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Arsenic Species in Marine Samples*

Kevin A. Francesconi[a,#] *and John S. Edmonds*[b]

[a]*Institute of Biology, Odense University, DK-5230 Odense M, Denmark*

[b]*Western Australian Marine Research Laboratories, PO Box 20, North Beach W.A. 6020, Australia*

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Arsenic occurs in seawater, in predominantly inorganic forms, at concentrations of about 1–2 μg/L. These concentrations are higher than those of most other potentially toxic metals and semimetals. Marine organisms have coped by exploiting the rich organic chemistry of arsenic to transform inorganic arsenic into a range of essentially non-toxic organoarsenic compounds. The resulting diversity of arsenic species found in marine samples is reviewed together with an overview of analytical methods for their determination. The relevance of the chemical form of arsenic to its bioavailability to marine organisms is also discussed.

INTRODUCTION

Although high concentrations of arsenic in marine samples were first reported almost 100 years ago, the large number and diversity of arsenic species in marine samples has been revealed only in the last 20 years. Arsenic occurs in seawater predominantly as the inorganic forms arsenate and arsenite. Marine organisms, unable to avoid exposure to the potentially toxic inorganic arsenic species, have developed novel mechanisms of biotransformation and detoxification. The result is a complex mixture of over 25 arsenic species occurring in marine systems. The distribution of these species,

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Author to whom correspondence should be addressed.

however, varies markedly among the four marine compartments, namely seawater, sediment/porewater, algae, and animals. This paper presents an overview of current knowledge of arsenic species in marine samples. Techniques for identifying and determining the species are described followed by a brief discussion of the importance of chemical form on the bioavailability and bioaccumulation of arsenic. The paper deals only with marine systems; the broader topic of environmental arsenic chemistry has been comprehensively covered in the excellent review of Cullen and Reimer.[1]

ARSENIC SPECIES IN MARINE SAMPLES

In the following, the term arsenic species refers to both compounds and ions of arsenic. We have adopted the convention[1] of not distinguishing between the different levels of protonation of the inorganic arsenic species by referring to them collectively as either arsenite or arsenate for the As(III) or As(V) forms, respectively. Similarly, level of protonation is not considered when describing methylated arsenic species, although with these species the recent comments of Howard[2] are also relevant.

Arsenic Species in Seawater and Sediment/Porewater

The first determination of arsenic species in seawater was carried out in 1926 by Atkins and Wilson,[3] and their results, showing significant concentrations of arsenite (As(III)) as well as the expected arsenate (As(V)), have been confirmed in subsequent studies.[4–6] Thermodynamic calculations indicate that arsenic in oxygenated seawater should exist almost entirely as arsenate; biological reduction, however, can produce appreciable levels of arsenite.[7,8]

Methyl- and dimethyl arsenic species, usually reported as methylarsonate (MA) and dimethylarsinate (DMA), are also detected in seawater (see Figure 1 for chemical structures and acronyms). Studies indicate that these species result from the uptake and subsequent biotransformation of arsenate by phytoplankton.[9–15] In addition to As(III), As(V), MA and DMA, other as yet unidentified arsenic species have been reported in seawater;[13–15] the possible identity of this arsenic is discussed further below.

Some information[16] on arsenic in sediments has been provided by selective extraction procedures. There have been, however, few studies on the arsenic compounds in sediments, largely because the methods necessary to extract the arsenic are likely to change its chemical form. Although arsenic concentrations in deep-sea sediments[17] may be high (up to 450 mg/kg), sediment-bound arsenic is generally regarded as unavailable to biota. The interstitial waters of sediments (porewaters), however, are thought to contain bioavailable arsenic, the chemical form of which has been the subject of

