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Review

ECOTOXICOLOGY OF ARSENIC IN THE MARINE ENVIRONMENT

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Abstract—Arsenic has a complex marine biogeochemistry that has important implications for its toxicity to marine organisms and their consumers, including humans. The average concentration of total arsenic in the ocean is about 1.7 μg/L, about two orders of magnitude higher than the U.S Environmental Protection Agency's human health criterion (fish consumption) value of 0.0175 μg/L. The dominant form of arsenic in oxygenated marine and brackish waters is arsenate (As V). The more toxic and potentially carcinogenic arsenite (As III) rarely accounts for more than 20% of total arsenic in seawater. Uncontaminated marine sediments contain from 5 to about 40 μg/g dry weight total arsenic. Arsenate dominates in oxidized sediments and is associated primarily with iron oxyhydroxides. In reducing marine sediments, arsenate is reduced to arsenite and is associated primarily with sulfide minerals. Marine algae accumulate arsenate from seawater, reduce it to arsenite, and then oxidize the arsenite to a large number of organoarsenic compounds. The algae release arsenite, methylarsonic acid, and dimethylarsinic acid to seawater. Dissolved arsenite and arsenate are more toxic to marine phytoplankton than to marine invertebrates and fish. This may be due to the fact that marine animals have a limited ability to bioconcentrate inorganic arsenic from seawater but can bioaccumulate organoarsenic compounds from their food. Tissues of marine invertebrates and fish contain high concentrations of arsenic, usually in the range of about 1 to 100 μg/g dry weight, most of it in the form of organoarsenic compounds, particularly arsenobetaine. Organoarsenic compounds are bioaccumulated by human consumers of seafood products, but the arsenic is excreted rapidly, mostly as organoarsenic compounds. Arsenobetaine, the most abundant organoarsenic compound in seafoods, is not toxic or carcinogenic to mammals. Little of the organoarsenic accumulated by humans from seafood is converted to toxic inorganic arsenite. Therefore, marine arsenic represents a low risk to human consumers of fishery products.

Keywords—Toxicity Bioaccumulation Arsenobetaine Arsenite Arsenate

INTRODUCTION

For hundreds of years, arsenic, in the form of tasteless and odorless arsenic trioxide, has been viewed by the public as the archetype poison, the suspected cause of several accidental mass poisonings, the theme of many mystery novels and plays, and even the suspected cause of the death of a former U.S. president, Zachary Taylor [1–3]. Inorganic arsenic, in the form of arsenite ion, AsO_2^{-1} [4], has been classified by the International Agency for Research on Cancer as a human carcinogen [5]. Most of the evidence for the carcinogenicity of inorganic arsenic comes from epidemiological studies [4,6,7]; much of the epidemiological evidence is circumstantial and confounded by lack of consideration of concurrent exposure to other potential carcinogens [2]. Most laboratory studies have failed to demonstrated the carcinogenicity of arsenic in laboratory mammals, even by prolonged exposures via several routes to high concentrations of arsenites, arsenates, and organoarsenicals [2,6,7]. Arsenite also has been reported to be as much as 60 times more toxic than arsenate and several hundred times more toxic than methylated arsenicals to mammals [8,9].

Based on the suspected human carcinogenicity of arsenite, the U.S. Environmental Protection Agency (U.S. EPA) has set a human health criterion for total dissolved arsenic in seawater of 0.0175 μg/L (at the 10^{-6} cancer risk level) for consumption of fishery products [10]. The human health criterion is based on a prediction of the bioaccumulation of arsenite from lifelong ingestion of the edible tissues of fish and shellfish. The human health criterion for consumption of marine fishery products is about two orders of magnitude lower than the average ambient concentration of inorganic arsenic in clean ocean water. The criterion apparently is based on the conservative assumption that all the arsenic in tissues of edible fishery products is present as inorganic arsenite or in a form that is readily reduced to arsenite. As discussed below, this almost never is the case.

The very low human health (fish consumption) criterion for arsenic in seawater often leads to the identification of an unacceptable risk to human health in human health risk assessments performed for marine and estuarine ecosystems. The human health criterion for arsenic in seawater should be revised to consider the natural concentration of total arsenic in clean seawater and the forms of arsenic in edible tissues of marine fishery products consumed by humans.

The quantitatively most important routes of exposure of humans to arsenic in its various forms are through inhalation of industrial dusts (particularly those from nonferrous metal smelters and coal-fired and geothermal plants), in drinking water, and in food, particularly seafood [11,12]. Total natural emissions of arsenic to the atmosphere (about 45,000 metric tons/year) are just about 1.5 times the estimated emissions of arsenic to the atmosphere from human activities (28,000 metric tons/year) [13]. Atmospheric arsenic apparently contributes little to the arsenic budget of the ocean [14]. Major sources of arsenic in surface waters of the ocean are riverine inputs and upwelling of deep ocean water enriched in arsenic [15,16]. Thus, human activities contribute little to the arsenic budget of the open ocean, but may be important in estuaries and coastal waters receiving arsenic-contaminated drainage from the land.

Growing evidence suggests that arsenic is an essential micronutrient in animals, including humans [17]. The maximum acceptable human intake of arsenic in food (2 μg/kg body weight/d, equivalent to 140 μg/d in a 70-kg person) [18] is only about 10 times higher than the recommended daily requirement of 12 μg As/d [17]. Several countries have regulations for the maximum permissible concentration (MPC) of arsenic in seafood consumed by humans [19]. These regulatory limits range from 0.1 mg/kg (Venezuela) to 10 mg/kg (Hong Kong). In some countries, the MPC for arsenic is for total arsenic; in others, it is for inorganic arsenic only [20]. Background or natural concentrations of arsenic in edible tissues of fishery products consumed by humans often exceed these limits, as discussed below.

