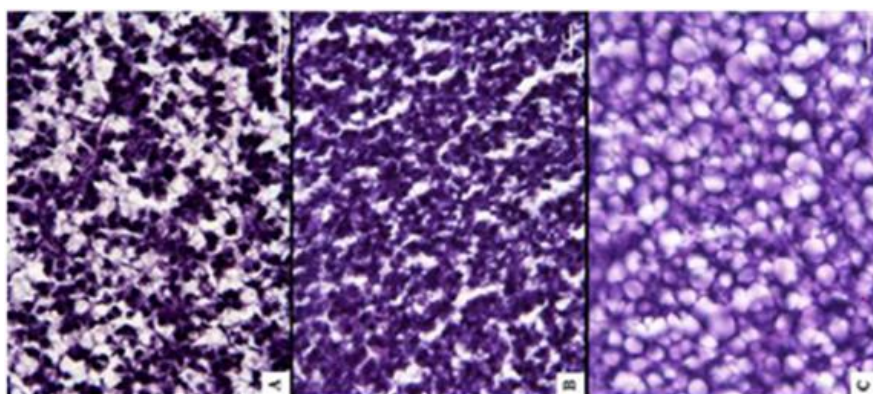


Figure 10 Histological images liver *Sparus Aurata* [102].

Finally, in coastal areas affected by mining activity, the bioavailability of trace elements was determined in two species of jellyfish, obtaining very high bioconcentration levels of As (3.57-130.01 mg/kg dry W) and other metals such as Al, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Sn and Pb [65].

3.6.2 Plants and Crops

The main pathways of AS entry to plants and crops are soil and water. However, As can be found naturally in plants, but concentrations in plant tissues rarely exceed 1 mg kg⁻¹ [59]. The maximum limit for consuming fruits, crops, and vegetables is 2.6 mg kg⁻¹ fresh weight [60]. Currently, the Food and Agriculture Organization (FAO) has recommended a safe limit of 0.2 mg kg⁻¹ As for rice grain (it is essential to consider that around 115 countries grow it and that approximately 3 billion people in the world, mainly Asian countries, use it as their primary source of food) [9].

In the context of the bioavailability of As species to plants, DMA < As (V) < MMA < As (III). As (V) is transported by the root using the phosphorus transport channel [80]. When plants grow naturally in soils that present high concentrations of As, for example, in soils influenced by mining activities, they can accumulate high concentrations of As in their tissues and constitute a public health problem since they can be part of the diet of natural fauna [22, 101, 102].

The behavior of arsenic is critical to its interaction with plants and humans, which makes it necessary to consider the chemical and physical properties of the element in the broad context of human toxicity and phytoremediation [103].

Furthermore, it is essential to underline that before starting a remediation program for contaminated soils, it is advisable to take into account the soil-plant transfer coefficients and thus be able to know the suitability of plant species for the different phytoremediation programs (phytostabilization, phytoextraction...). For example, in the studies by Pérez Sirvent [104], it was concluded that plant species such as *Dittrichia viscosa* can be considered suitable for phytoextraction and phytostabilization of soils contaminated by mining in southeastern Spain. This plant accumulates a high concentration of As in its roots (high value of Bioconcentration [BCF] = $CT_{\text{Total Plant}}/CT_{\text{Total Rhizosphere}}$). Still, it does not transfer in large quantities to the edible parts (low value of Displacement Factor [DF] = $CT_{\text{Total Leaf}}/CT_{\text{Total Root}}$). The microphotographs in Figure 11 show that the proportion of As to Fe is higher in the root than in the aerial parts. Therefore, *D. viscosa* does not represent a danger of As entering the food chain by feeding the fauna in the area where it is found.