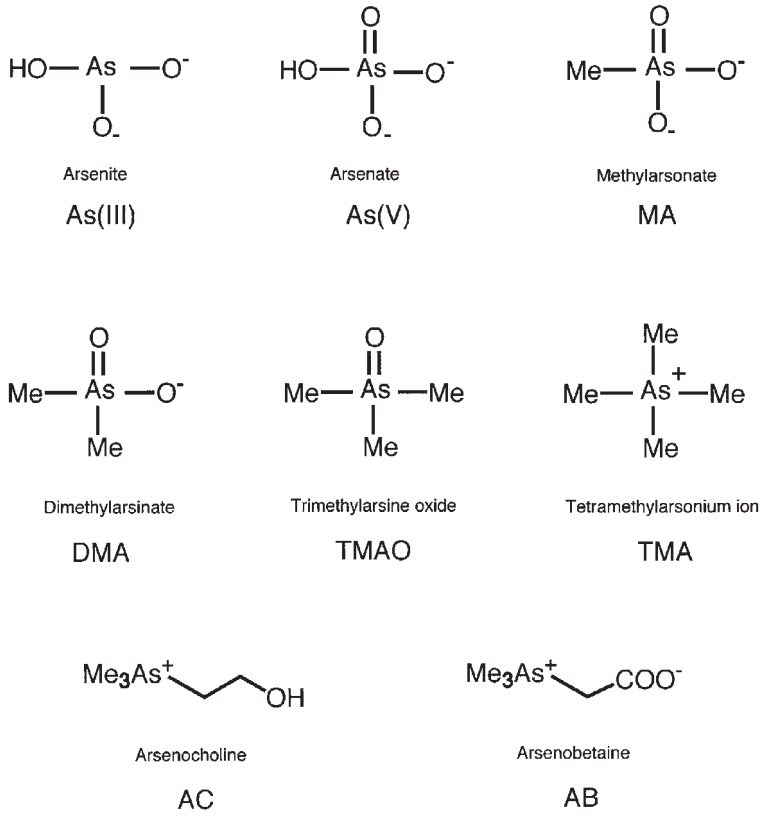

Figure 1. Chemical structures of some marine arsenic species.

several studies.[6,18,19] The results are similar to those reported for seawater: inorganic arsenic predominates and MA and DMA can occur at low but significant levels (*e.g.* 1–4% of total arsenic).[18] In addition to MA and DMA, a trimethylated arsenic species, presumably trimethylarsine oxide (TMAO), has been found in porewater samples.[19] The concentrations of total dissolved arsenic in porewaters are generally considerably higher than those in seawater.

Table I summarizes the arsenic species identified and quantified in seawater and sediment porewater. The data have been obtained using the hydride generation analytical procedure which detects only those arsenic species that give a volatile arsine following reduction (usually with a solution of sodium borohydride). In this regard, the report of »hidden« arsenic in seawater (recorded in Table I under »other cpds. and unknowns«) is of particular interest. Analysis of arsenic in seawater by the hydride generation method before and after a decomposition step (designed to transform all arsenic

TABLE I

Arsenic species in seawater and sediment porewater

Sample	Site	As concn. (μg/L)	As(V)	As(III)	MA	DMA	TMA	Other cpds. and unknowns	Ref.
Surface seawater	East Indian Ocean	0.87	***	**	*	**	NR	NR	12
Surface seawater	Antarctic Ocean	1.1	***	Tr	Tr	*	NR	NR	12
Surface seawater	North Indian Ocean	0.85	***	**	*	**	NR	NR	12
Surface seawater	China Sea	0.64	***	**	*	**	NR	NR	12
Seawater	North-east Pacific and California Shelf	≈ 1–2	***	Tr/**	Tr	Tr	ND	NR	6
Estuarine water	Southampton Water, UK	0.76–1.00	*** (As(V) + As(III))		**	**	ND	**	13
Estuarine water	Tagus estuary, Portugal	24.3	*** (As(V) + As(III))		* (MA + DMA)		ND	**	14
Sediment porewater	Northeast Pacific	≈ 1–2.5	***	Tr	ND	ND	ND	NR	6
Sediment porewater	Coastal British Columbia	3–52	**/***	**/***	Tr/*	Tr/*	Tr/*	NR	19
Sediment porewater	Tamar estuary, UK	5–62	*** (As(V) + As(III))		Tr/*	Tr/*	ND	NR	18