The objective of this review is to summarize the marine biogeochemistry of arsenic and evaluate whether arsenic is a hazard to marine organisms and human consumers of marine fishery products.

ARSENIC IN SEAWATER

Arsenic has a complex marine biogeochemistry that has important implications for its toxicity to marine organisms and their consumers, including humans. As a member of group Va of the periodic table, arsenic shares many chemical properties with its nearest neighbors in the group, phosphorus and antimony. Arsenic can occur in estuarine and marine waters and sediments in four valency states, +5, +3, 0, and −3 [21]. Elemental arsenic is very rare and As^{-3} is found only at extremely low Eh values in highly reducing environments. Arsenate (As V) and arsenite (As III) are the dominant forms of inorganic arsenic in marine ecosystems. The most abundant forms of inorganic arsenic at the normal pH of brackish and marine waters are anionic for arsenate ($H_2AsO_4^{-1}$ and $HAsO_4^{-2}$) and neutral for arsenite ($As[OH]_3^0$) [22,23]. Two organic forms of arsenic, methylarsonic acid (MMA) and dimethylarsinic acid (DMA), also are found frequently in seawater [24,25].

The concentration of total arsenic in clean coastal and ocean waters is 1 to 3 μg/L, with a mean of about 1.7 μg/L [24,26,27], a concentration about 100 times higher than the U.S. EPA human health water quality criterion (fish consumption) value (0.0175 μg/L). In continental shelf waters, the concentration of dissolved arsenic in surface waters varies seasonally due to natural cycling between sediments and the overlying water column [28]. Lowest concentrations occur in the spring when dissolved arsenate is scavenged by phytoplankton and suspended particles; concentrations increase in the fall due to remobilization of arsenic from sediments. The behavior of arsenate resembles that of phosphate [29], which is known to undergo seasonal remineralization and mobilization, with peak remobilization often in late summer [30]. A similar seasonal pattern occurs in some estuaries [31,32]. The concentration of total arsenic in the Patuxent River estuary, Maryland, USA, peaks at about 1 μg/L in July and August and then declines gradually to about 0.1 to 0.2 μg/L in January through April [32].

Arsenic is depleted in surface waters of the open ocean [16]. The average concentration in surface water of the eastern tropical Atlantic is 0.97 μg/L; below about 400 m, arsenic concentration is relatively constant with depth at an average of 1.5 μg/L. A good correlation usually exists between concentrations of arsenate and phosphate in ocean water, suggesting that the vertical distribution of arsenic in the ocean is controlled by biological activity.

Concentrations of inorganic arsenic in some estuaries and coastal waters may be higher than those in the open ocean, reflecting natural and anthropogenic inputs, primarily in runoff from the land [33]. In the Carnon/Restronguet Estuary system in southwestern England, which drains a metal-mining region, total arsenic concentrations decrease from 25 to 42 μg/L in the freshwater portion to 1.9 to 4.8 μg/L at the mouth of the estuary [34]. Sediments in freshwater streambeds draining metal-mining areas of southwestern England contain up to 14,000 μg/g total arsenic [35].

In most estuaries draining nonindustrial watersheds, concentrations of total arsenic in the water increase from the head to the mouth of the estuary, reflecting progressive mixing of arsenic-poor freshwater with arsenic-rich seawater [33,36]. Arsenic concentrations in fresh ground water range from less than 0.01 μg/L to more than 800 μg/L, with most concentrations falling below the current U.S. drinking water criterion of 10 μg/L average and 50 μg/L maximum [37,38].

ARSENIC SPECIATION

The thermodynamically most stable and, therefore, dominant form of inorganic arsenic in oxygenated fresh, brackish, and seawater is arsenate (As V) [33]. In open ocean seawater, the ratio of As V to As III may exceed 300 [27]. In coastal waters influenced by freshwater runoff and high primary production, the ratio may be much lower [26]. Between 1.6 and 13.2% of total arsenic in surface waters of the continental shelf off the southeastern United States is arsenite [39].

Although arsenate is the dominant form of arsenic in unpolluted fresh, estuarine, and marine waters [15,40,41], arsenite concentrations in oxygenated water bodies nearly always are higher than predicted, based on thermodynamic considerations alone [42]. Potential sources of thermodynamically unstable arsenite in oxygenated fresh, brackish, and marine waters include biotic and abiotic reduction of arsenate, deposition from the atmosphere, upwelling of anoxic waters, and input from hypoxic river basins [42]. In most coastal regions, atmospheric and riverine inputs of arsenic are primarily (≥90%) in the form of arsenate [42]. Upwelling of anoxic bottom water rich in arsenite may be important in water bodies, such as Chesapeake Bay, USA [43], that experience seasonal stratification leading to hypoxic or anoxic bottom waters. Concentrations of arsenite (0.1–0.2 μg/L) in the Patuxent River Estuary, a tributary of Chesapeake Bay, usually are highest in the spring, at about the time of the spring phytoplankton bloom [32,44].

Dimethylarsinic acid reaches a peak concentration of 0.2 to 0.6 μg/L in the water column of the estuary in May or June at a time when arsenate concentrations are low. Seasonal increases in concentrations of arsenite and DMA in seawater probably are caused by reduction followed by oxidative methylation of arsenate accumulated by phytoplankton, bacteria, and yeasts [40,43,45]. Arsenite and methylarsenic compounds are excreted to the ambient water by living microbiota [45,46], or are released when the microorganisms die [46–48]. Yeasts may convert some of the biosynthesized methylarsenic to volatile alkylarsines [45]. Microbes in aerobic and anaerobic sediments also are able to synthesize and release methylated arsenic compounds [49]. Although several species of anaerobic bacteria are able to reduce arsenite to arsines (AsH_3) in laboratory culture, there is no evidence that quantitatively significant arsine production occurs in anaerobic marine and estuarine sediments [50].

