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Review

Arsenic Environmental Biogeochemistry

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Abstract

Arsenic represents a ubiquitous element in the environment, characterized by high mobility, complex chemical speciation and a strong sensitivity to redox conditions and biological activity. The present review provides an integrated synthesis of arsenic biogeochemical cycling across terrestrial, freshwater and marine ecosystems, emphasizing the central role of chemical speciation in controlling the arsenic levels, mobility and bioavailability. Natural processes regulating arsenic distribution are examined from mineralogical sources and soil–water interactions to biologically mediated transformations in aquatic and marine biotic compartments, highlighting the contrast between inorganic arsenic dominance in abiotic reservoirs and the prevalence of organoarsenicals in tissues of living organisms. The review further explores arsenic behaviour under natural environmental alterations and in extreme or unconventional ecosystems, where redox constraints, sulphide chemistry or intense fluid–sediment exchanges lead to deviations from the baseline speciation patterns. Against this framework, anthropogenic perturbations are discussed through several documented case studies, illustrating how industrial releases, the long-term effects of mining activities, agricultural practices and the use of synthetic arsenical compounds may change the arsenic pathways primarily by altering geochemical and biological controls rather than the generalized increase of the total arsenic content. Overall, the topics covered provide an integrated framework for interpreting arsenic dynamics across environmental systems, emphasizing the complex biogeochemical processes governing arsenic cycling.

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1. Introduction

Arsenic (As) represents one of the most fascinating elements in environmental chemistry due to its elevated mobility, complex chemical speciation, widespread natural occurrence, and involvement in highly dynamic biogeochemical cycles [1,2]. Unlike many other trace elements, arsenic exhibits a remarkably variable environmental behaviour, modulated by both geochemical, biological and climatic conditions, which determines its distribution in the terrestrial, aquatic, atmospheric and biotic compartments [1,3]. Arsenic is relatively abundant in the Earth's crust, with an estimated average concentration of 1.5–2.0 mg kg^{-1} dry weight (d.w.) and a marked spatial variability due to local geological factors [4]. It occurs in more than 700 mineralogical species, primarily associated with metal sulphides such as arsenopyrite, realgar, and orpiment, and is released into the environment through natural weathering, erosion, and volcanic activity [5]. These processes form the basis of the global arsenic cycle, which in more recent times has been substantially modified by the anthropogenic influence [1,2,5].

A distinctive feature of arsenic is represented by its ability to exist in multiple chemical forms, both inorganic and organic, which can coexist within the same environmental compartment [6,7]. Chemical speciation exerts a primary control on arsenic mobility, bioavailability, and toxicity, rendering this element particularly sensitive to variations in redox conditions, pH, biological activity,

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and organic matter dynamics. The terrestrial ecosystems, soils in particular, represent major reservoirs of arsenic [1]. Global soil concentrations typically range between 0.1 and 40 mg kg^{-1} but values may exceed these baseline concentrations by orders of magnitude in the proximity of mineral deposits or naturally enriched geological formations. Within soils, arsenic is involved in adsorption, release, and transformation processes mediated by mineral surfaces, organic matter, and microbial communities, directly influencing its transfer to groundwaters, plants and its entry into the terrestrial food webs [8].

Groundwater constitutes one of the most critical compartments of concern with respect to arsenic, due to both its geochemical sensitivity and its relevance to human exposure. Worldwide, millions of people are exposed to groundwater arsenic concentrations exceeding the guideline value of 10 μg L^{-1} established by the World Health Organization (WHO) for drinking water, with concentrations in some aquifer systems reaching hundreds or even thousands of μg L^{-1} as a consequence of natural mobilization processes [1,9]. Surface waters generally exhibit lower arsenic levels, most commonly ranging from below detection limits to about 50 μg L^{-1}, but their arsenic dynamics are closely controlled by exchanges with sediments and by biological activity [1,6].

In marine environments, arsenic is typically present at lower and more uniform concentrations than in continental systems, with average dissolved concentrations in ocean waters of approximately 1–3 μg L^{-1} [10]. Despite this apparent chemical stability, the marine arsenic cycle is strongly influenced by biological processes. Phytoplankton and other marine organisms play a central role in arsenic uptake, transformation, and trophic transfer, mediating the formation of organic arsenic compounds that commonly represent the most abundant chemical species in tissues of the living organisms [7,10]. In this context, arsenic concentrations in marine biota vary within an extremely wide range, from less than 1 μg g^{-1} d.w. up to several thousand μg g^{-1} d.w. in selected taxa, often associated with species-specific physiological traits or ecological strategies rather than environmental bioavailability [10,11].

The atmosphere represents a quantitatively minor but dynamically relevant compartment in the global arsenic cycle. Atmospheric arsenic occurs predominantly in form of particulate and contributes mainly to both regional and long-range transport, facilitating the redistribution of arsenic among terrestrial and aquatic environments. However, the atmosphere does not constitute a domain of biological transformation. In addition, its role in controlling arsenic speciation and bioavailability is indirect, acting primarily as a vector rather than as an active processing compartment [1].

Over the last centuries, human activities have significantly altered arsenic cycling on a global scale. Both the mining activities, industrial emissions, agricultural practices, urban wastewater discharge and the extensive land exploitation have increased arsenic fluxes and modified the physicochemical conditions that regulate arsenic mobility and transformation. Furthermore, global environmental changes have introduced further perturbations, since variations in redox regimes, hydrology and salinity significantly influence the behaviour of arsenic in different environmental compartments [1,12].

In light of these considerations, the present review aims to provide a critical and integrated synthesis of arsenic biogeochemical cycling in the environment. A central focus is placed on the role of chemical speciation in mediating arsenic mobility and bioavailability across terrestrial, freshwater, and marine systems. The review also identifies common mechanisms governing arsenic behaviour under both natural and anthropogenically influenced conditions. While arsenic cycling is examined across all major environmental compartments, marine systems receive special attention, as they involve a wider range of biogeochemical equilibria, trophic interactions, and redox-driven transformations, offering a clear perspective on the balance between physicochemical constraints and biological regulation. Arsenic biogeochemical interactions were further explored in uncommon and extreme environments to highlight how modifications of environmental conditions may alter arsenic mobility and speciation, and how these changes are reflected in species-specific bioaccumulation and biotransformation features in selected biological taxa. Overall, the present review aims to

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complement compartment-specific and contamination-focused perspectives by framing arsenic as a sensitive tracer of geochemical and biological interactions across environmental systems.

2. Arsenic-Bearing Minerals and Natural Sources

Arsenic occurs in the lithosphere mainly hosted in a wide range of mineral phases, reflecting its elevated affinity for sulphur and transition metals. More than 700 arsenic-containing minerals have been identified, and in over 200 of these, arsenic is present as a major structural component rather than as a trace substituent. As shown in Table 1, listing the most common and widespread arsenic-bearing minerals, the arsenic content varies over a very wide range, from about 15–25 wt.% in complex arsenates and sulfosalts (e.g., erythrite, mimetite, or proustite) to 100 wt.% in native arsenic and arsenic polymorphs [5]. These arsenic-bearing phases include both primary minerals, formed during magmatic and hydrothermal processes, and secondary minerals resulting from the weathering and alteration of arsenic-rich assemblages under low-temperature oxidative conditions.

Table 1. *List of common and widespread arsenic-bearing minerals, according to Mindat.org mineralogy database (Ralph* et al.*, 2025) [5]. For each mineral, chemical formula, crystal system, typical colour, arsenic content (wt.%), and Mohs hardness (HR) are reported. Secondary minerals formed during weathering and oxidation processes are indicated by the symbol †.*

Name	Formula	Crystal System	Colour	As wt.%	HR (Mohs)
Arsenolamprite	As	Orthorhombic	Grey-white	100.0%	2
Arsenolite†	As_2O_3	Isometric	White to bluish	75.7%	1½
Arsenopyrite	FeAsS	Monoclinic	Silver-white to steel-grey	46.0%	5½ - 6
Claudetite†	As_2O_3	Monoclinic	Colourless to white	75.7%	2½
Cobaltite	CoAsS	Orthorhombic	Silver-white to grey	45.1%	5½
Duranusite	As_4S	Orthorhombic	Grey-black	90.3%	2 - 2½
Enargite	Cu_3AsS_4	Orthorhombic	Grey-black	19.0%	3
Erythrite†	$Co_3(AsO_4)_2 \cdot 8H_2O$	Monoclinic	Pink to crimson	25.0%	1½ - 2½
Ferroskutterudite	$FeAs_3$	Isometric	Tin-white	80.1%	5½ - 6
Gersdorffite	NiAsS	Isometric	Grey to silver-white	45.2%	5½
Löllingite	$FeAs_2$	Orthorhombic	Steel-grey to silver-white	72.9%	5 - 5½
Mimetite	$Pb_5(AsO_4)_3Cl$	Hexagonal	Yellow to brown	15.1%	3½ - 4
Native arsenic	As	Trigonal	Tin-white to dark grey	100.0%	3½
Nickelskutterudite	$NiAs_3$	Isometric	Tin-white to silver-grey	79.3%	5½ - 6
Paradimorphite	As_4S_3	Orthorhombic	Orange-yellow	75.7%	1 - 2
Pararsenolamprite	(As,Sb)	Orthorhombic	Grey	100.0%	2 - 2½
Proustite	Ag_3AsS_3	Trigonal	Red	15.1%	2 - 2½
Realgar	As_4S_4	Monoclinic	Red to orange-red	70.0%	1½ - 2
Scorodite†	$Fe^{3+}AsO_4 \cdot 2H_2O$	Orthorhombic	Green to blue-green	32.5%	3½ - 4
Skutterudite	$CoAs_3$	Isometric	Tin-white to silver-grey	79.2%	5½ - 6

Among the primary arsenic-bearing minerals, arsenopyrite (FeAsS) is the most abundant and geochemically significant, constituting a large fraction of the arsenic present in ore bodies worldwide. With an arsenic content of approximately 46 wt.% (Table 1), arsenopyrite is commonly found in hydrothermal systems associated with gold, copper, lead, and zinc mineralization. Other important primary minerals include various kind of arsenides (with arsenic occurring in the −3 oxidation state) and sulfosalts, including löllingite ($FeAs_2$), skutterudite-group minerals ($CoAs_3$, $NiAs_3$, $FeAs_3$), enargite (Cu_3AsS_4), and cobaltite (CoAsS), characteristic of magmatic-hydrothermal and epithermal environments [3,5]. Pure arsenic phases (0 oxidation state), including native arsenic, arsenolamprite and pararsenolamprite, although less abundant, indicate that arsenic can occur as a major element under specific geological conditions. The elevated arsenic content and moderate hardness (HR) of many of these minerals (Table 1) influence their reactivity during weathering and arsenic release [3,5].