*** Major arsenic constituent, > 50% of total arsenic.
** Significant arsenic constituent, 11–49% of total arsenic.
* Minor arsenic constituent, 1–10% of total arsenic.
Tr trace arsenic constituent, < 1% of total arsenic.
NR not recorded.
ND not detected.

species into arsenate) reveals additional detectable arsenic. The identification of this »hidden« arsenic is essential for a full understanding of arsenic transformations in marine systems. Possible candidates are quarternary arsonium compounds such as arsenobetaine (AB), arsenocholine (AC) and tetramethylarsonium ion (TMA) which cannot be reduced to an arsine without prior decomposition. Arsenosugars are also possible candidates for this »hidden« arsenic; although they can be reduced to arsines without prior decomposition these derivatives would be too involatile for analysis by the hydride generation method.

Arsenic Species in Marine Algae

Algae contain the greatest number of arsenic species among marine samples. Most of the arsenic in algae is bound to carbohydrate molecules; these arsenic compounds are referred to collectively as arsenosugars. Although a total of 15 arsenosugars have been found in marine algae,[20–29] most of the algal arsenic is present as one or more of the four major compounds shown in Figure 2. The structures of the arsenosugars were first determined by spectroscopic methods, mainly ^{1}H-NMR and ^{13}C-NMR spectro-

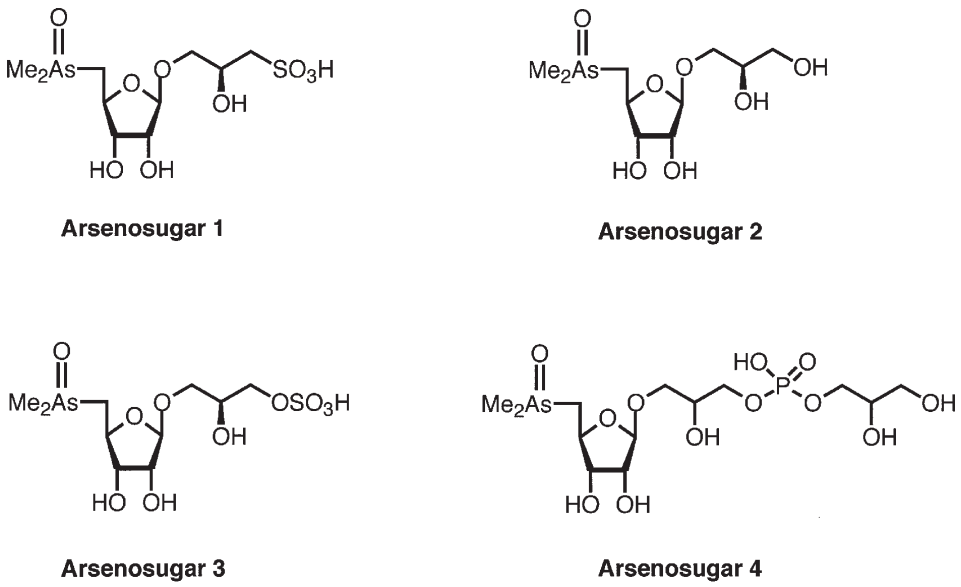

Figure 2. Chemical structures of the four major arsenosugars found in marine algae. A total of 15 arsenosugars have been reported as naturally-occurring constituents of marine algae.