Rates of release of methylarsenic compounds by estuarine and marine phytoplankton and macroalgae are temperature dependent [51]. There is only a slight increase with increasing temperature in the rate of release of MMA by algae; however, the rate of release of DMA increases by more than sixfold between 5 and 15°C. The dominant organoarsenical released from the algae to seawater at all temperatures is DMA.

In aerobic seawater, arsenite is oxidized rapidly to arsenate, both abiotically [52] and by bacteria [48,53]. In productive coastal and estuarine waters, the first order rate constant for arsenite oxidation is in the range of 0.5 to 2.2/d [42]. Particulate manganese oxides, often abundant in estuarine waters, may increase the rate of oxidation of arsenite [52].

In hypoxic and anoxic waters ($Eh < 0.1$ V), the reduced species of arsenic is favored thermodynamically. The abiotic rate of arsenate reduction is slow; the first order rate constant is in the range of 1.6×10^{-5} to 8×10^{-2}/d [52,54]. Most of the arsenate in anoxic bottom waters of lakes, estuaries, and seas (e.g., the Black Sea) can be attributed to downward fluxes of organic particles containing adsorbed arsenate, advection of oxidized surface waters down into the anoxic zone, and the slow rate of arsenate reduction [26,42].

Thus, arsenate, arsenite, and methylated arsenic species may occur together in seawater. The relative proportions of the different forms of inorganic and organic arsenic in marine and estuarine waters depend on the redox conditions, temperature, and the species composition and abundance of phytoplankton and bacteria present [43,55,56]. Arsenate is always the most abundant form of arsenic in oxygenated, biologically productive waters of the ocean, except when stratification of the water column breaks down and large amounts of deep hypoxic water are advected to the surface. However, arsenite is nearly always present in oxygenated surface waters at concentrations higher than predicted by the thermodynamics of oxidation and reduction of arsenic. This undoubtedly is due to the rapid reduction of arsenate and excretion of arsenite by marine phytoplankton, yeasts, and bacteria.

For example, freshwater entering the Chesapeake Bay, USA, from the Susquehanna River contains an average of 0.18 μg/L total arsenic [43]. Concentrations of total arsenic in surface water increase with distance down the bay and with increasing salinity to an average of 1.13 μg/L at the mouth of the bay and immediately offshore. In the summer, all the arsenic in Susquehanna River water is arsenate. Surface waters offshore the mouth of the estuary contain predominantly arsenate, with traces of arsenite and DMA. Surface waters in the middle reaches of the bay contain up to 62% arsenic as reduced or methylated arsenic species. Arsenite is most abundant at low salinities; MMA is present primarily in the region of the estuary with salinities between 8 and 20‰ and DMA occurs irregularly at salinities greater than 7‰. This pattern of arsenic distribution is attributed to a combination of reduction of arsenate in anoxic bottom waters during summer followed by advection of arsenite-rich anoxic water to the surface during the fall turnover and the presence in surface waters of the middle estuary of large numbers of arsenic-methylating species of phytoplankton. Nearly all the MMA and DMA in the middle reaches of Chesapeake Bay and the Charlotte Harbor estuary, Florida, USA, are derived from blooms of phytoplankton [32,57].

In the waters of the Carnon/Restronguet Estuary, draining a metal-mining area of southwestern England, the ratio of arsenite to arsenate decreases from the head to the mouth of the estuary. Following a release of a large volume of arsenite-contaminated mine drainage water to the Carnon River, concentrations of arsenite downstream in the Carnon Estuary increased to 9 to 27 μg/L and remained elevated for at least 6 months [58]. Oxidation of arsenite to arsenate in the estuary occurred slowly by biotic and abiotic pathways, probably because of high concentrations of reduced arsenic in sediments of this chronically arsenic-contaminated estuary.

ARSENIC IN SEDIMENTS

Concentrations of total arsenic in uncontaminated nearshore marine and estuarine sediments usually fall in the range of 5 to 15 μg/g dry weight [21]; however, the average concentration of arsenic in deep-sea sediments is about 40 μg/g [59]. Sediments from rivers in England and Wales contain 7 to 950 μg/g arsenic [60]. Sediments from estuaries receiving drainage from metal-mining areas may contain substantially elevated concentrations. For example, sediments from the Carnon/Restronguet Estuary in southwestern England contain from 9 to more than 5,000 μg/g total arsenic [61]. Sediments from the Tinto and Odiel Rivers in southwestern Spain contain less than 200 to 3,000 μg/g total arsenic [62].

Arsenate is the most abundant form of arsenic in oxidized marine sediments, whereas arsenite is the dominant dissolved and solid species in reduced sediment layers [56,63–65]. Bacteria in aerobic sediments can oxidize As III to As V [65]. Iron oxyhydroxides, which are abundant in oxidized marine sediments, also can catalyze oxidation of arsenite to arsenate [66]. In the oxidized layers of the sediment, much of the arsenic is associated (coprecipitated or adsorbed) with the hydrous iron and manganese oxide fraction or is present as $Fe_3(AsO_4)_2$ [19,26,66,67]. Sediment organic matter may also bind some arsenic [29]. Although the affinity of pelagic clays for sorption of arsenite is three orders of magnitude higher than that for arsenate [68], most of the arsenite that sorbs to iron oxides is rapidly oxidized to arsenate [66]. Because the dominant sorbent phase in most oxidized marine sediments is iron oxyhydroxide coatings on clays [69], most of the sorbed, nondetrital arsenic is in the pentavalent state. Under these conditions, the amount of arsenic in solution in sediment pore water is low and 65 to 98% is present as arsenate [64,65]. The concentration of arsenic in solution in sediment pore water and the fraction of the total dissolved arsenic that is pentavalent increase with increasing pH, providing further evidence that much of the nondetrital arsenic in the oxidized sediment layers is sorbed as arsenate to iron and manganese oxide surfaces [65,66]. Sorbed or bound arsenic is less bioavailable than is dissolved arsenic. Thus, much of the arsenic in oxidized marine sediments may not be bioavailable to sediment-dwelling marine organisms.

