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Contribution of Arsenic Species in Unicellular Algae to the Cycling of Arsenic in Marine Ecosystems

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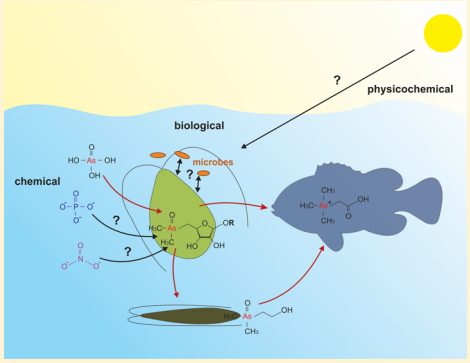
ABSTRACT: This review investigates the arsenic species produced by and found in marine unicellular algae to determine if unicellular algae contribute to the formation of arsenobetaine (AB) in higher marine organisms. A wide variety of arsenic species have been found in marine unicellular algae including inorganic species (mainly arsenate—As(V)), methylated species (mainly dimethylarsenate (DMA)), arsenoribosides (glycerol, phosphate, and sulfate) and metabolites (dimethylarsenoethanol (DMAE)). Subtle differences in arsenic species distributions exist between chlorophyte and heterokontophyte species with As(V) commonly found in water-soluble cell fractions of chlorophyte species, while DMA is more common in heterokontophyte species. Additionally, different arsenoriboside species are found in each phyla with glycerol and phosphate arsenoribosides produced by chlorophytes, whereas glycerol, phosphate, and sulfate arsenoribosides are produced by heterokontophytes, which is similar to existing data for marine macro-algae. Although arsenoribosides are the major arsenic species in many marine unicellular algal species, AB has not been detected in unicellular algae which supports the hypothesis that AB is formed in marine animals via the ingestion and further metabolism of arsenoribosides. The observation of significant DMAE concentrations in some unicellular algal cultures suggests that unicellular algae-based detritus contains arsenic species that can be further metabolized to form AB in higher marine organisms. Future research establishing how environmental variability influences the production of arsenic species by marine unicellular algae and what effect this has on arsenic cycling within marine food webs is essential to clarify the role of these organisms in marine arsenic cycling.



INTRODUCTION

In nature, arsenic (As) is widely distributed in all organisms, although it has no known biological function.[1] Although As is present in all environments, total arsenic concentrations in marine organisms are higher (1−1000 μg g^{-1} dry mass) than in terrestrial animals and plants (0.1−10 μg g^{-1} dry mass).[1,2] In uncontaminated environments, total arsenic concentrations in seawater are approximately 1−2 μg L^{-1}.[1,3,4] In most environments, arsenate—As(V) (Figure 1)— is the major arsenic species found in seawater, with arsenite—As(III) (Figure 1)—also present in appreciable concentrations.[3] In addition, inorganic arsenic species comprise the majority of arsenic found in marine sediments.[5] Inorganic arsenic species found in both seawater and sediments are highly toxic,[3] and therefore considerable research has investigated how marine organisms detoxify constant exposure to inorganic arsenic.[6−17]

Dimethylarsenoribosides, commonly known as arsenoribosides or arsenosugars, are the major arsenic species found in marine macro-algae.[18−23] The common arsenoribosides are differentiated by end groups containing glycerol (Gly-); phosphate (PO_4-), sulfonate (SO_3-), and sulfate (OSO_3-)[18−20] (Figure 1). Other arsenic species such as thio-arsenoribosides, thio-dimethylarsenoethanol (thio-DMAE), dimethylarsenoethanol (DMAE), dimethylarsenoacetate (DMAA), methylarsenate (MA), dimethylarsenate (DMA) (Figure 1) and As(V) have been associated with decomposing macro-algal tissue.[24−27] Arsenobetaine (AB) is the major arsenic species in almost all marine animals, typically accounting for more than 80% of the water-soluble arsenic content.[3,9,28−30] Other arsenic species such as thio-arsenoribosides, thio-DMAE, DMAE, DMAA, tetramethylarsonium ion (TETRA), arsenocholine (AC), dimethylarsenopropionate (DMAP), and trimethylarsenopropionate (TMAP) (Figure 1) are consistently found in marine animals, however, generally in low concentrations and proportions.[1,10,14,31]

Many published studies describe total arsenic concentrations and arsenic species in higher marine organisms such as macro-algae,[18−22,24−26,32−39] seagrasses,[12,13,32,40,41] invertebrates,[6−8,10,12,13,15,29,42−48] and fish,[6,7,9,10,12,13,49−53] with many of these investigating arsenic concentrations and species within food webs.[6−17] Unicellular algae (both pelagic and benthic) are integral components of marine food webs[54−56] but have been consistently overlooked with regard to their importance in marine arsenic cycling. In this context unicellular algae is the collective term given to single-celled photosynthetic organisms that occupy all aquatic ecosystems.[57] Although unicellular algae as a group are diverse, they all share a common trait in obtaining energy from sunlight for growth and cell division.[58] Unicellular algae are thus photoautotrophic and are responsible