TABLE II

Arsenic species in marine algae

Type/species	As concn. (mg/kg)#	As-sugar **1**	As-sugar **2**	As-sugar **3**	As-sugar **4**	Other As-sugars	As (V)	DMA	Other cpds. and unknowns	Ref.
Green algae										
Codium fragile	0.6 wet	ND	***	ND	**	ND	ND	*	*	27, 30
Ulva pertusa	17.1 dry	ND	**	ND	*	ND	ND	ND	**	30
Bryopsis maxima	19.4 dry	ND	*	ND	**	ND	ND	ND	**	30
Red algae										
Corallina pilulifera	21.6 dry	ND	*	ND	**	ND	ND	ND	*	30
Ahnfeltia paradoxa	11.7 dry	ND	*	*	**	ND	ND	ND	*	30
Coeloseira pacifica	23.1 dry	ND	*	ND	**	ND	ND	ND	**	30
Brown algae										
Ecklonia radiata	10 wet	***	**	NR	**	NR	NR	NR	NR	20, 22
Hizikia fusiforme	10 wet	*	NR	**	Tr	Tr	***	NR	NR	23
Laminaria japonica	4 wet	***	*	NR	**	NR	NR	NR	NR	24
Sphaerotrichia divaricata	2 wet	*	***	NR	**	NR	NR	NR	NR	26
Undaria pinnatifida	2.8-4.5 wet	***	**	NR	**	**	NR	NR	NR	30, 32
Sargassum thunbergii	4 wet	NR	NR	**	NR	Tr	NR	NR	NR	25
Sargassum lacerifolium	40 wet	*	*	***	**	Tr, (4 cpds.)	NR	Tr	Tr	28

\# Wet or dry weight basis as shown.
*** Major arsenic constituent, 50% of total water-soluble arsenic.
** Significant arsenic constituent, 11-49% of total water-soluble arsenic.
* Minor arsenic constituent, 1-10% of total water-soluble arsenic.
Tr trace arsenic constituent, < 1% of total water-soluble arsenic.
NR not recorded.
ND not detected.

scopy, following isolation of the compounds. Subsequent work employing chromatographic separations and arsenic-specific detectors demonstrated that these compounds were widespread in algae.[30] Table II provides a representative summary of arsenic compounds in marine algae. Although most of this work has been carried out on macroalgae, a recent study[31] has shown that the unicellular alga *Chaetoceros concavicornis* also contains arsenosugars, suggesting that these compounds are likely to be general algal metabolites.

The distribution of the arsenic compounds among algae may have taxonomic significance. For example, in brown algae the major compounds are the arsenosugars **1** and **3** whereas arsenosugars **2** and **4** predominate in red and green algae. Although the data are still relatively few, differences appear to exist between the orders of brown algae. Three species so far examined in the order Fucales (*Hizikia fusiforme* and *Sargassum spp*) contain arsenosugar **3** as the major arsenic compound, whereas the three Laminariales species (*Ecklonia radiata, Laminaria japonica,* and *Undaria pinnatifida*) contain arsenosugar **1** as the major compound.

Further work is required on the distribution of the arsenic compounds among algal orders. The possibility exists that these compounds may serve as highly specific tracers within marine food chains. Recent work[31] on arsenic transformations in short marine food chains has provided examples of the potential discriminating power of arsenosugars as food chain tracers.

Chemical syntheses have also been reported[28,29,33,34,35] for some of the arsenosugars. Three of the four major compounds (arsenosugars **1**, **3**, and **4**), however, remain to be synthesised. The availability of synthetic quantities of these arsenic compounds would greatly facilitate identification of arsenosugars in biota and studies on arsenic biotransformations in marine systems.

Other arsenic species commonly found in algae are arsenate and DMA. These species are generally minor constituents although high concentrations of arsenate were found in two species of brown algae.[23,36,37,38]

The origin of arsenosugars has yet to be established although a biogenetically sound scheme beginning with arsenate in seawater has been proposed.[39,] The scheme involves methylation and alkylation of trivalent arsenic compounds by *S*-adenosylmethionine (AdoMet), following the pathway first proposed by Challenger[40] for the conversion of arsenate to trimethylarsine by the mould *Scopulariopsis brevicaulis*. Although the arsenosugars in algae are thought to be detoxification end products, a possible biochemical role for these compounds was suggested.[39] Arsenosugars have also been proposed[39] as probable precursors of other arsenic compounds found in marine animals. This hypothesis awaits confirmation.