Under moderately reducing conditions, iron and manganese oxide phases begin to dissolve, releasing adsorbed arsenate into the pore water [64,65]. Arsenate is reduced to arsenite in reducing sediments and, if sulfur is abundant, as is the case in most marine sediments, most of the arsenic reacts with sulfides to form realgar (AsS), inclusions in copper and zinc sulfides, arsenopyrite (FeAsS), or orpiment (As_2S_3) [22,70–72]. These sulfides have a low solubility and mobility.

In oligohaline and freshwater sediments, which often contain low concentrations of sulfur, arsenic solubility is less limited by formation of insoluble sulfide minerals. Arsenite, often as arsenolite (As_2O_3), may remain quite mobile and tends to diffuse upward to be released into the overlying water column as either arsenite or arsenate [56,63,70,73, 74]. Thus, arsenic is much more mobile and probably more biovailable in freshwater than in marine ecosystems.

Marine sediments may also be an important source of MMA and DMA to the overlying water column. Several species of aerobic and anaerobic sediment bacteria are able to bioaccumulate arsenate and arsenite and convert them to MMA and DMA [75]. The organoarsenicals are released by the bacteria into the sediment pore water, from which the organoarsenic may be mixed up into the overlying water column. Release of MMA and DMA from marine sediments is not temperature sensitive and MMA is released more rapidly than is DMA [51].

Arsenic is most likely to be dissolved and mobilized from marine sediments at redox interfaces and during transitions in redox potential, either up or down [70]. During redox potential changes, arsenic is released into solution in the pore water due to dissolution of iron and manganese oxides (decreasing redox potential) or sulfides, especially pyrite (increasing redox potential). The arsenic-rich pore water may then be mixed up into the overlying water column by sediment resuspension and transport or by bioturbation [64,76]. Redox changes in coastal marine and estuarine sediments occur most frequently at times of seasonal change, particularly spring and autumn. Seasonal fluxes of arsenic from sediments may contribute to seasonal cycles of arsenic accumulation by marine organisms.

BIOACCUMULATION AND BIOTRANSFORMATION OF ARSENIC

Marine bacteria, micro- and macroalgae, and salt-marsh plants are able to accumulate dissolved arsenate from seawater [77–79]. The brown macroalgae *Fucus spiralis* and *Ascophyllum nodosum* accumulate four times more arsenate than arsenite from equivalent concentrations in seawater [80]. Bacteria and marine algae rapidly accumulate dissolved arsenate via a cellular phosphate transport system, but the bacteria excrete arsenate rapidly by another active transport system that prevents a net accumulation of arsenate inside the cells [81,82]. In many marine algae, arsenate does not compete with phosphate for uptake, suggesting that there is more than one mechanism for arsenate uptake by the algae [47].

Between about 1 and 50% of the arsenic in tissues of macroalgae is inorganic; the remainder is in the form of various organoarsenic compounds [83,84]. Marine bacteria, yeasts, and plants may reduce accumulated arsenate to arsenite and then oxidize it to form organoarsenic compounds [45,47,55]. The organoarsenic compounds synthesized by marine algae include MMA, DMA, an arsenotaurine derivative, and several arsenic-containing ribosides [40,85]. Methylation of arsenic may involve an enzymatically mediated methyl transfer via methylcobalamin or *S*-adenosylmethionine [86]. Methylarsonic acid and DMA are excreted rapidly, suggesting that arsenic methylation may be a detoxification mechanism for the algae [87]. Dimethylarsinic acid may be reduced further in a reaction with adenosylmethionine to form dimethylarsinyladenosine [40]. Glycosidation of this intermediate leads to formation of dimethylarsinoribosides, which may be reductively methylated to form trimethylarsonioribosides. The arsenotaurine derivative may be formed by a similar mechanism. Trialkylarsinyl compounds, such as the dimethylarsenylribosides, readily undergo reduction and oxidation and may participate in cellular oxidation/reduction reactions in bacteria and algae [40,50].

Table 1. Concentrations of total arsenic in the whole or muscle tissues of marine organisms from throughout the world. Concentrations are in μg/g dry weight

Taxon	Number of samples	Range	Geometric mean
All taxa	544	0–2,739	11.10
Algae	50	0.1–382	43.70
Seagrass	5	0.16–0.59	0.28
Zooplankton	4	0.2–24.4	2.10
Polychaetes	18	5.0–2739	29.19
Crustaceans	96	<0.1–270.5	14.86
Crustacean larvae	7	26.95–79.90	41.67
Bivalves	151	<0.6–214	10.44
Snails	41	8.0–533	51.97
Cephalopods	7	4.0–49.5	16.11
Fish	156	0.05–449.5	5.59
Marine mammals	6	0.05–0.90	0.25

Much of the organic arsenic in the tissues of marine animals may be derived directly or indirectly from consumption of marine algae [88–90]. Concentrations of arsenic reach values in excess of 1,000 mg/kg in the kidneys of the giant clams *Tridacna maxima* and *Tridacna derasa* from the Great Barrier Reef off Australia [91]. Symbiotic zooxanthellae in the clam mantle tissues accumulate arsenate from seawater, convert it to organic forms, such as arsenoribosides and arsenotaurine [84], and pass it on to the host. Edmonds and Francesconi [92,93] showed that in unpolluted waters of western Australia, the brown alga *Ecklonia radiata* accumulates inorganic arsenate from seawater and converts it to a variety of arsenosugars. The organoarsenic compounds appear to be accumulated by detritivorous polychaetes, and then by school whiting, *Sillago bassensis*, that feed on the polychaetes. The major form of arsenic in the fish is arsenobetaine.