From a geochemical perspective, the mineral HR provides a first-order indication of resistance to mechanical breakdown and surface abrasion, which in turn influences the exposure of reactive surfaces during weathering processes [5]. Minerals characterized by low to moderate HR (commonly

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in the range 1–4 Mohs) are more readily fragmented and altered, promoting faster dissolution kinetics and enhancing the release of structurally bound arsenic into soils and groundwaters. On the contrary, harder phases (>5 Mohs) tend to weather more slowly, potentially delaying arsenic mobilization and favouring its persistence within solid reservoirs [3,5].

Oxidative dissolution of sulphide minerals, particularly arsenopyrite and enargite, represents a key natural process controlling arsenic release. During weathering, arsenic may be temporarily retained through adsorption onto newly formed iron oxides and hydroxides or incorporated into discrete secondary minerals [1,3]. Secondary arsenic minerals, such as scorodite ($FeAsO_4{\cdot}2H_2O$) and erythrite ($Co_3(AsO_4)_2{\cdot}8H_2O$), are common in the oxidation zones of arsenic-rich deposits and contain substantial arsenic contents (25–33 wt.% As; Table 1, †). Under specific redox and pH conditions, these phases may act as transient sinks for arsenic, while remaining potentially unstable under reducing or alkaline environments. In soils and sediments, arsenic is more frequently associated with poorly crystalline or amorphous phases rather than well-defined minerals, reflecting the predominance of surface complexation processes under typical oxic to mildly reducing conditions [1,5,8].

Natural arsenic fluxes from the lithosphere to surface environments are generally mediated by mineralogical composition, weathering intensity and physical redistribution processes. Chemical erosion of arsenic-rich minerals provides a continuous source of arsenic to soils, groundwater, and surface waters, with a release rate strongly dependent on mineral type and environmental conditions [3,8]. Physical erosion and sediment transport commonly redistribute arsenic-bearing particles from source ores to alluvial, lacustrine, and coastal environments, where arsenic may be further mobilized or immobilized [1]. In addition, volcanic and geothermal activity represents an additional natural source, contributing to the arsenic input through gas emissions, hydrothermal fluids, and ash deposition [9]. At the global scale, these processes establish background arsenic levels typically below 10 $\mu g\ L^{-1}$ in surface waters and around 0.1–10 $mg\ kg^{-1}$ in soils, although marked spatial heterogeneity is common [1,2,8].

3. Chemical Speciation and Environmental Reactivity of Arsenic

Arsenic occurs in the environment in various chemical forms, both inorganic and organic, characterized by different structures, stabilities, and distributions. Representative molecular structures of the main inorganic, methylated, and more complex organic species discussed in the present section are shown in Figure 1 [6,7,10].

Inorganic arsenic (iAs) occurs predominantly in the trivalent and pentavalent oxidation states, as arsenite (As(III)) and arsenate (As(V)). In aqueous systems, As(III) is mainly present as arsenious acid and its conjugate species (H_3AsO_3, $H_2AsO_3^-$), while As(V) occurs as arsenate oxyanions ($H_2AsO_4^-$, $HAsO_4^{2-}$), with relative abundances controlled primarily by redox conditions and pH. From a thermodynamic perspective, As(V) represents the more stable oxidation state of iAs. It therefore tends to dominate in abiotic matrices under typical oxic environmental conditions [1,6,7]. These inorganic forms constitute the primary precursors from which more complex arsenic species may be generated through physical and biological processes. A relevant fraction of iAs is associated with solid phases, including iron and manganese oxides and hydroxides, sulphide minerals, and mixed Fe–As–S assemblages. In these associations, arsenic may be adsorbed onto mineral surfaces, incorporated in the mineral structures, or present as surface complexes. The continuous exchange between dissolved inorganic species and solid-associated arsenicals results in a dynamic partitioning that strongly influences arsenic mobility and persistence in environmental matrices [13].

It is well known that iAs undergoes extensive biological transformation in natural systems, resulting in the formation of a range of methylated compounds. The most common methylated arsenic compounds are constituted by monomethylarsenicals (MMA) and dimethylarsenicals (DMA) groups, which are often detected in soils, waters, and biological samples [1,6,14]. These compounds are primarily produced through biological processes mediated by microorganisms and plants via enzymatic methylation pathways. On the contrary, abiotic contributions to methylation may arise

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from redox-driven transformations at mineral–water interfaces, particularly under strongly reducing or oxidizing conditions and in the presence of reactive organic matter or sulphide-rich environments [15].

In natural systems, biological arsenic methylation occurs through a sequence of redox-coupled transformations. These processes link the uptake of iAs to the formation of progressively more substituted organoarsenic species. In oxidizing environments, thermodynamically stable As(V), which is structurally analogous to phosphate, can be readily accumulated by microorganisms and plants via phosphate transport systems. However, only trivalent arsenicals represent a suitable substrate for enzymatic methylation. The initial intracellular conversion of As(V) to As(III) is therefore catalysed by arsenate reductases (ArsC) through thiol-dependent electron transfer systems, commonly involving glutaredoxin–glutathione (Grx/GSH) or thioredoxin (Trx) pathways [14,15]. Subsequently, methylation is mediated by S-adenosylmethionine (SAM) dependent arsenic methyltransferases (ArsM/AS3MT), which utilize SAM as methyl-group donor. In this pathway, As(III) is first converted to monomethylarsonic acid (MMA(V)), which can undergo reduction to the trivalent intermediate monomethyl-arsenite (MMA(III)) and further methyl transfer to produce dimethylarsinic acid (DMA(V)). Overall, arsenic methylation proceeds through alternating cycles of reduction and methyl transfer, with trivalent methylated intermediates acting as key substrates within the transformation sequence [14–16]. Therefore, reduced methylated intermediates such as MMA(III) and dimethyl-arsenite (DMA(III)), which are generally short-lived and difficult to detect, are thought to play an important role in the overall transformation pathway. Further methylation of DMA leads to trimethylated species, with trimethylarsine oxide (TMAO) representing a key metabolic endpoint of the conventional methylation sequence [15–18].

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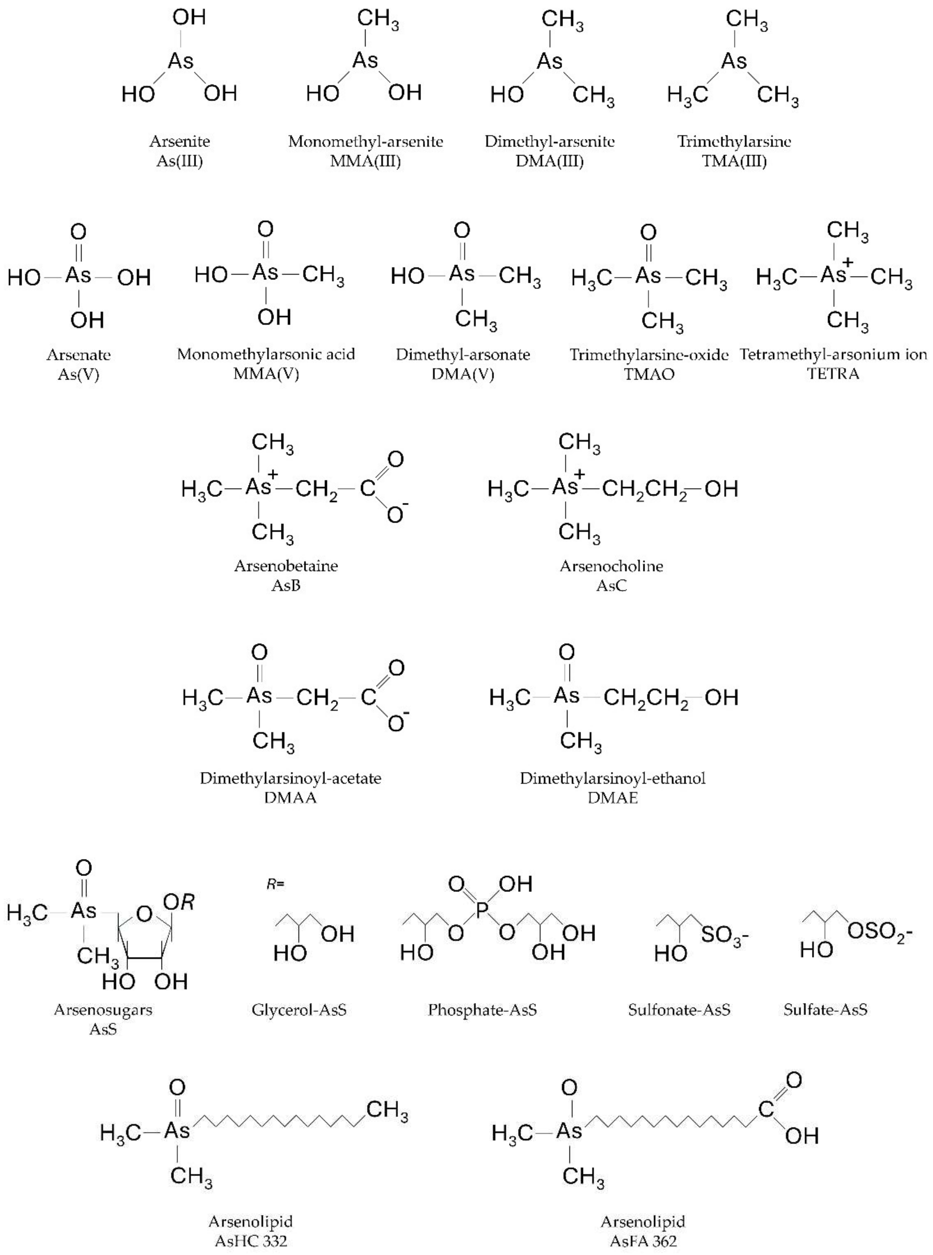

Figure 1. *Common inorganic and organic forms of arsenic in the environment and biota, according to relevant literature [7,10,15].*

Reduction of TMAO can generate volatile trimethylarsine (TMA(III)), while further methylation or structural rearrangement can lead to the formation of tetramethylarsonium (TETRA) or incorporation into more complex organoarsenic compounds. In aquatic systems, particularly those dominated by algal and microbial activity, TMA(III)/TMAO intermediates are further transformed into arsenobetaine (AsB), arsenocholine (AsC), arsenosugars (AsS) and arsenolipids, thereby redistributing methylated arsenic into more stable, biologically associated forms that predominate in the tissues of most of the marine organisms [10,15,19].