Arsenic Species in Marine Animals

The major arsenic compound in marine animals is arsenobetaine. Since its isolation and identification from the western rock lobster 21 years ago,[41] this stable quaternary arsonium compound has been shown to be present in virtually all marine animals, and in most cases it is by far the predominant arsenic species.[42]

The tetramethylarsonium ion is also commonly found in marine animals,[43–47] particularly in bivalve molluscs where it can be the major form.[47] Trimethylarsine oxide and arsenocholine also occur, generally as minor arsenic constituents although exceptions have been reported.[48] Arsenosugars are found in herbivorous marine animals[39] where the source is almost certainly the marine algae on which the animals feed. With few exceptions, however, arsenosugars are minor arsenic species in herbivorous marine animals, and they are generally absent at higher trophic levels.

Table III summarises the arsenic species recently identified in marine animals. The ubiquity and predominance of arsenobetaine is perhaps not fully represented by this table. With the recent availability of analytical techniques with low detection limits, interest in examining minor arsenic species, often in unusual marine animals, has increased. A compilation[42] of the early work demonstrating the ubiquity of arsenobetaine in marine animals was published in 1993.

DETERMINATION OF ARSENIC SPECIES

Methods for the identification and quantification of arsenic species may be divided into three categories depending on the level of information that they provide. First level techniques distinguish only between inorganic and organic arsenic; second level techniques are capable of analysing the two inorganic forms in addition to three of the simple methylated arsenic species (MA, DMA, and TMAO); and third level techniques extend the range to quaternary compounds such as arsenobetaine, and other more complex arsenic species such as arsenosugars. Each of these methods has a role in the determination of arsenic compounds in marine samples.

A method that distinguished only between inorganic and organic arsenic was employed widely in the 1970s and 1980s (*e.g.* Ref. 53). The method is based on the conversion of inorganic arsenic to $AsCl_3$ by treatment of the sample with KI (to reduce As(V) to As(III)) and strong HCl. The $AsCl_3$ is then separated from the organoarsenic constituents by distillation or by extraction with a non-polar solvent; arsenic in the two fractions is subsequently determined by standard techniques. Although the method appears to be little used today, possibly because it provides only limited information on arsenic species, it remains relevant for human health studies which gen-

TABLE III

Arsenic species in marine animals

Type/species	As concn. (mg/kg)#	AB	AC	TMA	TMAO	DMA	MA	As(III)	As(V)	As-sugars	Other cpds. and unknowns	Ref.
FISH												
– mackerel	3.8 dry	**	NR	NR	NR	*	ND	NR	**	NR	*	49
– mixed (4 species)	13.7–30.7 dry	***	NR	NR	NR	ND	ND	NR	ND	NR	NR	49
– mixed (3 species)	62.2–196.1 dry	***	NR	NR	NR	ND	ND	NR	ND	NR	NR	49
– plaice (*Pleuronectes platessa)*	41.9 dry	***	Tr	Tr	Tr	NR	ND	NR	ND	NR	Tr	50
– tuna	3.2 dry	***	Tr	Tr	Tr	NR	NR	NR	NR	NR	Tr	50
– silver drummer (*Kyphosus sydneyanus)*	1 wet	ND	ND	*	***	ND	ND	ND	ND	*	ND	31
– Estuary catfish (*Cnidoglanus macrocephalus*)	≈0.5 wet	***	NR	NR	**	NR	NR	NR	NR	NR	NR	51
CRUSTACEANS												
– shrimp (3 species)	15.1–44.1 dry	***	Tr/ND	*	ND	NR	ND	Tr/NR	Tr/ND	NR	Tr	50
– crab (*Cancer pagurus)*	118 dry	***	ND	Tr	Tr	NR	ND	Tr	Tr	NR	Tr	50
– amphipods (*Allochestes compressa)*	NR	***	ND	ND	ND	ND	ND	ND	ND	**	ND	31
– krill (*Euphausia superba)*	NR	***	ND	ND	ND	**	ND	ND	ND	*	ND	31
MOLLUSCS												
– *Meretrix lusoria*												
foot muscle	3.6 wet	***	ND	**	NR	NR	NR	NR	NR	NR	**	43
midgut gland	6.6 wet	**	ND	*	NR	NR	NR	NR	NR	NR	**	43
gill	23.8 wet	*	ND	***	NR	NR	NR	NR	NR	NR	*	43