Most marine animals have only a limited ability to accumulate arsenate from solution in seawater [77,94,95]. Despite this limited ability, concentrations of total arsenic vary widely in tissues of marine plants and animals, irrespective of the trophic position of the organisms in the local food web [77,88,96] (Table 1).

Concentrations of total arsenic in whole or muscle tissues of marine organisms worldwide range from below the detection limit of the analytical method (usually 0.01–0.6 μg/g dry weight, depending on the method) to more than 2,500 μg/g dry weight (ppm). Because of the wide range of concentrations found in a particular taxon, the geometric mean value best represents the ‘‘typical’’ concentration.

Natural concentrations of total arsenic in the tissues of marine animals, other than marine mammals, often are in the range of a few tens of parts per million, although much higher concentrations are reported often, even in tissues of marine animals from seemingly uncontaminated marine environments. Geometric mean concentrations range from 0.25 and 0.28 μg/g in marine mammal tissues and sea grasses, respectively, to 43.7 and 52 μ/g in marine macroalgae and marine snails, respectively. Bivalve mollusks, *Modiolus capax*, from several locations along the west coast of the Gulf of California, Mexico, contain 6.62 to 44.7 μg/g dry weight arsenic in soft tissues [97]. Oysters, *Crassostrea virginica*, from coastal waters of the U.S. Gulf of Mexico contain 4.1 to 39 μg/g total arsenic [98]. Highest concentrations are in oysters from coastal areas along the west coast of Florida, USA, receiving drainage from natural phosphate mineral deposits, which are rich in arsenic.

Several species of oceanic decapod, mysid, and euphausiid crustaceans from offshore waters of the eastern North Atlantic Ocean contain mean concentrations of total arsenic ranging from 17.4 μg/g in the penaeid shrimp *Gennadas valens* to 59.3 μg/g in the euphausiid *Meganyctophanes norvegica* [99].

Highest concentrations of arsenic appear to be present in tissues of marine animals that feed primarily on phytoplankton or macroalgae, which often contain high concentrations of inorganic and organic arsenic. These taxa include planktonic crustaceans, bivalve mollusks, herbivorous snails, and some polychaete worms.

Marine organisms from arsenic-contaminated environments usually contain higher concentrations of total arsenic than do organisms from uncontaminated sites. For example, the brown macroalga *Fucus vesiculosus* from Restronguet Creek, United Kingdom, which is heavily contaminated with arsenic from mine drainage, contains 38.5 to 184 μg/g dry weight total arsenic [34]. Other species of marine macroalgae from the same estuary also contain elevated concentrations of arsenic. *Fucus vesiculosus* from less contaminated British estuaries, from the Baltic Sea, and from the North Sea contain 10.2 to 59 ppm total arsenic (Table 1). Plaice, *Pleuronectes platessa*, from the Irish Sea contain 26 to 102 μg/g total arsenic in muscle tissue; the highest concentrations are in fish from the sludge disposal ground in Liverpool Bay [100]. More than 99% of the total arsenic in all the plaice samples is organic.

Some marine invertebrates accumulate exceedingly high concentrations of arsenic. For example, the polychaete worm *Tharyx marioni* often has a whole-body concentration of arsenic greater than 2,000 μg/g dry weight [101]. Most of the arsenic is present in the organic form in the palps (6,000–13,000 μg/g), which comprise only 4% of the mass or the worm. Gills of the large edible snail *Hemifusus ternatanus* may contain more than 100 μg/g wet weight (equivalent to about 500 μg/g dry weight) total arsenic, 49 to 100% of which is inorganic [102]. Other soft tissues of the snails contain lower concentrations of total arsenic and much of it (33 to >99%) is in organic forms. The edible foot contains 4 to 50 μg/g wet weight (about 20–250 μg/g dry weight) arsenic, more than 95% of which is organic.

Bottom-living marine animals often contain higher concentrations of arsenic than do pelagic animals. Edible muscle tissue of Atlantic cod, *Gadus morhua* (a demersal feeder), from waters off Labrador and Newfoundland, Canada, contains 7 to 52 μg/g dry weight total arsenic (average 19 and 11 μg/g from two locations) [103]; muscle tissue of bluefin tuna, *Thunnus thynnus* (a pelagic feeder), caught off eastern Canada contains an average of 3.2 μg/g arsenic [104]. The average concentration of arsenic in edible muscle tissue of *T. thynnus* caught in the Arabian Sea off Pakistan is 2.9 μg/g and increases slightly with weight of the fish [105]. The reasons for this wide variability in tissue concentrations of arsenic in marine invertebrates and fish are not fully understood, but may be related to variations in the bioavailability of arsenic due to environmental temperature; salinity; concentrations of dissolved phosphate; seasonal variations in ratios of arsenite, arsenate, and organic arsenic in seawater; and to differences among species in trophic status.