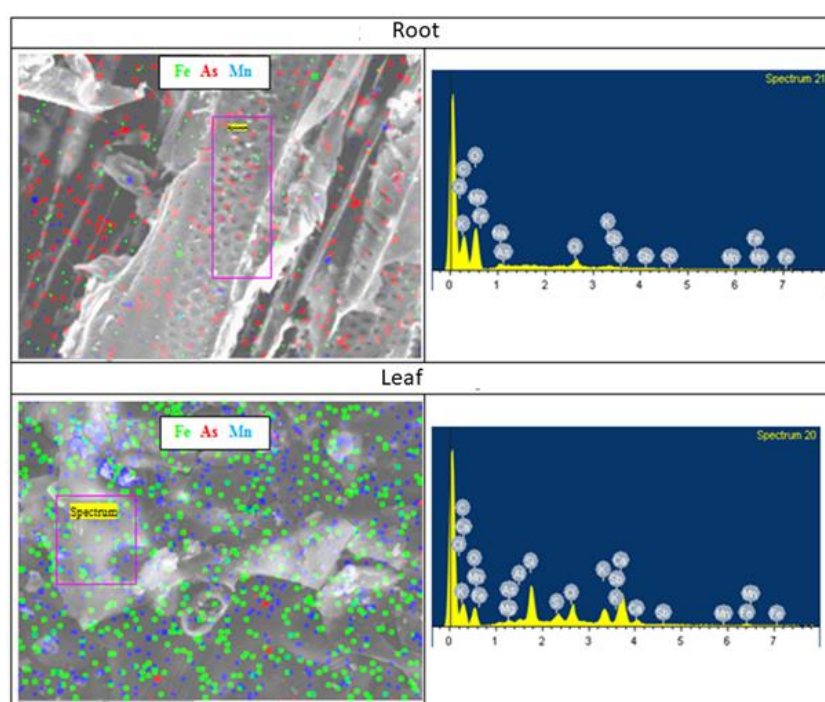


Figure 11 Representative scanning electron microscopy images of root and leaves of *Dittrichia viscosa* [104].

As mentioned above, the transfer of trace elements to crops constitutes a potential risk of entry of Potentially Toxic Elements (PTE) into the trophic chain. An experimental greenhouse study on different plant species, using mineral soils with high As content and other PTEs with varying treatments of restoration (technosols), provided data on the transfer of As to plants. The results showed a lot of variability, not only changes by families and species, but it is even sensitive to plant variety. The Transfer Factors were always less than 1 for crops such as onion, lettuce, leek, and broccoli, so the As content in edible parts rarely presented problems for intake [105].

Rice is the cereal that contains the most arsenic, compared to other foods, because it grows in a flooded environment with anaerobic conditions [106, 107]. Rice is considered the leading food in the diet of many consumers, especially in Asian countries [63, 106, 108, 109]. It is estimated that a

population of >3.5 billion inhabitants depends on rice as a staple food [110]. Long-term rice consumption is a public health problem that needs to be addressed [111-114].

3.6.3 Fauna

Terrestrial invertebrates are an important part of the food chain since they are consumed by higher animals such as shrews, frogs and birds but knowledge about the mechanism of arsenic uptake and flux is very scarce [115]. Ali and Khan [116] assessed that carnivorous animals accumulate more arsenic than omnivores.

The main route of As entry to wildlife organisms is through plant consumption. To evaluate this entry pathway into the food chain, [117] studied the transfer to the food chain through plants and natural fauna inhabiting soils affected by heavy metals in abandoned mining areas. That study analyzed 165 soil samples and the same number of plants. The mammals selected were sheep (is important for the human diet) [118] and mice. The results of studying bioconcentration and displacement factors determined that As transfer depends mainly on plant species and soil characteristics (pH, carbonate content and metal concentration). It was concluded that plants such as *D. viscosa* (already mentioned) do not represent a risk of As ingestion when consumed by the fauna studied, and that it is highly recommendable for soil remediation programs.

Other species, such as *Arthrocnemum macrostachyum* and *Glaucium flavum*, can also be used but with caution. In contrast, the use of *Helichrysum decumbens*, *Carduus bourgeanus* and *Lygeum spartum* for these purposes is discouraged. It was concluded that in a phytoremediation program, the plant's contribution to the animals' diet should be studied because this indicator can be used to select plant species [119].

3.6.4 Human Beings

Curiously, humans' highest dietary intake of As comes from consuming marine products, mainly fish, which accounts for 90% of the As consumed. In 2003, the European Union established that the maximum total As content in food products derived from both fish and fur-bearing animals is 6 $\mu\text{g g}^{-1}$. Another important As entry route is ingesting groundwater, which presents a significant public health problem. It has been estimated that approximately 200 million people worldwide are currently at risk of As poisoning, either by direct ingestion of contaminated groundwater or indirectly through ingestion of crops, such as rice grown with As-contaminated water [9].

It is essential to assess the adverse effects on human health of arsenic present at a potentially contaminated site by considering the possible pathways of entry of the contaminant into the human body and the uses of the site. The toxicity of the metal(loid) is not only a function of the total concentration but depends on potential leachability, solubility, bioavailability, and bioaccessibility [120, 121]. In a possible human health risk analysis project of a contaminated site, it cannot be assumed that 100% of the ingested dose is bioavailable [122] because the risk is overestimated and the results are higher than the reality [115, 122, 123].