Type/species	As concn. (mg/kg)#	AB	AC	TMA	TMAO	DMA	MA	As(III)	As(V)	As-sugars	Other cpds. and unknowns	Ref.
– clams (5 species)	1.2–2.2 wet	**	NR	**	ND 4sp *(1 sp)	NR	NR	NR	NR	NR	**	47
– *Tectus pyramis*												
foot muscle	4.2 wet	***	ND	*	NR	NR	NR	NR	NR	NR	**	44
midgut gland	7.5 wet	**	ND	**	NR	NR	NR	NR	NR	NR	**	44
– *Haliotis roeii*												
foot muscle	1.0 wet	***	ND	*	ND	ND	ND	ND	ND	*	ND	31
midgut gland	NR	**	ND	*	ND	ND	ND	ND	ND	***	ND	31
OTHER												
– Turtle (*Dermochelys coriacea*)												
muscle	4.4 wet	***	ND	ND	ND	ND	ND	ND	Tr.	ND	ND	48
heart	0.7 wet	***	*	ND	ND	ND	ND	ND	*	ND	ND	48
liver	1.2 wet	***	**	ND	ND	ND	ND	ND	**	ND	ND	48
MARINE REFERENCE MATERIALS												
DORM-1 (dogfish muscle)	17.7 dry	***	Tr	*	Tr	NR	ND	ND	ND	NR	*	50
DOLT-1 (dogfish liver)	10.1 dry	***	Tr	Tr	Tr	**	ND	ND	*	NR	*	50
TORT-1 (lobster midgut gland)	24.6 dry	***	Tr	Tr	Tr	*	ND	ND	ND	NR	*	50
NIES No. 6 (mussel)	9.2 dry	**	Tr	Tr	Tr	***	ND	ND	*	**	*	50, 52
NIST SRM 1566a (oyster)	13.4 dry	**	Tr	Tr	ND	***	Tr	ND	*	**	**	50, 52

\# Wet or dry weight basis as shown.
*** Major arsenic constituent, 50% of total water-soluble arsenic.
** Significant arsenic constituent, 11–49% of total water-soluble arsenic.
* Minor arsenic constituent, 1–10% of total water-soluble arsenic.
Tr trace arsenic constituent, < 1% of total water-soluble arsenic.
NR not recorded.
ND not detected.

erally consider only the inorganic portion of total arsenic in seafoods.[54] The method also has the advantage of being accessible to laboratories with only routine analytical instruments such as atomic absorption spectrometers. In addition, the method determines the inorganic/organic arsenic quantities on the whole sample, not an extract thereof. Consequently, potential problems associated with extraction of biological tissue needed for the solubilization of arsenic compounds are avoided.

Second level analyses for arsenic species are provided by hydride generation techniques. These methods were reported[55] for arsenic in 1973, and they find widespread application to marine samples today. Reduction of inorganic arsenic, MA, DMA or TMAO produces characteristic volatile derivatives (arsines) which may be flushed from the sample matrix, collected in a cold trap, and then separated from each other by fractional distillation or chromatography prior to arsenic specific detection.[56] Hydride generation techniques are particularly suitable for seawater samples in which most of the arsenic present forms volatile arsines. However, the limitation of the technique has been highlighted by the reported presence of arsenic species in estuarine water which do not form a volatile arsine.[13,14] These arsenic compounds may well be important in the cycling of arsenic and techniques need to be developed for their quantitative determination.