The limited bioaccumulation (bioconcentration factors of 2–10) of arsenate by a marine shrimp, *Lysmata seticaudata*, and a mussel, *Mytilus galloprovincialis*, is inversely correlated with salinity, suggesting that arsenate is less bioavailable to marine than to estuarine animals [106,107]. Arsenic loss from tissues is rapid initially with a half-time of about 3 d. Mussels excrete much of the accumulated arsenate in byssal threads. More than one half of the arsenate accumulated by shrimp is in the exoskeleton and is lost during the molt. When shrimp accumulate arsenic from food, they assimilate about 75% of the dose, and excrete it with a half-time of 14 d. Crabs, *Carcinus maenas*, accumulate both inorganic and organic arsenic from food [108]. However, they are not able to convert organic arsenic to inorganic forms or vice versa in their tissues; they tend to excrete the inorganic forms more rapidly than the organic forms. Fowler and Ünlü [106 to 108] suggested that arsenic assimilated from food is present in the tissues in a persistent, organic form, whereas that accumulated from water remains inorganic and is excreted rapidly or sequestered in nonliving tissue compartments. Arsenate accumulated from solution apparently is sequestered in or absorbed to surface tissues, from which it is readily partitioned back into the ambient water; arsenic accumulated from food is mostly organic and is assimilated into the tissues where it may be persistent.

Sanders et al. [95] reported that the copepod *Eurytemora affinis*, the barnacle *Balanus improvisus*, and the oyster *C. virginica* do not accumulate inorganic arsenate from seawater into soft tissues. Arsenate is accumulated in the calcified shell material of the barnacles and oysters. Several species of phytoplankton do accumulate arsenate from the water. When the contaminated algae are fed to the invertebrates, the invertebrates accumulate some arsenic in their tissues, probably in the form of organoarsenic compounds. However, the amount of arsenic accumulation from the algae is small. Similar results are obtained in a simple artificial food chain of phytoplankton, brine shrimp, *Artemia* spp., and grass shrimp, *Palaemonetes pugio* [78]; however, grass shrimp do not accumulate arsenic from either water or food (brine shrimp). It is possible that the phytoplankton in these experiments were not in the optimal physiological state for maximal synthesis of organic arsenic compounds.

Langston [77] showed that the deposit-feeding clam *Scrobicularia plana* accumulates arsenic from ingestion of sediment particles and direct contact of the labial palps with sediments; the filter-feeding bivalves *Cerastoderma edule* and *Mytilus edulis* accumulate arsenic from ingested living and dead particles; snails, *Littorina* spp., accumulate arsenic from grazing on macroalgae, *Fucus* spp., which are able to accumulate arsenate from solution in the water.

Arsenobetaine is the most abundant form of arsenic in tissues of most marine animals examined to date [40,88,109]. It usually represents 50 to more than 95% of the total arsenic in tissues of marine crustaceans and elasmobranch and teleost fish; 10 to more than 95% of the total arsenic in sponges, coelenterates, molluscs, and echinoderms is arsenobetaine [110]. A variety of other organoarsenic compounds has been detected in the tissues of marine animals [88,90,109,111]. These include MMA, DMA, arsenocholine, trimethylarsine oxide, tetramethylarsonium ion, phosphatidylarsenocholine, and a variety of arsinylribosides. Concentrations of arsenocholine, a possible precursor of the dominant arsenobetaine, range from less than 0.016 to 0.084 μg/g in several species of marine invertebrates and fish [109].

The source(s) of arsenobetaine in the tissues of marine animals is uncertain. Marine invertebrates and fish apparently are not able to synthesize arsenobetaine from accumulated inorganic arsenic [40]. Cooney and Benson [112], Hanaoka et al. [89], and Edmonds et al. [90] proposed that herbivorous marine animals accumulate arsinylribosides, other arseno-sugars, and arsenic-containing phospholipids from algal foods and convert them through arsenocholine and other intermediates to arsenobetaine ($[CH_3]_3As^+CH_2COO^-$), which is accumulated in the tissues. However, Klumpp and Peterson [34] and others have been unable to demonstrate direct transformation of organoarsenic compounds accumulated from algal foods to arsenobetaine in the tissues of marine animals.

Francesconi and Edmonds [40,113] and Phillips [84] proposed a pathway involving decomposition of dimethylarsinylribosides and trimethylarsonioribosides to dimethy-arsinylethanol or arsenocholine by anaerobic bacteria in sediments. The degradation products may then be bioaccumulated by benthic and demersal marine animals, converted to arsenobetaine, and transferred through the marine food web in this form. Dimethylarsinylethanol may be oxidized to dimethylarsinylacetic acid, which in turn can be methylated to form arsenobetaine; alternatively, dimethylarsinylethanol can be methylated to form arsenocholine. Arsenocholine formed from dimethylarsinylethanol or trimethylarsonioribosides may then be oxidized to form arsenobetaine. Arsenobetaine is metabolically stable and usually is the major end product of arsenic metabolism; it is readily bioaccumulated but not readily excreted by marine animals [40,113].

Organoarsenic compounds, including arsenobetaine, that are released to the marine environment are converted rapidly to arsenate in aerobic seawater, sediments, and the tissues of dead marine animals [89, 114–117]. Thus, there is a complex cycle of arsenic in the ocean, involving biologically mediated interconversions among arsenate, arsenite, and several organoarsenic compounds. In this cycle, concentrations of the most toxic form, arsenite, remain very low in all but anoxic microenvironments.

If the hypothesis of Francesconi and Edmonds [40,113] and Phillips [84] is correct, there actually are two arsenic cycles in the marine environment, one for inorganic arsenic species, and the other for organoarsenic compounds. The two cycles are linked at the level of sediment microbes and marine algae where inorganic arsenic is converted to organic forms. Inorganic arsenic is accumulated by marine plants, but only to a limited extent by marine animals, and is not transferred efficiently through marine food webs. Organoarsenic compounds are synthesized by marine plants and sediment microbes, are bioaccumulated efficiently by marine animals, and are readily transferred through marine food webs. Organoarsenic, but not inorganic arsenic, may be biomagnified to some extent in marine food webs [118]. However, Andreae [25] reported that the ratio of phosphorus to total arsenic increases with increasing trophic level in marine food chains, suggesting a biodiminution of total arsenic. The increase of the phosphorus to arsenic ratio up the marine feed web suggests that the biochemical depletion of arsenic relative to phosphorus and its conversion to relatively harmless organic forms represent a natural control on arsenic toxicity up the food chain [25,119].