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These divergent transformation pathways provide the chemical basis for the predominance of complex organoarsenic species observed in aquatic and marine environments. AsB is the most widespread and abundant organoarsenic compound in tissues of marine organisms often accounting for almost the totality of the arsenic in the higher trophic levels, while AsC is more commonly detected in lower trophic organisms [7,10,11]. Primary producers and macroalgae play a central role in this context, acting as major sources of AsS, a diverse group of compounds that include glycerol-, phosphate-, sulfonate-, and sulphate-AsS [7,10]. These species are formed during biological uptake and intracellular processing of iAs and constitute key intermediates in the transfer of arsenic through aquatic food webs. In addition to AsS, more specialized organoarsenic metabolites such as dimethylarsinoyl-acetate (DMAA) and dimethylarsinoyl-ethanol (DMAE) have been identified in aquatic organisms, including brown algae and molluscs, where they are interpreted as products of further biochemical modification of methylated arsenic species [7,10].

In addition to these compounds, arsenic can also be incorporated into lipid-soluble organoarsenic species, collectively referred to as arsenolipids, including arsenic fatty acids (AsFA), arsenic hydrocarbons (AsHC) and arsenic phospholipids (AsPL). These compounds have been principally reported in algae and higher-trophic-level consumers and represent a distinct pool of biologically associated arsenic. Although typically occurring at lower concentrations than AsB or AsS, arsenolipids are of increasing interest due to their structural diversity and potential implications for arsenic bioaccumulation and trophic transfer [10].

A significant proportion of environmental arsenic is associated with particulate matter, including suspended particles, sediments, and biological material. Particulate-bound arsenic represents an important reservoir that can act as both a sink and a source of dissolved arsenic, depending on environmental conditions such as redox state, pH, and organic matter dynamics. Under strongly reducing conditions, arsenic may also occur in volatile form. Arsine (AsH_3) and methylated volatile arsines, including MMA(III), DMA(III) and TMA(III), can be produced through microbial activity or abiotic reactions. Although these species generally represent a minor fraction of total arsenic, they provide a pathway for arsenic transfer from soils and sediments to the atmosphere [15].

In specific environments, arsenic can form less common chemical species that reflect local geochemical conditions. Thioarsenates are characteristic of sulfidic systems, where arsenic interacts with reduced sulphur species, and are particularly relevant in anoxic sediments and geothermal environments. Additional unusual or polyarsenic species, such as As–As bonded clusters and polymeric arsenic sulphide complexes, have been reported in hydrothermal and highly mineralized settings [20,21].

Although a detailed discussion of arsenic toxicology lies beyond the scope of the present review, it is nonetheless important to acknowledge that the environmental and biological relevance of arsenic species is closely linked to their markedly different toxicological properties. In general, iAs forms are associated with the highest toxicity, with As(III) being the most reactive and potentially hazardous species, followed by As(V). Toxicity then tends to decrease with increasing molecular complexity, with simple methylated arsenicals such as MMA and DMA typically considered as moderately toxic, and more highly substituted species such as TMA(III), TMAO and TETRA exhibiting substantially lower biological reactivity. In contrast, complex organoarsenic compounds that dominate aquatic and marine food webs, including AsB, AsC and AsS, are generally considered to exhibit low toxicological relevance under typical exposure scenarios. Notably, AsB, which represents the major arsenic species in most of the marine organisms, has been shown to be rapidly excreted in humans largely unchanged following dietary intake, typically within 24-48h, indicating minimal metabolic transformation and biological interaction [10,15,17]. Although toxicological aspects are not further addressed in the present review, this broad hierarchy in arsenic species toxicity provides an essential contextual framework for the discussion that follows.

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4. Arsenic in Terrestrial Environments: Soil, Groundwater and Biogeochemical Controls

Terrestrial environments represent one of the major reservoirs and dynamic regulators of arsenic on the Earth surface. Within soils, groundwaters, surface waters, and terrestrial biota, arsenic distribution and mobility are governed by the interplay between mineralogical sources, chemical speciation, redox conditions, and biological processes. A synthesis of typical arsenic concentrations, dominant chemical forms, and key controlling processes across the main terrestrial environmental compartments is provided in Table 2 [1,22,23].

Table 2. *Summary of common arsenic concentrations, dominant speciation, and controlling processes in soils, waters, and terrestrial biota, according to relevant literature [1,22,23].*

Compartment	Typical As concentration	Dominant speciation	Key controlling processes
Soils	0.1 – 10 mg kg^{-1}	As(V) > As(III)	pH Adsorption on Fe/Mn oxides Phosphate competition
Enriched terrains	> 100 mg kg^{-1}	As(V) dominant As(III) locally significant	Mineralogical source control Weathering of As-bearing minerals Adsorption/desorption on Fe oxides Redox conditions
Groundwater	< 1 to > 1,000 μg L^{-1}	As(III) in reducing conditions	Reductive dissolution of Fe oxides Microbial reduction
Surface waters	< 1 to 50 μg L^{-1}	As(V) Particulate iAs	Sediment–water exchange Particulate transport
Vegetation	1 to 10 mg kg^{-1} (d.w.)	iAs	Uptake via phosphate transporters Sequestration
Hyperaccumulator plants	10,000 to 100,000 mg kg^{-1} (d.w.)	As(III) in leaf system	Rapid accumulation Reduction Vacuolar storage

Soils constitute a primary storage compartment for arsenic in terrestrial systems, with concentrations reflecting both geogenic background levels and localized enrichment associated with mineralized or volcanogenic settings [4,5,8,9]. Typical arsenic concentrations in uncontaminated soils range globally from approximately 0.1 to 10 mg kg^{-1} [4,8,22]. On the other hand, arsenic concentrations ranging from approximately 20 to 500 mg kg^{-1} have been reported in areas influenced by arsenic-rich lithologies or natural mineralization, including major alluvial basins, volcanic and geothermal regions, and mineralized terrains in Asia, the Americas and Europe [1,8,9,22,24].

The chemical speciation of arsenic in soils is closely linked to redox potential, pH, and the availability of reactive mineral surfaces. A substantial fraction of soil arsenic is associated with iron and manganese oxides and hydroxides, which represent the dominant sorbents for both As(V) and As(III) [1,6,8]. Adsorption processes are typically strong under acidic to neutral pH conditions and decrease at higher pH, where desorption, mobilization and leaching may occur [1,8]. Although As(V) is normally the predominant species in well-aerated soils, in the presence of localized reducing microenvironments, the proportion of As(III) can increase compared to background conditions, particularly in water-saturated soils or within organic-rich aggregates where oxygen availability is limited.

Competition with other anions, particularly phosphate and silicate, plays a critical role in controlling arsenic retention in soils. Due to its chemical similarity to phosphate, As(V) competes for sorption sites on mineral surfaces. Increases in phosphate availability, whether natural or anthropogenic, can therefore enhance arsenic mobility by displacing As(V) [8,13,25,26]. Soil organic

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matter further modulates arsenic behaviour through complexation, alteration of redox conditions, and indirect effects on microbial activity. Depending on its composition and degree of humification, organic matter can promote arsenic immobilization or facilitate its release into soil porewater [6,8,9,13]. Furthermore, soil microbial communities mediate redox transformations between As(V) and As(III), influencing arsenic mobility and bioavailability. Although biological methylation of arsenic can occur in soils, the diversity and abundance of methylated and complex organoarsenic species are generally lower than in aquatic systems, due to differences in microbial communities and environmental conditions [14,15].

Arsenic concentrations in groundwater exhibit wide variability, primarily controlled by geogenic factors [9]. In aquifers affected by arsenic-rich lithologies or natural mineralization, concentrations generally range between about 100 and 1,000 µg L^{-1}, with locally higher values reported in specific areas. Such conditions are widely documented in regions such as the Ganges-Brahmaputra-Meghna Basin, the Mekong Delta, northern Chile, and mineralized areas of China [1,9,12,24,27]. Occasionally in some aquifer systems, elevated arsenic levels result from the reductive dissolution of iron oxides and hydroxides that host adsorbed or coprecipitated arsenic, resulting in the release of the element into solution [1,9,12]. Under such reducing conditions, As(III) generally predominates the dissolved speciation, reflecting both thermodynamic stability and microbial reduction processes [15]. Arsenic in groundwater is strongly influenced by hydrological connectivity with soils and surface environments [9]. Vertical transport from soil horizons, lateral migration within aquifers, and exchange with river systems collectively contribute to the dynamics of arsenic mobility across terrestrial compartments [1,9]. In surface waters, arsenic concentrations are typically lower than in groundwater, often ranging from <1 to 50 µg L^{-1}. Distribution between dissolved and particulate phases is controlled by water chemistry, suspended sediment load, and interactions with bottom sediments, which may act as temporary sinks or secondary sources [6,9].

Terrestrial biota, and plants in particular, play an important role in arsenic cycling by mediating uptake, internal transformation, and transfer within food webs [8,14,23]. Plant uptake of arsenic is strongly influenced by its chemical speciation. As previously noted, As(V) is accumulated primarily via phosphate transporters while As(III) may be transported through aquaporin channels [8,23,28]. Once internalized, arsenic may undergo reduction, chelation, and compartmentalization, limiting its interference with essential metabolic processes [14,23,28,29]. In most terrestrial plants, arsenic speciation remains characterized by inorganic forms, with limited conversion to organic species relative to aquatic organisms [8,14]. Nevertheless, substantial interspecific variability exists in arsenic uptake efficiency and tolerance [23,28,29]. Of particular relevance are arsenic-hyperaccumulating plant species, which can concentrate arsenic to extraordinarily high levels without exhibiting phytotoxic effects [18,23]. The most widely studied example is *Pteris vittata*, a fern capable of accumulating arsenic in the aerial parts of the plant at concentrations typically ranging from approximately 1,000 to 5,000 mg kg^{-1} (d.w.) in naturally enriched soils, with reported values frequently reaching up to about 8,000 mg kg^{-1} in mineralized terrains. Related species such as *P. cretica* and *P. multifida* also display enhanced arsenic accumulation, although generally to a lesser extent [18,23,28].