The third level methods combine chromatographic separation of the native arsenic compounds with arsenic-specific detection. High performance liquid chromatography (HPLC) with ion exchange or reversed phase columns is the most common separation method. In practice, the separation of the arsenic species obtained on these systems is partly determined by the sensitivity of the detector; for less sensitive detectors, a large quantity of sample must be injected onto the column which in turn compromises the chromatographic resolution. Although atomic absorption and atomic emission spectrometers can be directly connected to a HPLC system and used as arsenic-specific detectors, they usually lack the low detection limits necessary to examine crude marine extracts. Mass spectrometry following decomposition of the arsenic species and ionisation to the $^{75}As^{+}$ ion by inductively coupled plasma (ICP-MS) provides the necessary low detection limits.[56] Such HPLC/ICP-MS systems allow the separation and determination of arsenic species in crude marine extracts without pretreatment. When combined with appropriate standard compounds, HPLC/ICP-MS can provide comprehensive data on arsenic species in marine samples.[31,48–50,52]

Detection limits for third level analyses can be lowered by derivatisation of the arsenic compounds after the chromatographic separation. For example, on-line decomposition of organoarsenic compounds to inorganic arsenic in the HPLC column effluent permits hydrides to be generated and detected.[57] Peak broadening caused by diffusion of arsenic species during decomposition and derivatisation can compromise the separation. The resolu-

tion can be considerably improved with the technique of argon-segmented flow in the post-column effluent.[58] The incorporation of the decomposition/derivatisation step allows relatively simple instruments such as atomic absorption spectrometers to be used for the analysis of crude marine extracts.

Third level techniques should not be viewed as providing full information of the arsenic species present – at least not in all cases. Clearly, they are restricted by the availability of standard compounds. Arsenic species with, as yet, unknown structures occur in marine samples, and although third level techniques may detect the presence of these species they can provide no structural data. Newer techniques[59–62] for determining arsenic species using MS/MS systems for both separation and detection may overcome this restriction. These methods are not yet in common use. The structural information provided by MS/MS techniques may enable identification of arsenic species without standard compounds. These techniques also have the potential to provide structural elucidation of novel arsenic species. In addition, the combination of molecular ion and fragment ion specificity available with MS/MS systems may enable determination of arsenic species without prior chromatographic separation.

Information on arsenic species from third level methods can also be restricted by problems associated with extraction (solubilization) of the arsenic compounds. Mild, polar solvents such as water or water/methanol mixtures are generally used to solubilize the arsenic species prior to their determination. Although water-soluble arsenic species predominate in marine samples, lipid-soluble arsenic species do also occur and can be the major forms in some marine samples. Routine chromatographic procedures have not yet been developed for lipid-soluble arsenic species.

Methanol is probably the most commonly used solvent for extracting arsenic species from marine biological tissue. Evaporation of the methanol and partitioning the residue between diethyl ether/water can provide information on the relative quantities of lipid-soluble and water-soluble arsenic. Alternatively, methanol/chloroform/water mixtures can be used on the original biological tissue. The extraction efficiencies of a chloroform/methanol/water mixture and an enzymatic digestion procedure were determined with fish muscle tissue.[49] Both procedures recovered the majority of the arsenic in the extract. However, because the samples contained virtually all of their arsenic as arsenobetaine, the effectiveness of the extraction procedures on other arsenic species can not be evaluated.

Arsenic remaining after methanol extraction may be residue-bound, or may reflect incomplete extraction of some of the more polar arsenic species. For example, although HPLC/ICP-MS analysis of the methanol extract of freeze-dried turtle liver indicated that arsenate was only a trace constituent, a subsequent aqueous extraction of the same material showed that ar-

senate constituted 35% of the total extractable arsenic.[48] Some of the organoarsenic compounds (arsenosugar **4** for example) are also very polar and their concentrations in biological samples may be underestimated if methanol is used as the extractant. Thus, for some marine samples at least, the pattern of arsenic species is likely to depend on the extraction methodology. There is an increasing body of data on arsenic species in marine biological samples. Evaluation and comparison of these data might well be simplified by the adoption of standard extraction procedures for solubilizing the arsenic species prior to analysis.

INFLUENCE OF CHEMICAL FORM ON ARSENIC BIOACCUMULATION

Striking differences in the distribution of arsenic species among the various marine compartments exist (Tables I, II, III). Inorganic arsenic predominates in seawater, arsenosugars in algae, and arsenobetaine in marine animals. These differences may be due, at least in part, to the relative bioavailability and bioaccumulation of the arsenic species.