Inorganic arsenic represents between about 0.5 and 1% of the total arsenic in the edible portions of most marine invertebrates and fish examined to date [110]. The fraction of total arsenic that is inorganic tends to decrease as the concentration of total arsenic in the tissues increases. Concentrations of inorganic arsenic in the edible portions of marine invertebrates and fish from uncontaminated marine environments generally range from less than 0.001 to about 0.5 μg/g wet weight [110]. These concentrations are below the MPCs for total arsenic in seafoods set by most countries. However, an edible marine macroalga, *Hizikia fusiforme*, contains up to about 5 μg/g inorganic arsenic [120] and, therefore, could be toxic to humans if eaten in large amounts.

There is no published information on seasonal cycles of concentrations of inorganic and organic arsenic in tissues of marine organisms. Marine bivalve molluscs and fish from offshore waters of the western Gulf of Mexico do show large seasonal variations in tissue concentrations of total arsenic (J. Trefry, Florida Institute of Technology, personal communication). These seasonal variations may reflect seasonal changes in absolute and relative concentrations of different forms of inorganic and organic arsenic in seawater, surficial sediments, and phytoplankton. Ratios of inorganic to organic arsenic in edible tissues of fishery products consumed by humans may vary seasonally as they do in different species of marine invertebrates and fish. Research is needed on seasonal cycles of inorganic and organic arsenic in edible tissues of marine organisms consumed by humans.

Mammals, including humans, readily accumulate inorganic and organic forms of arsenic from their food [121]. The form of arsenic excreted in the urine of human volunteers depends on the forms of arsenic ingested [122]. After eating a meal of Dungeness crab, *Cancer magister*, containing 2,000 μg of unidentified organoarsenic compounds, human volunteers excrete most of the arsenic as an unidentified organic compound (probably arsenobetaine) that yields DMA upon alkaline treatment. Small amounts of MMA and DMA also are excreted, but concentrations of inorganic tri- and pentavalent arsenic remain constant in the urine, indicating that the organic arsenic in the crab tissues is not converted in human tissues to inorganic forms. Vahter [123] suggested that inorganic and organic arsenic from food are detoxified in mammalian liver by the route: As (V) → As (III) → MMA → DMA, explaining the predominance of DMA in human urine.

These observations were recently confirmed by Buchet et al. [121], who showed that when human volunteers are fed mussels containing known amounts of inorganic and organic arsenicals, they excrete more than the expected amount of DMA in the urine, suggesting possible conversion of some ingested inorganic arsenic (3% of the total arsenic in the mussels is inorganic) to DMA. When the volunteers are fed filets of three species of fin fish (ray, cod, and plaice) containing averages of 4.7 to 16.4 μg/g total arsenic, most of it organic, the volunteers excrete 74 to 86% of the ingested arsenic within 48 h [121]. In all cases, the amount of inorganic arsenic excreted in the urine is similar to or less than the amount expected based on the relative amounts of inorganic and organic arsenic in the food, indicating that little or none of the organic arsenic ingested in food is converted to inorganic forms in human tissues.

Complex organic arsenic compounds, such as arsenobetaine, seem to be excreted unchanged by mammals. Human volunteers accumulate organoarsenic when fed marine fish and shellfish, but excrete more than three quarters of the administered dose, most as arsenobetaine, in the urine within a few days [124,125] The half-life of trimethylarsenic (mostly arsenobetaine) in humans is 6 h.

Arsenobetaine and other organoarsenic compounds found in seafoods are not toxic, mutagenic, or carcinogenic when ingested in food by mammals [126,127]. The relative toxicity of arsenic in mammals is As (III) $>$ As (V) $\gg$ MMA, DMA [8].

TOXICITY OF ARSENIC TO MARINE ORGANISMS

Inorganic arsenic is moderately toxic to marine organisms. Laboratory bioassays seem to show that arsenite and arsenate have similar toxicities to marine organisms; this could be caused by speciation of inorganic arsenic in exposure media during the bioassay.

Different species of marine organisms differ widely in their sensitivity to inorganic arsenic. Growth and survival of the microalgae *Tetraselmis chui* and *Hymenomonas carterae* are not affected during exposure to concentrations as high as 1,000 μg/L of arsenite or arsenate [81]. However, growth of the diatom *Skeletonema costatum* is inhibited at a concentration of 20 μg/L arsenite or 13 μg/L arsenate [128]. Growth of *Dunaliella* sp. is inhibited during exposure for 3 d to arsenate concentrations of 100 μg/L or greater, but during continued exposure, growth rate recovers and is normal after 12 d at concentrations up to 2,000 μg/L [129]. Mature cystocarp formation (sexual reproduction) is inhibited in the macroalga *Champia parvula* during exposure to 95 μg/L arsenite; the alga is killed by exposure to 300 μg/L arsenite [130]. A concentration of 10,000 μg/L arsenate in seawater does not kill *Champia.* However, the toxicity of arsenate increases as phosphate concentration in the exposure water decreases, suggesting that dissolved phosphate affects the bioavailability of arsenate.

These results suggest that the toxicity of inorganic arsenic to marine algae is related to its bioavailability. Arsenite is more bioavailable and toxic than arsenate, particularly in the presence of high concentrations of dissolved inorganic phosphate.