Hyperaccumulation in these species has been associated with sequestration within vacuole compartments [23,28]. These mechanisms minimize arsenic interference with cellular metabolism and allow sustained growth under high-arsenic conditions. From an environmental perspective, arsenic-hyperaccumulating plants influence arsenic redistribution at the soil–plant interface and have received attention for their potential role in phytoremediation [18,23]. Arsenic accumulated by plants can be transferred to higher trophic levels, although terrestrial food webs typically exhibit lower diversity of organoarsenic compounds than aquatic systems. The predominance of iAs in plants markedly contrasts with the prevalence of complex organoarsenic species observed in marine ecosystems, highlighting fundamental differences in arsenic biogeochemistry between terrestrial and aquatic environments [8,10,11].

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5. Arsenic in Marine Environments: Abiotic Matrices, Bioaccumulation Patterns and Species-Specific Features

In marine environments, arsenic levels reflect the combined influence of geological background, large-scale biogeochemical cycling and local environmental conditions [1,19]. In open seawater, dissolved arsenic concentrations are relatively low and remarkably stable, typically between 1 and 3 $\mu g\ L^{-1}$, with As(V) being the most thermodynamically stable and abundant chemical species under oxic conditions [7,10,19]. Minor contributions of As(III) may occur in reducing microenvironments, stratified water columns or in proximity to sediments separated by intense organic matter degradation. In contrast, marine sediments exhibit a greater variability in total arsenic concentrations, with values from typically <1 up to a maximum of about 50 $\mu g\ g^{-1}$ (d.w.), depending on lithology, redox regime, sediment texture and the abundance of iron and manganese phases [6,24].

In coastal and estuarine ecosystems on continental shelves, arsenic in sediments is predominantly present as inorganic species, typically accounting for 60–90% of total arsenic, and is largely associated with Fe/Mn oxides and hydroxides or, under reducing conditions, incorporated into sulphide phases [6,24]. Similar associations between arsenic and iron- or manganese-containing phases are consistently observed in both temperate, tropical estuaries and mangrove wetlands, even in the absence of identifiable anthropogenic sources of arsenic. This indicates that relatively high arsenic concentrations in coastal sediments may primarily reflect natural sediment composition and redox-controlled partitioning processes, rather than direct contamination inputs [1,12]. However, the environmental relevance of sedimentary arsenic is closely linked to its potential mobility, since variations in redox conditions, salinity, hydrodynamics or pH can transiently increase the amount of labile arsenic species available to the water column and ultimately bioavailable to biota [6,13].

In estuarine and coastal mixing zones, the transition from fluvial to marine conditions promotes the rapid oxidation of dissolved Fe(II) and the formation of poorly crystalline Fe(III) oxides and hydroxides, which effectively capture dissolved arsenic through adsorption and coprecipitation. This flocculation process is enhanced by increasing salinity and pH and is particularly effective for As(V), while Mn oxides can further contribute by oxidizing the more mobile As(III) to As(V). Together, these processes act as an efficient natural sink for fluvial arsenic, limiting its direct transfer to open marine waters. However, within estuarine sediments, subsequent reductive dissolution of Fe and Mn oxides can remobilize arsenic previously processed during early diagenesis. In subsurface estuaries, similar reactions can give rise to so-called “iron curtains”, where Fe precipitation locally limits arsenic fluxes to the ocean [6,12,24].

Despite the predominance of iAs in abiotic matrices, marine organisms exhibit a markedly different and highly conserved pattern of arsenic accumulation. In most of the marine species, total arsenic concentrations range from about 5 to 200 $\mu g\ g^{-1}$ (d.w.) [11,30], with chemical speciation largely characterized by organoarsenic compounds [7,10,31]. Under baseline environmental conditions, iAs typically represents less than 1–5% of the total arsenic burden in tissues, while AsB constitutes the main arsenic species, often accounting for 60–95% of total arsenic. Secondary contributions of AsC, DMA, TMAO and TETRA are commonly observed, with relative proportions varying among taxa [10,32]. A synoptic overview of typical arsenic concentrations, dominant chemical forms and controlling processes across marine abiotic and biotic compartments is reported in Table 3 [1,6,7,10,11,30,31].

Table 3. *Summary of common arsenic concentrations range, arsenic speciation forms, and controlling processes in seawater, marine sediments and selected marine taxa, according to relevant literature [1,6,7,10,11,30,31].*

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Compartment / group	Typical As concentration	Common As forms	Key controlling processes
Seawater	1 to 3 µg L^{-1}	As(V)	Redox equilibrium Large-scale mixing
Marine sediments	<1 to 50 µg g^{-1} (d.w.)	iAs (60–90%)	Fe/Mn oxides binding Redox conditions
Macroalgae Phytoplankton	10 to 200 µg g^{-1} (d.w.)	AsS Arsenolipids DMAA, DMAE	Biological transformation Detoxification
Bivalves	10 to 40 µg g^{-1} (d.w.)	AsB dominant AsC as secondary specie DMAA, DMAE as minor metabolites	Dietary uptake Osmoregulation
Crustaceans	30 to 150 µg g^{-1} (d.w.)	AsB dominant AsC as secondary specie	Carapace formation Molting processes
Marine fish	2 to 35 µg g^{-1} (d.w.)	AsB dominant Arsenolipids in lipid-rich tissues	Trophic transfer Lipid partitioning
Selected polychaetes	50 to >1,000 µg g^{-1} (d.w.)	iAs, MMA, DMA, TMAO, TETRA Insoluble or mineralized As	Species-specific metabolism Tissue compartmentalization

This general pattern has been documented across a wide range of marine organisms, including invertebrates and fish, and appears to be largely independent of latitude as well as broad geographical setting [11,30]. Comparative surveys have shown that organisms collected from polar, temperate, and tropical environments often display overlapping arsenic concentrations and similar speciation profiles, whereas substantial differences are frequently observed among species inhabiting the same site [11,33,34]. These observations may suggest that species-specific physiological and metabolic traits override environmental gradients in determining arsenic accumulation and speciation in marine biota [31,32].

Bivalve molluscs provide one of the most informative examples of this behaviour. In species such as *Mytilus galloprovincialis*, *Crassostrea virginica* or *Meretrix meretrix*, total arsenic concentrations typically range between about 10 and 40 µg g^{-1} (d.w.), although seasonal variations may reach 30–50 µg g^{-1} (d.w.) or higher [11,30,33,35]. Long-term field studies have shown that arsenic in bivalves exhibits pronounced seasonal and inter-annual variability, often differing from patterns observed for other trace elements [30,33]. Unlike elements such as cadmium or zinc, whose tissue concentrations commonly decrease during gametogenesis due to biological dilution, arsenic frequently follows independent temporal patterns, showing weak or absent correlation with reproductive cycles [31,33].

A key environmental driver of this variability is represented by salinity gradients, particularly in estuarine and semi-enclosed basins [36,37]. Along estuarine–marine transitions, bivalves consistently exhibit increasing arsenic concentrations with increasing salinity, even in the absence of identifiable anthropogenic sources [33,36]. This pattern has been documented, for example, in the Adriatic Sea (Mediterranean, Italy), which is characterized by a pronounced north–south salinity gradient driven by the substantial freshwater input from the Po River in its northern sector. Along this gradient, *M. galloprovincialis* exhibits progressively higher arsenic concentrations moving from the low-salinity, river-influenced northern Adriatic toward the more saline central and southern basins [30,33]. Importantly, this spatial trend is not accompanied by similar increases in other trace elements, supporting the interpretation that arsenic bioaccumulation may reflect salinity-dependent physiological processes related to biological regulation [31,33]. The salinity dependence of arsenic accumulation has been linked to the predominance of AsB, which has been proposed to represent an adventitiously accumulated compound potentially contributing to osmotic regulation. According to this hypothesis, AsB is not actively synthesized by bivalves but is accumulated through the diet and retained because it contributes to osmotic balance under seawater salinity [36,38].

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Crustaceans often exhibit higher arsenic concentrations than bivalves, with values commonly ranging from 30 to 150 μg g^{-1} (d.w.), and occasionally exceeding this range [11,34]. This pattern has been repeatedly observed in temperate species such as the Mediterranean crab *Carcinus mediterraneus*, the mantis shrimp *Squilla mantis*, the Norway lobster *Nephrops norvegicus*, and penaeid shrimps like *Melicertus* (*Penaeus*) *kerathurus*, which typically show arsenic concentrations markedly higher than those measured in co-occurring bivalves. In contrast, tropical crustaceans such as *Callinectes sapidus*, *Farfantepenaeus notialis* and *Litopenaeus schmitti* generally display lower arsenic levels, often below 30 μg g^{-1} (d.w.), despite inhabiting environments with comparable environmental arsenic levels [11,34,39]. Chemical speciation in crustaceans is largely dominated by AsB, frequently accounting for more than 80–90% of total arsenic, although DMA, TETRA and AsC may represent variable secondary contributions in selected taxa (Table 3) [7,10,11,31]. As observed for other marine organisms, these interspecific and latitudinal differences cannot be readily explained by environmental exposure alone. Worthy to note, similar temperature gradients appear to produce no comparable effects on arsenic concentrations in marine fish tissues or bivalve molluscs, suggesting that temperature per se is unlikely to be the determining factor in arsenic accumulation in crustaceans [11,34].

An alternative and intriguing explanation may involve crustacean-specific physiological and structural features, particularly those related to the formation, mineralization and periodic turnover of the chitinous carapace. Experimental and comparative studies have shown that temperature-dependent differences in cuticle permeability, composition and moulting dynamics can significantly influence the accumulation and regulation of several trace elements in crustaceans, including zinc, copper, cadmium and cobalt [39–41]. On this basis, a similar mechanism may be hypothesized for arsenic. The exoskeleton represents a major interface for ion exchange and trace element incorporation, and arsenic, predominantly accumulated as AsB, may be temporarily or partially associated with carapace components or with tissues involved in moulting processes. Differences in moulting frequency, cuticle composition, and metabolic regulation of osmolytes between temperate and tropical crustaceans could therefore contribute to the higher arsenic burdens observed in temperate species [40,41]. While this hypothesis remains to be fully explored, it is consistent with the recurrent observation that arsenic exhibits accumulation patterns distinct from those of most trace elements, and enrichment in crustaceans may reflect the influence of intrinsic biological traits in regulating arsenic accumulation [11,34,39].