The half-life of ingested inorganic As is approximately 10 hours, and 50 to 80% is excreted around 3 days, while methylated arsenic has a half-life of 30 hours. As is absorbed into the body and stored mainly in the liver, kidney, heart, and lung [115, 124, 125]. Ingestion can have health effects, ranging from general malaise to even death [126-128]. Exposure to inorganic As through drinking water and food intake can cause health effects such as skin effects or skin, bladder, kidney, and lung cancers.

Long-term exposure also leads to blood vessel diseases of the legs and feet, diabetes, cardiovascular diseases, hypertension, and reproductive disorders [126].

3.6.5 Microorganisms

As present in flora, fauna or even human beings can return to sediments through the action of different microorganisms. Within the biogeochemical cycle, microorganisms play a vital role in the biotransformation of arsenic [127, 128].

Fungi, yeasts and bacteria can volatilize arsenic as a detoxification mechanism. As can be volatilized in the form of arsine and its methylated species, such as mono-, di- and tri-methylarsine. However, this As volatilization rate is considered low [129]. Soil microorganisms are considered to be the most sensitive to changes produced by the presence of As in contaminated soils [130]. The presence of arsenic can negatively affect microbially mediated processes, however, there are microbial communities that have become resistant to high concentrations of arsenic [115]. Many microorganisms involved in the biogeochemical cycling of As have now been described [131]. Microorganisms play a key role in As cycling and toxicity, such that anaerobic bacteria can reduce As^{5+} , while aerobic organisms can oxidize As^{3+} [132].

3.6.6 Interference of Arsenic with Other Biogeochemical Cycles

The As cycle represents the interactions between abiotic, geological, and biotic (especially bacterial) systems. The biogeochemistry of As is like that of heavy metals, where microorganisms play a vital role in As cycling and toxicity. In this As transformation process, the microorganisms do not directly benefit from the degradation of the compound, and it can even be harmful and inhibit the growth and metabolism of these microorganisms. This process is favored by the phytodegradation processes carried out by plant roots [132]. Changes in hydrochemistry associated with the hydrological cycle, anthropogenic activities, and dynamic boundaries between different environmental compartments can trigger the release of arsenic into the subsoil [133]. The main interferences of the arsenic cycle with the primary biogeochemical cycles are summarized below.

Arsenic and Sulphur (S). As and S often coexist in geothermal environments and undergo similar chemical and microbial redox transformations [134-136]. The microbiological cycling of S in hot springs exerts a relevant direct or indirect effect on As speciation, forming different thioarsenate species [132, 133, 137, 138].

There is some evidence that S, iron, and As can be reduced simultaneously under the action of anaerobic microorganisms [138]. The presence of sulfide ion (S^{2-}) can not only generate mackinawite (FeS) with Fe^{2+} but also reacts with As^{3+} to form orpiment (As_2S_3) and realgar (AsS). Other studies confirm that As in solution and a reducing medium can co-precipitate with FeS , thus interfering with speciation and favoring its immobilization. Therefore, the alteration of the biogeochemical S cycle, which is caused, for example, by the input of Acid Mine Drainage (AMD), may influence the speciation and transformation of arsenic, i.e., the bioavailability of arsenic in cultivated soils such as rice fields [92]. During flooded conditions, SO_4^{2-} in the soil-water system reduces into S^{2-} [139]. As(III) in the paddy soil solution can react with S^{2-} and precipitate as an As_2S_3 -like complex [140]. Therefore, the bioavailability of As(III) for the uptake by rice plants is decreased [34].

Authors such as Glodowska et al., 2021 showed that the presence of SO_4^{2-} in Pleistocene aquifers in Vietnam is related to lower As concentrations in the groundwater samples analyzed. The S cycle is also associated with the formation of minerals such as FeS, FeAsS, and AsS, leading to the sorption of As to these minerals in this zone [141].

Arsenic and Phosphorus (P). The nature of As interactions with other biogeochemical cycles, such as phosphorus, is currently poorly understood. Woolson [137, 142] states that P is the most influential fertilizer material on As toxicity. The uptake of arsenate, but not arsenite, is affected by phosphate. This is because arsenate and phosphate are chemically similar and compete for the same sites in soils and transport systems. The amount of phosphorus in the soil solution seems to govern arsenic uptake in the plant because when P in the solution is high, uptake is reduced [62]. Numerous reports have shown that As uses phosphorus entry channels to enter the plant [27, 141, 143-147]. It is, therefore a topic where further research is needed to deepen our understanding of the biogeochemical cycle of As.