Limited published data exist for the toxicity of arsenite and arsenate to marine animals. The median lethal concentration at 96 h (96-h LC50) of arsenite to juvenile bay scallops, *Argopecten irradians,* is 3,490 μg/L [131]. Larvae of Dungeness crabs, *C. magister,* have a 96-h LC50 of 232 μg/L arsenite [132]. The acute toxicities of arsenite to the estuarine amphipods *Corophium insidiosum* and *Elasmopus bampo* are 1,100 μg/L and 2,750 μg/L, respectively [133]. The 96-h LC50 of arsenic trioxide to the crab *Scylla serrata* is 17,000 μg/L [134]. The highest concentration of arsenite tolerated by crabs for 96 h without mortalities is 7,500 μg/L. Acute exposure of the crabs to the 96-h LC50 of arsenite produces a variety of histopathological lesions in the hepatopancreas of the crabs.

The acutely lethal concentration of arsenate to a mysid, *Mysidopsis bahia,* is 2,319 μg/L [135]. Arsenate concentrations in excess of 25,000 μg/L are required to affect survival of adult shrimp of the species *Crangon crangon* [136]. Small individuals are more sensitive than are large individuals. Respiration rates of the shrimp decrease during short-term exposures to 10,000 to 50,000 μg/L arsenate.

The limited available toxicity data do not show a substantial difference in the toxicity of arsenite and arsenate to marine animals. Arsenite is more bioavailable than arsenate to marine animals and, therefore, should be more toxic than arsenate if cellular mechanisms of toxicity of the two arsenic species are similar. In laboratory toxicity tests, arsenite may oxidize to arsenate or may complex with dissolved or colloidal organic matter in the exposure media, reducing the apparent toxicity of the arsenite. Nothing is known about the mechanisms of acute toxic action of inorganic arsenic in tissues of marine animals.

The U.S. EPA acute and chronic water quality criteria (protection of marine life) for arsenite are 69 μg/L and 36 μg/L, respectively [135]. No marine criteria values are available for arsenate or organoarsenic compounds. The acute and chronic criterion concentrations for arsenite are much higher than the concentrations of arsenite or even total inorganic arsenic that have been observed in marine waters. However, concentrations of arsenite could be high enough in estuarine waters subjected to chronic inputs (e.g., from mining and metal smelting) or periodic episodes of bottom water hypoxia to affect some sensitive species of estuarine phytoplankton.

The effects range low (ERL) and effects range median (ERM) guidelines for total arsenic in marine sediments are 8.2 and 70 μg/g dry weight, respectively [137]. The two guidelines define three concentration ranges for total arsenic in sediments. Arsenic concentrations below the ERL are expected to rarely cause adverse effects in benthic organisms; concentrations of arsenic in sediments between the ERL and ERM may occasionally cause adverse effects. Concentrations of arsenic above the ERM value of 70 μg/g are expected to be associated frequently with adverse effects in benthic organisms. The ERM value is several times higher than concentrations of arsenic expected in uncontaminated marine sediments and may well be associated with adverse effects in benthic fauna. However, the ERL concentration seems low for marine sediments, which, even in uncontaminated coastal areas, usually contain between 5 and 15 μg/g arsenic [18]. Concentrations of apparently dissolved arsenite and arsenate in pore water of marine sediments usually are less than about 5 μg/L and, depending on sediment redox potential, much of the arsenic is present as arsenate, MMA, and DMA [24,56,63]. These concentrations of apparently dissolved arsenic in sediment pore water are an order of magnitude or more below concentrations known to be toxic to marine animals. Much of the data upon which the guidelines were based may be from freshwater and low-salinity estuarine sediments, in which much of the arsenic remains in a mobile form as arsenolite.

CONCLUSIONS

Arsenic has a complex biogeochemistry in marine and brackish water ecosystems. In well-oxygenated water and sediments, nearly all the arsenic is present in the thermodynamically more stable pentavalent state. Small amounts of inorganic arsenite and organic compounds of pentavalent arsenic may also be present. In most oxygenated, productive marine ecosystems, arsenite usually represents less than one to no more than about 10 to 20% of the total arsenic. Concentrations of arsenite measured in even the most heavily contaminated estuaries are well below concentrations known to be harmful to marine animals, but approach or occasionally exceed concentrations that could be toxic to sensitive species of phytoplankton. Therefore, inorganic arsenic, at concentrations found in productive, oxygenated seawater and brackish waters does not represent a significant hazard to marine organisms and ecosystems. Natural concentrations of arsenic in coastal marine and ocean waters are always much higher than the U.S. EPA human health (fish consumption) water quality criterion for total arsenic in seawater. This criterion should be revised to reflect the actual concentrations of total and arsenite arsenic in the ocean and in the tissues of marine organisms consumed by humans.

Marine animals have only a limited ability to bioaccumulate inorganic arsenic from solution. Marine plants accumulate arsenate from seawater and convert it to arseno-sugars that can be bioaccumulated from food by marine animals. Nearly all the arsenic in the tissues of marine animals is in the form of nontoxic arsenobetaine. Arsenobetaine and other organoarsenic compounds are excreted rapidly by mammals, and are not toxic to human consumers of fishery products. Because arsenic in marine foods is not present as, nor is it readily converted in marine food chains to inorganic arsenite, it cannot be considered to be a human toxin or carcinogen when ingested by this route [11]. However, marine organisms living in coastal waters and estuaries that are heavily contaminated with inorganic arsenic may accumulate inorganic arsenic to high concentrations in some tissues, particularly the gills and digestive gland/liver, which ordinarily are not consumed by humans. Some species of marine algae contain high concentrations of inorganic arsenic. These could be toxic to humans if consumed in large quantities. More information is needed on the relative concentrations of different forms of arsenic in edible tissues of marine organisms and how these concentrations change seasonally or during the life cycle of the marine organism.

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