In marine fish, arsenic concentrations in muscle tissues are generally lower than those observed in many invertebrates, typically ranging from about 2 to 35 μg g^{-1} (d.w.), although higher values may occur in specific species or tissues. Studies on pelagic and demersal fish such as *Gadus morhua*, *Merluccius merluccius*, *Scomber scombrus*, *Clupea harengus* and *Pleuronectes platessa* have consistently shown that arsenic concentrations in muscle are relatively homogeneous across taxa and habitats, despite differences in diet and trophic position [10,34,39]. By contrast, internal organs involved in metabolism and detoxification, particularly the liver and gastrointestinal tissues, may contain substantially higher arsenic levels, in some cases exceeding muscle concentrations by one order of magnitude, reflecting tissue-specific partitioning rather than enhanced whole-body accumulation [10,34]. Chemical speciation in fish tissues is largely dominated by AsB, which generally accounts for 85–95% or more of total arsenic in muscle, while iAs or methylated arsenicals typically represents only minor fractions. Simple methylated species such as DMA may occur preferentially in liver and bile, indicating active metabolic processing without resulting in progressive concentration increases along trophic levels [10,34,39]. As a consequence, arsenic concentrations in marine fish do not display a biomagnification pattern, and species occupying different trophic levels often exhibit overlapping concentration ranges (Table 3) [10,34].

While the general AsB-dominated pattern characterizes most of the marine organisms (Table 3), selected taxa exhibit markedly different arsenic accumulation and speciation profiles, reflecting specialized and species-specific metabolic strategies rather than deviations from biological control [10,31,32]. A clear example is represented by the sabellid polychaete *Sabella spallanzanii*, a sedentary

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tube-dwelling worm that lives permanently enclosed within a self-constructed protective tube and exposes to the surrounding water column only its branchial crown for filter-feeding and respiration activities [32,42]. In this species, arsenic accumulates to extraordinarily high concentrations in the branchial crowns, frequently exceeding 1,000 μg g^{-1} (d.w.), and is almost entirely present as DMA, which typically accounts for 80–95% of total arsenic, while AsB represents only a minor fraction [32,42–44].

Following stress-induced autotomy, *S. spallanzanii* is able to rapidly regenerate branchial tissues and re-accumulate arsenic to restore baseline concentrations of approximately 1,000 μg g^{-1} (d.w.), even when ambient arsenic levels in the surrounding water column remain within typical marine background values (about 1 μg L^{-1}). Experimental observations further show that both tissue growth and arsenic re-accumulation proceed more rapidly under natural field conditions than under laboratory housing, probably reflecting differences in nutrient and trace-element availability [42]. In addition, controlled exposure experiments provide mechanistic insight into the metabolic basis of this behaviour. When *S. spallanzanii* is exposed to iAs, bioaccumulation of DMA was observed in the branchial crowns of the organisms, suggesting the involvement of a rapid methylation pathway. Direct exposure to DMA results in its preferential accumulation without any transformation, while exposure to more complex organoarsenicals such as AsB and TETRA leads to their active degradation and conversion to DMA [43]. Worthy to note, the biological breakdown of highly stable organoarsenic compounds represents one of the first experimental demonstrations of such processes occurring in a marine invertebrate under environmentally realistic conditions. Such observations suggest that *S. spallanzanii* may possess metabolic pathways enabling both iAs methylation and the degradation of organoarsenicals, supporting a biological role of DMA in the branchial crown [42,44]. The branchial appendages, which are the only tissues exposed outside the protective tube and accessible to predators, have been shown to be unpalatable for benthic consumers; accordingly, the pronounced accumulation of DMA in these structures has been associated with a biologically mediated antipredatory strategy [42–44].

The unusual arsenic accumulation and speciation pattern documented in *S. spallanzanii* is also observed in other polychaetes inhabiting coastal and shelf environments, although expressed through species-specific metabolic strategies and degrees of modulation [32,45]. For example, the cirratulid polychaete *Aphelochaeta* (*Tharyx*) *marioni* has been reported to accumulate exceptionally high total arsenic concentrations, approaching 1,000 μg g^{-1} (d.w.) at the whole-body scale and reaching up to about 6,000 μg g^{-1} (d.w.) in highly exposed tissues such as the palps [46]. While chemical speciation data are not available for this species, the occurrence of such extraordinarily elevated arsenic levels represents a clear similarity with *S. spallanzanii*, indicating a remarkable capacity for arsenic enrichment in specialized appendages. In contrast, deposit-feeding polychaetes such as *Arenicola marina*, *Hediste* (*Nereis*) *diversicolor* and *Neanthes* (*Nereis*) *virens* are characterized by a relatively lower total arsenic concentrations under natural conditions, typically in the range of about 10–50 μg g^{-1} (d.w.) [32,47,48]. However, these polychaetes exhibit unusually high proportions of iAs or methylated arsenic species, as well as MMA, DMA and TETRA. In addition, *H. diversicolor* and *N. virens*, exhibit the ability to actively methylate iAs leading to the formation of TETRA [32,47,48] (Table 3), thus supporting previous hypotheses regarding possible biological roles of selected arsenic species in polychaetes [32].

Organoarsenic compounds such as DMAA, DMAE, arsenosugars (AsS) and arsenolipids are closely associated with trophic transfer within marine food webs, originating from primary producers and organic matter and contributing to arsenic accumulation patterns in selected marine organisms depending on species-specific metabolic processing [10,49]. These compounds are particularly abundant in macroalgae, microalgae and planktonic organisms, where arsenic is actively transformed from inorganic forms into complex organic molecules through cellular metabolic processes [6,49]. In many marine algae, including brown macroalgae such as *Laminaria digitata* and *Fucus vesiculosus*, AsS constitute the dominant arsenic species, often accounting for more than 80–90% of total arsenic, with concentrations reaching about 50–200 μg g^{-1} (d.w.) [10,49]. These

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compounds are readily transferred to herbivorous and detritivores invertebrates, where they are often partially transformed into simpler methylated arsenicals through metabolic processing [10,31,32]. For example, bivalves such as *M. galloprovincialis* and *Cerastoderma edule* typically contain low but detectable levels of DMAA and DMAE (generally <1–5 μg g^{-1} d.w.), indicating metabolic processing of dietary AsS following trophic transfer (Table 3) [10,49].

Arsenolipids, including AsHC and AsFA, have been reported mainly in marine fish where they form a chemically distinct, lipid-associated arsenic pool that can reach concentrations of approximately 1–20 μg g^{-1} (d.w.) in lipid-rich tissues of species such as *Scomber scombrus*, *Clupea harengus* and *Salmo salar* [10,49,50]. These compounds are generally derived from planktonic primary producers and are transferred through marine food webs, reflecting their hydrophobic character and limited metabolic processing in higher trophic levels [49,51]. Worthy to note, although these compounds are transferred through marine food webs largely unmodified, no evidence of biomagnification has been reported for arsenolipids or other complex organoarsenic species. In this context, it is therefore plausible to hypothesize that organoarsenic compounds may be subject to tissue-level regulation and turnover at multiple trophic levels, governed by species-specific metabolic traits and physiological constraints rather than by passive accumulation processes [10,49–51]. Among the arsenolipids identified to date, those containing a dimethylarsinoyl group, such as 1-dimethylarsinoylpentadecane (AsHC 332) and the dimethylarsinoylhexadecanoic acid (AsFA 362), reported as representative examples in Figure 1, are among the most common and widely documented forms, together with structurally related homologues differing in chain length and degree of unsaturation [49,51].

Overall, the evidence discussed in the present section indicates that arsenic distribution and speciation in marine environments are controlled by natural geochemical settings, trophic interactions and species-specific metabolic traits [10,31,39]. The predominance of AsB in most of the marine organisms, together with the occurrence of distinct arsenic speciation strategies in selected polychaetes and the trophic transfer of complex organoarsenic compounds, highlights that arsenic biogeochemistry in marine systems is strongly mediated by biological processes rather than simply reflecting abiotic availability. This intrinsic biological control results in a wide natural variability of arsenic concentrations and chemical forms, which provides the essential baseline against which any perturbation of arsenic cycling in marine environments must be interpreted. In this respect, assessments of arsenic dynamics in marine systems require explicit consideration of biological context and chemical forms in addition to total concentrations [10,31,49].

6. Arsenic in Perturbed or Extreme Environments

In marine environments, arsenic distribution and chemical speciation reflect a dynamic balance between environmental forcing and biological regulation [6,10,31]. Growing evidence indicates that changes in key environmental conditions, as well as pH, redox state, temperature, and water-column stratification, can significantly modulate arsenic behaviour. These effects may occur even in the absence of changes in external arsenic inputs. [20,21,43,52]. Such drivers may act both directly, by altering arsenic speciation and mobility in seawater and sediments, and indirectly, by influencing organism physiology, metabolic rates, and detoxification pathways. As a result, their effects are often subtle and primarily expressed through changes in chemical forms and tissue distribution rather than through uniform increases in concentration levels [7,10,31,43,52].

To date, direct field evidence documenting systematic shifts in levels and arsenic speciation in tissues of marine organisms along natural gradients of pH, oxygen availability or water-column stratification is largely lacking, representing a knowledge gap to be further investigated. Controlled laboratory experiments, nevertheless, indicate that arsenic speciation in marine organisms is sensitive to specific environmental drivers that interfere with intracellular transformation pathways. In cultures of marine diatoms (*Asteroplanus karianus*, *Thalassionema nitzschioides*, *Nitzschia longissima*, *Skeletonema* spp., *Ditylum brightwellii* and *Chaetoceros didymus*), temperature departures from physiological optima induced marked shifts in arsenic speciation, including altered As(V)-to-As(III)

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conversion rates and a decline in arsenic methylation efficiency. Under thermal stress conditions, the contribution of methylated species typically decreased by about 40–70% and was accompanied by reduced growth and cellular performance [53].

At the same time, experimental simulations of ocean acidification in shallow marine systems demonstrated that environmentally realistic pH decreases (moderated acidification, pH=7.5, pCO2 about 2500 ppm; elevated acidification, pH=7.0, pCO2 about 5000 ppm) can significantly alter iAs speciation and mobility, promoting the release of dissolved iAs from sediments and favouring the relative persistence of As(III) over As(V). Under progressively lower pH conditions, both total dissolved iAs concentrations and the As(III) fraction increased, while the As(V)/As(III) ratio declined, highlighting pH-driven geochemical controls on arsenic speciation and bioavailability in coastal waters [54]. Along simplified marine food chains controlled arsenic exposure experiments involving the flagellated microalga *Diacronema lutheri* and the blue mussel *Mytilus edulis* further demonstrated that tissue-level arsenic speciation is metabolically regulated rather than passively inherited from the exposure source. In blue mussels, arsenic speciation patterns diverged markedly from those of the microalgal diet and evolved over time, reflecting strong organism-specific metabolic regulation [55]. On the other hand, these experimental findings suggest that while arsenic speciation is tightly controlled through both geochemical and biological mechanisms under baseline marine conditions, this regulatory balance may become increasingly vulnerable when key environmental parameters, such as pH, redox conditions, or exposure intensity, depart from the physiological ranges [52–55].