Arsenic and Iron-Manganese (Fe-Mn). Precipitation of Fe and Mn oxides can contribute to the natural attenuation of As. Arsenic retention can occur by co-precipitation (occurs when Fe minerals are formed in the presence of As) or adsorption (when As is added after forming Fe minerals). Since the environmental conditions are unknown when Fe minerals are included, it is unclear whether As attenuation is by co-precipitation or adsorption to Fe minerals [34, 148].

In groundwater, the presence of dissolved sulfide affects As mobility as it causes the dissolution of Iron (hydro) oxides (effective sorbents of As) [138]. The effects of nitrogen (N) and S on As transfer and migration in groundwater are not well known [149]. However, authors such as Li et al., 2017 and Gao et al., 2021 showed that the N cycle is essential for mobilization and As-enrichment as it is involved in dissolved Fe(II) [149-152].

Arsenic and Antimony (Sb). These two metalloids have a similar biogeochemistry, behaving as extremely toxic elements [153-155]. Recently, the pollution produced by these elements, mainly due to mining activities and smelters, has received much attention [156]. The toxicity of both depends on speciation. However, few Sb studies are available to fully assume this statement [132, 156]. The factors that influence the mobility of As and Sb in soils have not been sufficiently studied [155-157]. The results obtained by Zhao [158] showed that attention should be paid to the relationship between soil particle size and As and Sb concentrations, which increase as particle size decreases. Researchers such as Wilson [159] determined significant proportions of As and Sb retained in organic matter. In addition, increases in clay and organic matter in the soil influence the decrease in the solubility of Sb [160]. Natasha [161] observed that Sb is less well mobilized in soil than As. Other authors [27] showed that iron oxides' mineralogical transformations are significant to understanding the behavior of As and Sb in the environment. The biogeochemical cycles of As and Sb interact with other cycles such as C fixation, nitrate/nitrite reduction, N fixation and sulfate reduction [150].

Arsenic and Organic Matter. Authors such as Feng et al., 2023 showed that migration and transformation of As can be affected by the decomposition of organic matter in groundwater [149].

The results of the research conducted by Martínez López [162] show that As present in sediments is susceptible to mobilization in the event of soluble organic matter content increases, such as

accidental spills from a wastewater treatment plant or intensive agricultural practices. The presence of soluble organic compounds increases the leaching of As adsorbed on minerals, contributing to its increased mobility [163]. Likewise, As can be accumulated in living organisms (as arsenobetaine) by incorporating organic matter into sediments. This can mineralize and leave As integrated as a mineral component (clays, sulfides, etc.) or undergo a fossilization process and become coal or oil, with variable As contents. In this way, the arsenic passes back to the sources, closing the cycle, and is released naturally by geological processes or by anthropic actions (fossil fuels).

4. Conclusions and Perspective's

Following the review, it is clear that the scale of the problem represented by this element is classified as carcinogenic, mutagenic, and teratogenic. In this regard, it is considered the most problematic element on earth and presents numerous impacts. Arsenic in the ecosystem interferes with the biogeochemical cycles of other elements, but the nature of arsenic interactions with different biogeochemical cycles is still unknown. It is a subject that deserves much more research. Millions of people worldwide are exposed to a high risk of arsenic contamination, mainly through groundwater consumption and foodstuffs such as rice [46]. In other areas, it is due to the proximity of abandoned mining areas that lack soil recovery programs.

For the future development of a strategy for the management and recovery of the whole contaminated area, it is recommended:

- Identification of mining critical zone hazards. To locate the foci of contamination and the ways of transfer from the source.

- Study soil mineralogy and arsenic mobilization to prioritize areas for action.

- To avoid or decrease the main impacts of altered areas.

- Implement risk assessment study.

- To select a suitable management strategy for decision-making. When integrating phytostabilization techniques, prioritize plant species that do not transfer large amounts of heavy metals to their aerial part. When dealing with phytoextraction techniques, prioritize species with high rates of heavy metal transfer to their tissues.

- Study materials for the immobilization of PTE to recover contaminated soils and construct technosols [164].

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Author Contributions

Conceptualization, S.M.-L.; C.P.-S. and M.A.E-A; methodology, S.M.-L.; A.B.-G.; validation, S.M.-L.; writing-original draft preparation, S.M.-L.; A.B.-G.; M.A.E-A.; writing-review and editing, C.P.-S.; S.M.-L.; visualization and supervision, S.M.-L.; M.J.M.-S.; M.A.E-A.

Competing Interests

The authors have declared that no competing interests exist.

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