Arsenate in seawater is bioavailable to algae, probably because of its chemical similarity to the essential phosphate anion, and is readily taken up in that form. However, algae generally do not accumulate this arsenate but rapidly detoxify it by a process of methylation and alkylation, and accu-

TABLE IV

Arsenic concentrations in mussels (*Mytilus edulis)* following exposure to various arsenic compounds

Treatment	Mean arsenic concn.* mg/kg wet wt. $n = 10$
Control	4.7
Arsenite	5.8
Arsenate	3.9
Methylarsonate	5.4
Dimethylarsinate	5.4
Trimethylarsine oxide	4.9
Tetramethylarsonium ion	15.1
Arsenocholine	45.4
Arsenobetaine	139

* Following a ten day exposure to seawater spiked with the arsenic species at a concentration of 100 μg As/L (Ref. 65).

mulate the resultant end products, namely arsenosugars. Proposed mechanisms for this process of accumulation/detoxification have been discussed.[63]

The origin of arsenic species found in marine animals is more speculative. Arsenobetaine and the tetramethylarsonium ion (TMA), present at high concentrations in marine animals, have not yet been detected in seawater, sediments or algae. Their presence in marine animals may represent a process of selective bioaccumulation. Experimentation so far suggests that the bioavailability of arsenic compounds to marine animals is highly dependent on chemical form, with laboratory experiments demonstrating that arsenobetaine is accumulated much more readily than inorganic arsenic or other organoarsenic compounds. For example, feeding experiments showed that mullet (*Aldrichetta forsteri*) retain about 40% of their ingested arsenobetaine but only ≈ 0.3% of their ingested arsenate.[64] Similarly, uptake of arsenic from water by mussels *Mytilus edulis* is highly dependent on the form of arsenic (Table IV); arsenobetaine was avidly bioaccumulated by the mussels, whereas other forms of arsenic showed no detectable accumulation.[65] Tetramethylarsonium ion is also bioaccumulated by the mussels but to a lesser extent than arsenobetaine, in keeping with the observed relative quantities of these arsenic species in marine animals. Both arsenobetaine and TMA are bioaccumulated unchanged by the mussels.

Arsenocholine behaves differently; it is readily biotransformed by both fish[64] and mussels[65] to arsenobetaine. Other arsenic species, perhaps those present in seawater and algae, may also be transformed to arsenobetaine within animals. The presence of arsenobetaine in so many diverse marine animals, however, suggests an alternative hypothesis: that the biogenesis of arsenobetaine occurs outside the animal, perhaps by microbially mediated processes. Strong support for this hypothesis was provided by experiments indicating that arsenobetaine might be formed from MA and DMA by microbial activity in seawater.[66,67] Recent work[68] describing the arsenic species in deep-sea vent organisms also suggests a microbial role in the formation of arsenobetaine.

All data indicate that arsenobetaine is highly bioavailable to marine animals. Consequently, mere traces of arsenobetaine in seawater or sediment porewaters might be sufficient to result in the demonstrated ubiquity of arsenobetaine in marine animals. Techniques for the determination of arsenic species are constantly improving and they may soon enable the detection of trace, but possibly significant, concentrations of arsenobetaine in seawater and porewaters.

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SAŽETAK

Kemijski oblici arsena u marinskim uzorcima

Kevin A. Francesconi i John S. Edmonds

Arsen se u morskoj vodi pojavljuje pretežito u anorganskom obliku, u koncentracijama približno 1–2 μg/L. Te su koncentracije više od koncentracija ostalih potencijalno toksičnih kovina i polukovina. Marinski organizmi koriste složene organsko-kemijske reakcije arsena transformirajući anorganske kemijske oblike arsena u niz uglavnom netoksičnih organskih spojeva arsena. Posljedica toga je raznolikost kemijskih oblika arsena koju nalazimo u marinskim uzorcima. U radu se daje pregled specija arsena kao i analitičkih metoda koje se koriste za njihovo utvrđivanje. Također se diskutira važnost kemijskih oblika arsena za njegovu biološku dostupnost morskim organizmima.