A similar acidification-driven modification of arsenic speciation has also been reported for *S. spallanzanii* in a natural CO_2-vent system in Ischia (Gulf of Naples, Italy), where organisms have been exposed in situ to reduced pH and elevated pCO_2 conditions (pH 7.5-7.8, pCO2 400-1000 µatm, with local variability). In this context, *S. spallanzanii* exhibited the reappearance of iAs together with altered proportions of methylated species in the branchial tissues [43]. As mentioned above, DMA in the branchial crown of *S. spallanzanii* has been associated with a chemical deterrence against predation; therefore, the shift in arsenic speciation observed under naturally acidified conditions is more consistent with a disruption of function-oriented methylation processes, leading to a depletion of this biological defence role. Given that *S. spallanzanii* does not naturally inhabit persistently acidified environments, these changes may be interpreted as a stress-induced disruption of physiological regulation rather than an adaptive response [43].

Such speciation shifts were accompanied by indications of increased energetic costs associated with the maintenance of arsenic processing pathways, suggesting that acidification influences arsenic dynamics not only through changes in chemical equilibria and uptake competition, but also by constraining metabolic efficiency and intracellular transformation capacity. Under reduced pH conditions, the ability of organisms to finely regulate internal arsenic cycling may therefore be compromised, rendering arsenic speciation more susceptible to modulation by additional environmental drivers acting concurrently in natural systems [43].

Marine environments characterized by extreme physicochemical conditions represent natural laboratories in which the limits of biological control over arsenic bioaccumulation and speciation can be explored [20,21,52,56]. Extreme environments expose organisms to persistent and often simultaneous stressors that approach or exceed physiological tolerance thresholds. Under these conditions, arsenic biogeochemistry frequently departs from common patterns, giving rise to accumulation levels, chemical forms and tissue distributions that cannot be fully explained by classical models developed for coastal and shelf ecosystems [10,20,52,56].

Among extreme marine environments, deep-sea hydrothermal vents provide the most emblematic examples of uncommon arsenic behaviour. These systems are characterized by steep gradients in temperature, redox potential and chemical composition, with vent fluids enriched in reduced sulphur species, transition metals and metalloids, including arsenic [20,21,52,56]. Although dissolved arsenic concentrations in vent fluids and surrounding seawater may vary widely among vent fields, reported values typically range from about 5 to 200 µg L^{-1} in vent effluents and immediately adjacent waters, thus exceeding by one to two orders of magnitude the relatively

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uniform concentrations of approximately 1–3 μg L^{-1} typical of the open ocean. Under these conditions, resident fauna experience chronic exposure to elevated and chemically variable arsenic availability, coupled with extreme gradients in temperature and redox state [10,19,21,56].

The biological communities inhabiting hydrothermal vents are taxonomically distinct from those of shallow-water marine systems and are dominated by a limited number of highly specialized taxa, including polychaetes and bivalves hosting chemosynthetic symbionts, vent-associated crustaceans and fishes [56–58]. Data compiled from multiple vent sites across the Pacific and Atlantic oceans indicate that arsenic concentrations in vent-associated fauna span several orders of magnitude, but follow coherent, group-specific patterns. Despite the markedly elevated arsenic availability characterizing hydrothermal vent fluids and surrounding mixing zones, not all vent-associated invertebrates exhibit proportionally enhanced arsenic accumulation. In particular, bivalves such as bathymodiolins (*Bathymodiolus* spp.) and vesicomyids (*Calyptogena* spp., *Archivesica* spp.), as well as vent-associated crustaceans including alvinocaridid shrimps (*Alvinocaris* spp., *Rimicaris* spp.) and bythograeid crabs (*Bythograea* spp.), generally display arsenic concentrations comparable to those reported for related taxa inhabiting temperate or tropical coastal environments [56–61]. For instance, data from multiple hydrothermal vent systems worldwide suggest that arsenic concentrations in selected bivalves and crustaceans show considerable site- and tissue-specific variability but nonetheless remain relatively constrained, with levels often below 30 μg g^{-1} (d.w.) and only sporadically approaching about 50 μg g^{-1} in specific tissues or localities [56].

Selective hydrothermal vent endemic polychaetes represent a clear departure from the common arsenic accumulation patterns observed in most vent invertebrates. For instance, species belonging to the genus *Alvinella*, including *A. pompejana* and *A. caudata*, exhibit some of the most extreme arsenic accumulation and speciation patterns reported from hydrothermal vent ecosystems. Despite *A. pompejana* and *A. caudata* occupying different zones along vent chimneys and thus experiencing potentially distinct fluxes from the vent, both species exhibit comparably elevated arsenic concentrations, generally ranging from about 400 to up to 1,500 μg g^{-1} (d.w.), with the highest values consistently observed in branchial appendages directly exposed to vent effluents. In both species, arsenic was mainly present in a weakly insoluble form, while chemical speciation revealed a major contribution of methylated arsenicals, including DMA(V) and, to a lower extent, MMA(V) and TMAO [56]. Worthy to note, the vestimifera *Riftia pachyptila* shows a chemical speciation of arsenic very similar to that of the alvinellids, with high and predominant rates of insoluble species and DMA, although it never exhibits total arsenic concentrations exceeding 10 μg g^{-1} (d.w.) in its tissues [56]. A recent study has highlighted a further unusual arsenic related feature in *Paralvinella hessleri* [58]. This species is able to accumulate arsenic as mineral particles, including orpiment (As_2S_3), associated with exposed tissues such as the branchial appendages and chaetal structures. Concentrations of arsenic in these tissues can reach or exceed 1,000 μg g^{-1} (d.w.), with a substantial fraction occurring in insoluble, particulate form. This result is partly similar to what was previously observed for alvinellids, which share extremely high concentrations in specific tissues and are able to accumulate insoluble forms of arsenic, although the mineral composition of such deposits has not been investigated in *A. pompejana* and *A. caudata* [56,58]. Overall, hydrothermal vents illustrate how extreme physicochemical forcing can weaken the link between environmental arsenic availability and biological accumulation, while enabling highly specialized arsenic bioaccumulation and biotransformation strategies in selected vent-endemic polychaetes.

Beyond hydrothermal vents, other marine systems characterized by extreme or anomalous physicochemical conditions also show marked departures from baseline arsenic cycling. Strongly sulfidic environments provide especially clear examples. The Black Sea, the world’s largest permanently anoxic marine basin, is characterized by a stable euxinic deep layer below approximately 100–150 m, where dissolved sulphide is persistently present [62]. In this system, dissolved iAs concentrations remain relatively uniform throughout the water column, typically in the range of about 2–5 μg L^{-1}, while arsenic speciation changes sharply across the redox transition. Across the oxic–anoxic interface, arsenic shifts from predominantly oxidized forms to reduced

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species, with As(III) becoming dominant and sulphur-associated arsenic species becoming progressively more abundant relative to other arsenic forms as sulphide concentrations increase [63]. Similar patterns have been documented in other strongly stratified marine systems, such as the Baltic Sea, where anthropogenic inputs and redox-driven diagenetic processes exert first-order control on arsenic partitioning, mobility and chemical form, leading to pronounced shifts in chemical form along redox gradients, even where dissolved concentrations vary only moderately [64]. In strongly redox-stratified and sulfidic basins, such physicochemical gradients reorganize arsenic speciation at the scale of entire water columns, promoting reduced arsenic species and sulphur-associated forms under euxinic conditions [62,63].

A further emblematic case is provided by the Cariaco Basin (Venezuela), a permanently stratified marine system characterized by persistent anoxia below approximately 250 m and a sharply defined redoxcline separating oxic surface waters from sulfidic deep layers [65,66]. In this basin, intense organic-matter fluxes associated with seasonal upwelling sustain high microbial respiration rates and rapid oxidant consumption at the redoxcline, maintaining steep and long-lived chemical gradients within the water column [66]. Under these conditions, arsenic transformations are closely related to sulphur and iron cycling, with strongly reducing and sulphide-rich environments favouring the stabilization of reduced and sulphur-associated arsenic species [65–68].

Modification of the arsenic behaviour is even more pronounced in hypersaline and sulfidic coastal systems, including restricted lagoons and saline basins in arid regions [1,6,21]. Hypersaline lagoons of the Atacama Desert (Chile) and saline lakes of the Andean Altiplano (Northern Chile, southwestern Bolivia, and northwestern Argentina) exhibit extreme arsenic enrichment in waters, with dissolved arsenic concentrations typically ranging from about 100 to 1000 μg L^{-1} and locally exceeding this range in highly evaporative settings [69]. In these environments, arsenic speciation is typically dominated by inorganic forms, including As(V) and reduced sulphur-bearing species, while biogenic methylated arsenic is often absent or represents only a minor fraction [1,70,71]. Benthic microbial mats and invertebrates inhabiting these systems may accumulate arsenic to elevated levels, but the retained chemical forms differ markedly from those typical of oxygenated marine environments, reflecting the dominant role of sulphide chemistry, extreme salinity, and redox constraints rather than trophic transfer or classical marine biogeochemical pathways [6,20,70].

Beyond baseline coastal and open-ocean settings, a number of marine environments characterized by fluid escape and localized reducing conditions display arsenic behaviour that departs from common marine patterns [1,6,63]. These include marine pockmark fields, natural seepage areas and deep-sea methane hydrate fields, which are linked by episodic or sustained fluid migration from sediments to the overlying water column. Despite major differences in spatial extent, intensity and biological structure, these systems share geochemical conditions that promote arsenic mobilization and drive pronounced shifts in chemical speciation, again largely independent of sustained arsenic inputs from the overlying water column [72–74].

Marine pockmark fields, widely documented on continental shelves and slopes of the North Sea, Mediterranean Sea and NW Atlantic margins, are typically associated with the episodic release of methane-rich and reduced fluids [72]. In these settings, arsenic mobilization follows the same redox-controlled pathways, leading to elevated porewater concentrations and dominance of reduced inorganic species [74]. While quantitative data on arsenic accumulation in benthic fauna from pockmark fields remain limited, the geochemical evidence indicates enhanced local bioavailability driven by redox-controlled release rather than by sustained external inputs [75]. As a result, pockmarks function primarily as geochemical hotspots of arsenic remobilization, with biological effects likely restricted to localized benthic communities [72,74,75].

More persistent arsenic perturbations are observed at marine natural seepage areas, including cold seeps and diffuse hydrocarbon or methane-rich fluid escape zones on continental margins such as those of the Gulf of Mexico, eastern Mediterranean and Pacific margins [72–74,76]. These environments are characterized by long-lived reducing conditions, elevated sulphide production associated with anaerobic methane oxidation, and well-developed chemosynthetic communities

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[70,73,76,77]. In seep sediments and bottom waters, arsenic frequently occurs in reduced forms and may be associated with sulphur-bearing species, reflecting strong coupling between arsenic cycling, sulphur metabolism and microbial activity [20,21,70,71,73,74,76]. At methane-dominated cold seep systems, similar redox-driven processes control arsenic mobilization and redistribution at the sediment–water interface [78]. Geochemical surveys show that, while bulk sediment arsenic concentrations may not differ markedly from adjacent non-seep deep-sea settings, arsenic speciation departs substantially from open-ocean baselines, with a clear dominance of reduced inorganic forms and sulphur-bound species in porewaters and reactive sediment fractions [73,76,78]. Reductive dissolution of Fe oxides and hydroxides and the subsequent formation of authigenic sulphide minerals favour both the release of arsenic into porewaters and its re-sequestration as sulphide-associated phases, including incorporation into pyrite under sustained seepage conditions [79]. As a result, arsenic availability is primarily dictated by sediment–water redox chemistry and sulphur cycling rather than by input from the overlying water column [78,79].

Comparable geochemical patterns have been documented across geographically distinct cold seep provinces, including the South China Sea and other methane-rich continental margin settings, where arsenic occurs predominantly as As(III) and thioarsenate species stabilized under sulfidic conditions [76,78]. Overall, cold seeps represent environments in which methane-driven microbial processes indirectly regulate arsenic biogeochemistry by reshaping sedimentary redox structure and sulphur availability, thereby controlling arsenic speciation, mobility, and sequestration pathways in abiotically dominated compartments [73,76,79].

Deep-sea methane hydrate provinces represent a further class of unconventional environments in which arsenic behaviour is indirectly regulated by hydrate stability and sedimentary redox dynamics. Widely documented along continental margins, these systems are characterized by pronounced vertical redox gradients across the sulphate–methane transition zone, which strongly influence arsenic mobilization and chemical speciation. [74,80,81]. Although direct observations of arsenic cycling in hydrate-bearing settings remain limited, available geochemical evidence consistently indicates a predominance of reduced inorganic forms, including As(III), and an overall increase in arsenic lability under conditions of intensified methane fluxes or hydrate destabilization [71,74,82]. In this context, methane clathrate fields can be regarded as latent arsenic sources, in which variations in physical forcing, such as pressure–temperature perturbations or changes in methane supply, translate into shifts in arsenic mobility and chemical form, even in the absence of direct biological mediation.

On the other hand, these fluid-escape-related environments extend the concept of uncommon arsenic cycling beyond classical extreme systems. They demonstrate that modifications of sedimentary redox structure and sediment–water exchange alone are sufficient to alter arsenic speciation even in absence of modification of arsenic total contents and to enhance arsenic mobility under methane-dominated geochemical regimes [71,74,80–82].

7. Anthropogenic Perturbation of Arsenic Mobility, Speciation and Bioavailability

Human activities can influence the environmental arsenic cycle both by directly increasing concentration levels and by altering the physicochemical and biological mechanisms that regulate its mobility, chemical speciation, and bioavailability [1,31,52]. In many polluted systems, anthropogenic perturbations act by destabilizing naturally regulated arsenic chemical species, shifting redox conditions, modifying sorption equilibria, and redistributing legacy arsenic associated with historical mining and industrial activities, particularly in long-impacted coastal and shelf regions such as the Mediterranean Sea [30,64]. In this context, a series of well-documented case studies is examined to reconstruct the links between anthropogenic forcing, environmental modification and the resulting biogeochemical response of arsenic across marine and terrestrial systems [30,52].

A paradigmatic example of acute anthropogenic perturbation is provided by the accidental arsenic release in Cienfuegos Bay (southern Cuba) in December 2001 [31]. The event involved the

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discharge of approximately 3.7 tonnes of arsenic, predominantly as As(V) oxides, from a nitro-fertilizer plant located within the urban area of Cienfuegos. Within days to weeks, this single-point release altered arsenic levels and speciation across multiple environmental compartments, including seawater, sediments and marine biota. Total arsenic concentrations in fish muscle tissues collected fifteen days after the event reached exceptionally high values of about 500 µg g^{-1} (d.w.) in species such as *Caranx latus* and *Lutjanus synagris* sampled at the most impacted sites, values therefore an order of magnitude higher than those of reference organisms [31]. Most notably, chemical speciation analysis revealed a near-complete dominance of iAs in exposed fish, representing about 97–99% of total arsenic in muscle tissues, in sharp contrast to the AsB predominance profiles (>85–90%) observed in fish from reference sites and generally considered common for marine organisms. In algae and crustaceans collected from the same bay, total arsenic concentrations remained within typical background ranges (approximately 5–25 µg g^{-1} d.w.), and arsenic occurred predominantly as organic forms, indicating that the impact was highly species- and habitat-specific. This episode illustrates how acute anthropogenic inputs can temporarily overwhelm biological regulation of arsenic speciation [31].

Historical mining and metallurgical activities represent well-documented examples of chronic anthropogenic perturbations, in which arsenic mobility and chemical speciation are modified over decades to centuries without discrete release events. In these systems, prolonged exposure of arsenic-bearing sulphides, mine wastes, and tailings progressively alters sediment geochemistry through redox-driven processes that regulate arsenic partitioning and availability [30,52,64]. In the Andean mining districts of northern Chile (Antofagasta–Atacama), more than a century of copper, gold, and polymetallic mining has resulted in extensive exposure of arsenic-bearing sulphides. Oxidative weathering and long-term storage of poorly contained mine wastes have generated sustained arsenic release to soils, river sediments, and alluvial deposits [83]. Mine tailings and contaminated sediments typically contain total arsenic concentrations of approximately 200–1,500 mg kg^{-1} (d.w.), with arsenic occurring predominantly as As(V) adsorbed to iron oxides and hydroxides under oxic conditions [83,84]. Episodic flooding, burial, or hydrological confinement may locally induce reducing conditions, promoting partial remobilization of arsenic as As(III) through reductive dissolution of iron phases [52,64].

In southwest China, particularly the Guizhou and Yunnan mining provinces, long-term exploitation of gold, antimony, and base-metal deposits has produced extensive arsenic-rich tailings and mine-affected sediments [85]. Reported solid-phase arsenic concentrations commonly range between 100 and 1,000 mg kg^{-1}, with arsenic largely associated with amorphous and poorly crystalline iron oxides and hydroxides under oxic conditions [84,85]; by contrast, hydrological confinement and reducing conditions promote the reductive dissolution of iron phases and associated arsenic release as As(III) into porewaters, where dissolved concentrations may locally reach values in the range of 100 to 500 µg L^{-1}, highlighting the dominant role of redox dynamics rather than renewed inputs [52,64,84].

In Central Europe, including Germany (Ore Mountains, Saxony), the Czech Republic, Slovakia, Austria, and parts of Poland and Romania, legacy arsenic contamination reflects historical waste disposal and long-term interaction between tailings, mine workings, and groundwater systems [86]. At decommissioned sites, arsenic concentrations in solid materials and mine-affected sediments typically range between approximately 50 and 500 mg kg^{-1} (d.w.), with mobility regulated by iron-controlled redox cycling rather than ongoing anthropogenic loading [52,64,86]. In the Mediterranean basin, the legacy of mining activities is most evident in coastal and near-shore marine environments where terrestrial tailings have been transported or disposed of. In these settings, restricted circulation, semi-enclosed basins, and long sediment residence times promote the persistence of arsenic in marine sediments long after mining activities have ceased. [30]. Mediterranean case studies document that mine tailings deposited in marine settings retain elevated arsenic contents (typically about 20–80 mg kg^{-1} d.w.), with arsenic predominantly hosted by sedimentary phases and interacting with benthic

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ecosystems via sediment–water exchange regulated by redox conditions and early diagenesis [30,52,87].

In several regions of the world, naturally elevated arsenic concentrations in groundwater have long constituted a major environmental and public-health concern, particularly in large alluvial basins such as the Ganges–Brahmaputra–Meghna delta, as well as in parts of Southeast Asia, South America and China [1,9,12,24]. In these settings, arsenic enrichment originates from geogenic processes affecting young, Holocene sedimentary aquifers and frequently results in groundwater arsenic levels far exceeding the WHO guideline value of 10 µg L^{-1} [1,9,12,27].

Critically, however, widespread human intervention has been the key factor translating this natural geochemical condition into large-scale environmental contamination. In Bangladesh and adjacent regions, the extensive installation of tube wells since the 1970s, promoted to avoid pathogen-rich surface waters, has led to the systematic extraction and use of arsenic-rich groundwater for drinking and domestic purposes, in the absence of adequate chemical monitoring [1,9]. This anthropogenic shift in water sourcing has resulted in chronic exposure of tens of millions of people and, importantly, has progressively extended arsenic contamination from groundwater to agricultural soils through irrigation practices. Against this background, diffuse agricultural activities provide a particularly instructive example of anthropogenic control over arsenic behaviour. In irrigated rice-growing regions of South and Southeast Asia, including the Bengal Basin (Bangladesh and eastern India) and parts of the Mekong Delta (Vietnam and Cambodia), the combined use of arsenic-rich groundwater for irrigation and intensive phosphate fertilization has profoundly altered arsenic cycling and speciation at the soil–water–plant interface [8,12,22,88,89]. Flooded paddy soils rapidly develop reducing conditions, favouring the microbial reduction of As(V) to As(III) and its release into soil porewaters at concentrations commonly ranging from 50 to 200 µg L^{-1} [9,14,15,90,91]. Competition between phosphate and As(V) for sorption sites further enhances mobilization [13,25,26], while As(III), being neutrally charged at circumneutral pH, exhibits higher mobility and plant uptake efficiency [8,23]. As a consequence, arsenic accumulation in rice grains typically reaches 0.1–2 mg kg^{-1} (d.w.), with iAs constituting 40–80% of total arsenic in polished rice, depending on cultivar and local conditions [12,14,23,92]. Importantly, these speciation patterns occur even where total soil arsenic concentrations remain within moderate ranges (often <15–25 mg kg^{-1}), indicating that anthropogenic alteration of hydrology and nutrient regimes plays a key role in controlling arsenic bioavailability and dietary exposure [8,22,90].

A particularly illustrative class of anthropogenic perturbations involves synthetic organoarsenic compounds deliberately introduced into the environment. Roxarsone (4-hydroxy-3-nitrophenylarsonic acid), extensively used as a feed additive in poultry and swine production from the 1950s until the early 2000s in the United States, China, and parts of Southeast Asia, exemplifies this mechanism [93,94]. Although roxarsone was originally considered less toxic than iAs, environmental investigations demonstrated its rapid transformation following animal excretion and land application of contaminated manure [93,95]. Under aerobic conditions, photochemical and microbial degradation pathways convert roxarsone predominantly into As(V), while under reducing conditions partial conversion to As(III) has been documented [93,95]. In poultry-impacted soils of the southeastern United States, repeated manure application increased total arsenic concentrations from background levels of approximately 3–5 mg kg^{-1} (d.w.) to 15–40 mg kg^{-1} (d.w.), with iAs accounting for more than 70% of the total soil arsenic pool within a few years [93,95]. Runoff from these amended soils resulted in dissolved arsenic concentrations of 10–30 µg L^{-1} in adjacent surface waters during high-flow events, thereby enhancing off-site transport and exposure [93]. Similar environmental transformation pathways have been documented for related organoarsenic feed additives and veterinary compounds, including arsanilic acid (4-Aminobenzenearsonic acid) and nitarsone (4-Nitrobenzenearsonic acid), which undergo progressive conversion to iAs species following soil application [94,95]. These findings indicate that synthetic organic arsenic compounds may generate a persistent environmental presence through post-application transformation processes, resulting in the secondary release of environmentally mobile and bioavailable iAs [93–96].

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Finally, the historical production, deployment, and disposal of arsenic-based chemical weapons represent a distinctive source of long-term arsenic contamination whose environmental relevance is increasingly recognized in post-conflict settings. Large quantities of arsenic-containing warfare agents, notably lewisite (2-chlorovinyl dichloroarsine), adamsite (10-chloro-5,10-dihydrophenarsazine), and the arsenical irritants Clark I (diphenylchloroarsine) and Clark II (diphenylcyanoarsine), were manufactured during the First and Second World Wars and subsequently disposed of at sea as part of post-war demilitarization practices. These activities resulted in well-documented legacy contamination in the Baltic Sea, as well as in parts of the Mediterranean basin, with arsenic release from corroding munitions persisting over decadal time scales [97,98]. In Italian marine waters, the most comprehensive reconstruction of these practices is provided by the RED COD project [99]. Archival records and post-war remediation activities indicate that approximately 20,000 chemical weapons were dumped, predominantly in the Adriatic Sea, with a significant fraction containing arsenic-based agents. The main documented dumping areas include the southern Adriatic Sea off Bari, Molfetta, Manfredonia, and Brindisi (Apulia, Italy), at distances of 20–40 nautical miles from the coast and depths ranging from roughly 300 to over 1,000 m. Recovered or identified ordnance comprised aerial bombs, artillery shells, and chemical containers filled with lewisite, adamsite, and arsenical irritants, often in association with sulphur mustard mixtures [99].

Although these sites were initially considered isolated, the RED COD investigations indicate that long-term corrosion of thin-cased munitions has promoted intermittent release of arsenic compounds to surrounding sediments. Measurements conducted in the late 1990s and early 2000s reported sediment arsenic concentrations on the order of 20–40 mg kg^{-1} (d.w.) in proximity to confirmed dumping areas, exceeding regional background values, with arsenic predominantly present in inorganic forms following hydrolysis and oxidation of parent organoarsenicals [99]. In addition to the documented Adriatic and Ionian dumping areas, historical accounts suggest that arsenic-based chemical ordnance may also have been scuttled offshore of other sections of the Italian coast, including the central Adriatic sector off Pesaro (Marche, Italy). However, in these latter cases no dedicated environmental investigations are presently available, and the presence and condition of such munitions remain inferred from military archives rather than direct analytical evidence [99].

The compounds summarized in Table 4 illustrate how synthetic organic arsenic formulations, developed for agronomic, veterinary, or military purposes, converge in the environment toward a limited set of iAs species, thereby generating persistent and spatially decoupled contamination regardless of their original intended use.

Table 4. *Selection of synthetic arsenical compounds deliberately produced and released into the environment for specific agricultural, veterinary or military purposes. The compounds listed represent some of the most environmentally relevant examples in terms of documented use, spatial distribution and long-term impact, according to relevant literature [93–99].*

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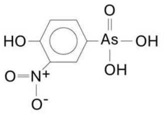
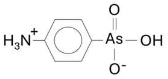
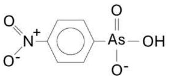
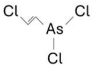
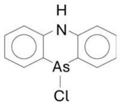
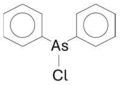
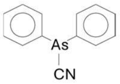
Compound	Formula	Intended use	Main areas of use or release	Period of use	Key environmental issues
Roxarsone		Feed additive and growth promoter in poultry and livestock production	China Southeast Asia USA	1950s – early 2000s	Environmental transformation into iAs Accumulation in agricultural soils Runoff to surface waters Long-term legacy contamination
Arsanilic acid		Feed additive and veterinary antimicrobial	China Europe USA	1940s – 1990s	Conversion to iAs in soil Persistence following manure application Enhanced As mobilization in agro-ecosystems
Nitarsone		Antiprotozoal feed additive in poultry	China USA	1960s – 2010s	Degradation to iAs Contamination of soils and sediments Contribution to dietary iAs exposure
Lewisite		Chemical warfare vesicant	Adriatic Sea (Italy) Baltic Sea	1917 – 1945 Post-war dumping	Corrosion of munitions Slow release in marine sediments Long-term sedimentary exposure
Adamsite		Chemical warfare irritant agent	European seas	1917 – 1945 Post-war dumping	Environmental persistence Gradual degradation Input to sedimentary As chemical species
Clark I		Chemical warfare irritant agent	Baltic Sea Mediterranean Sea	1917 – 1945 Post-war dumping	Release from corroding shells Transformation into iAs Localized sediment contamination
Clark II		Chemical warfare irritant agent	Baltic Sea Mediterranean Sea	1917 – 1945 Post-war dumping	Long-term environmental presence Secondary As release Long-term sedimentary exposure

8. Conclusions

The present review highlights arsenic as an element whose environmental behaviour is governed by a complex interplay of mineralogical, geochemical and biological processes rather than by concentration alone. Across terrestrial, freshwater and marine systems, arsenic mobility, bioavailability and toxicity emerge as properties intrinsically linked to chemical speciation, redox dynamics and biological processing, often not directly proportional to total arsenic levels. Natural systems exhibit a wide spectrum of arsenic behaviours, from strongly mineral-controlled reservoirs to biologically mediated transformations that dominate in aquatic and marine ecosystems, providing an essential baseline against which disturbed conditions must be interpreted.

Human activities alter this balance not merely by introducing additional arsenic into the environment, but also by perturbing the physicochemical controls that regulate its speciation and partitioning. Industrial releases, mining legacies, agricultural practices and the dissemination of synthetic arsenical compounds reshape arsenic pathways, frequently increasing the fraction of labile and toxic species without proportional increases in total concentrations. Accordingly, interpretation of arsenic dynamics requires a process-based perspective that integrates speciation, redox conditions and biological regulation.

The arguments developed throughout this review necessarily point toward analytical considerations. Determination of arsenic speciation remains analytically challenging, relying largely on hyphenated techniques and non-standardized protocols that are not routinely accessible in many monitoring frameworks [6,7,31,49,95]. Moreover, sample handling and extraction procedures may introduce significant biases, particularly through the oxidation of trivalent arsenicals during collection, storage or preparation, potentially obscuring environmentally relevant redox distributions. Although a detailed discussion of analytical methodologies lies beyond the scope of the present review, acknowledging these constraints is essential for the correct interpretation of speciation data and for avoiding over-simplified conclusions.

Overall, the evidence discussed in the present review highlights arsenic as a sensitive tracer of the interactions between geochemical conditions and biological regulation across environmental

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systems. Arsenic cycling emerges as the product of multiple, interconnected processes that operate across solid, dissolved and biological compartments and shape its mobility, chemical form and ecological relevance. Across a wide range of environments, recurrent patterns of arsenic behaviour reflect broadly shared modes of regulation, while departures observed in extreme, redox-forced or highly specialized systems clarify the conditions under which these controls are modified or overcome. Framing arsenic within this process-based perspective enables a more coherent interpretation of its environmental dynamics, particularly in systems increasingly influenced by human activities.

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Abbreviations

The following abbreviations are used in this manuscript:

ArsC	Arsenate reductases
ArsM	Arsenite S-adenosylmethionine methyltransferase
As(III)	Trivalent inorganic arsenic (arsenite)
As(V)	Pentavalent inorganic arsenic (arsenate)
As3MT	Arsenite methyltransferase
AsB	Arsenobetaine
AsC	Arsenocholine
AsFA	Arsenic fatty acids
AsFA 362	Dimethylarsinoylhexadecanoic acid
AsHC	Arsenic hydrocarbons
AsHC 332	1-Dimethylarsinoylpentadecane
AsPL	Arsenic phospholipids
AsS	Arsenosugars
d.w.	Dry weight
DMA	Dimethylarsenicals
DMA(III)	Dimethyl-arsenite
DMA(V)	Dimethyl-arsonate
DMAA	Dimethylarsinoylacetic acid
DMAE	Dimethylarsinoylethanol
Grx	Glutaredoxin
GSH	Glutathione
HR	Hardness
iAs	Inorganic arsenic
MMA	Monomethylarsenicals
MMA(III)	Monomethyl-arsenite
MMA(V)	Monomethylarsonic acid
SAM	S-adenosylmethionine
TETRA	Tetramethylarsonium
TMA(III)	Trimethylarsine
TMAO	Trimethylarsine oxide
Trx	Thioredoxin
WHO	World Health Organization
wt.%	Weight percent

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