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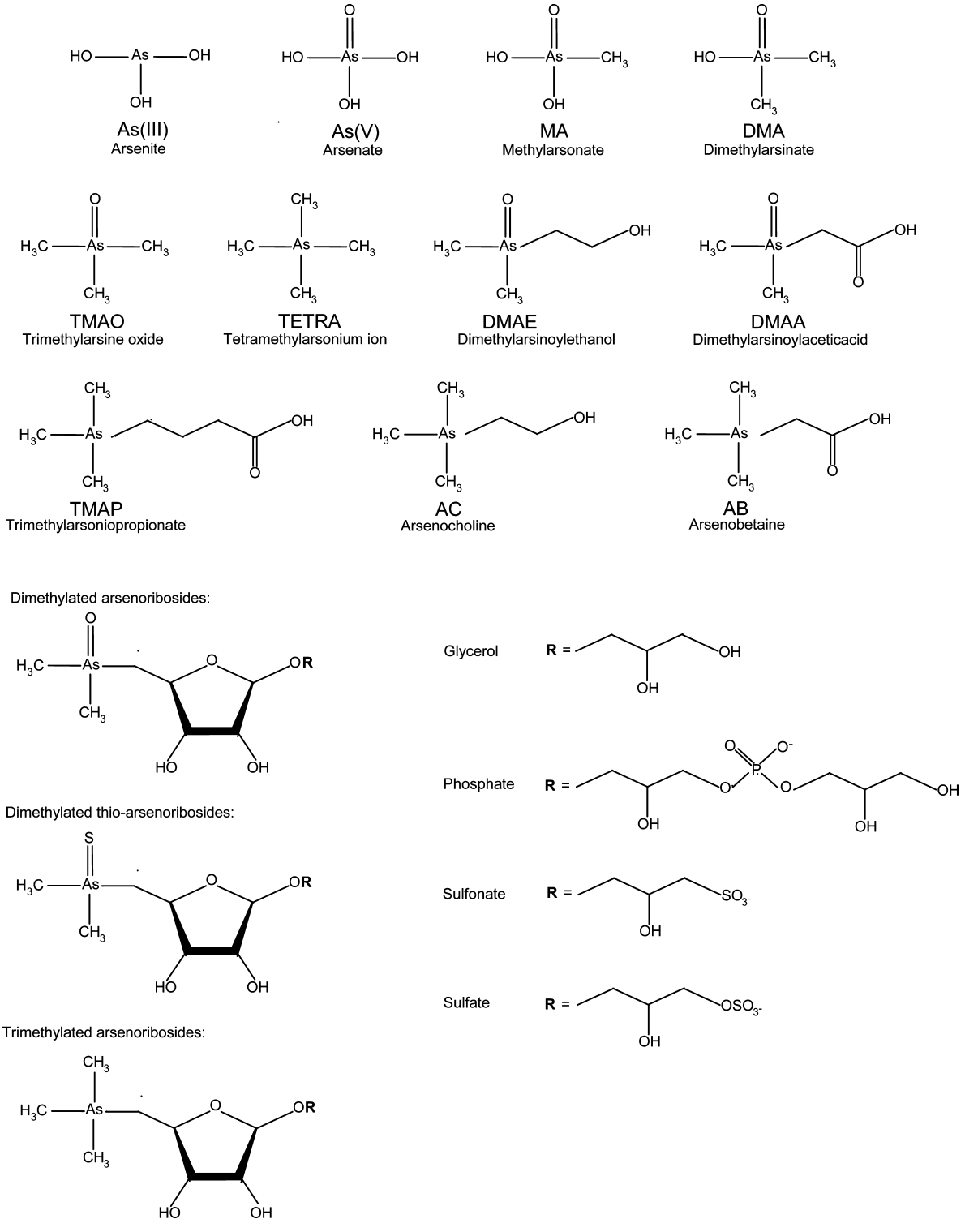

Figure 1. Structures of common arsenic species.

for the bulk (>70%) of primary production in marine ecosystems.[55,56] Because unicellular algae are a major food source in marine ecosystems, they are also likely to be a source of many of the precursors in the formation of AB, the major water-soluble arsenic species in marine animals (Figure 2).[11,14,15]

Recently there has been a renewed interest in the arsenic species found in marine unicellular algae[59−65] and the influence of these organisms in the cycling of arsenic in marine ecosystems. Although research on arsenic species distributions in marine unicellular algae is in its infancy with only 10 species encompassing two phyla (Tables 1−3) currently assessed, a review on the current state of the peer-reviewed literature is required to illustrate how these organisms contribute to marine arsenic cycling and also highlight important areas of future research. This review synthesizes current published research reported on the arsenic species present in marine unicellular algae to answer the following questions:

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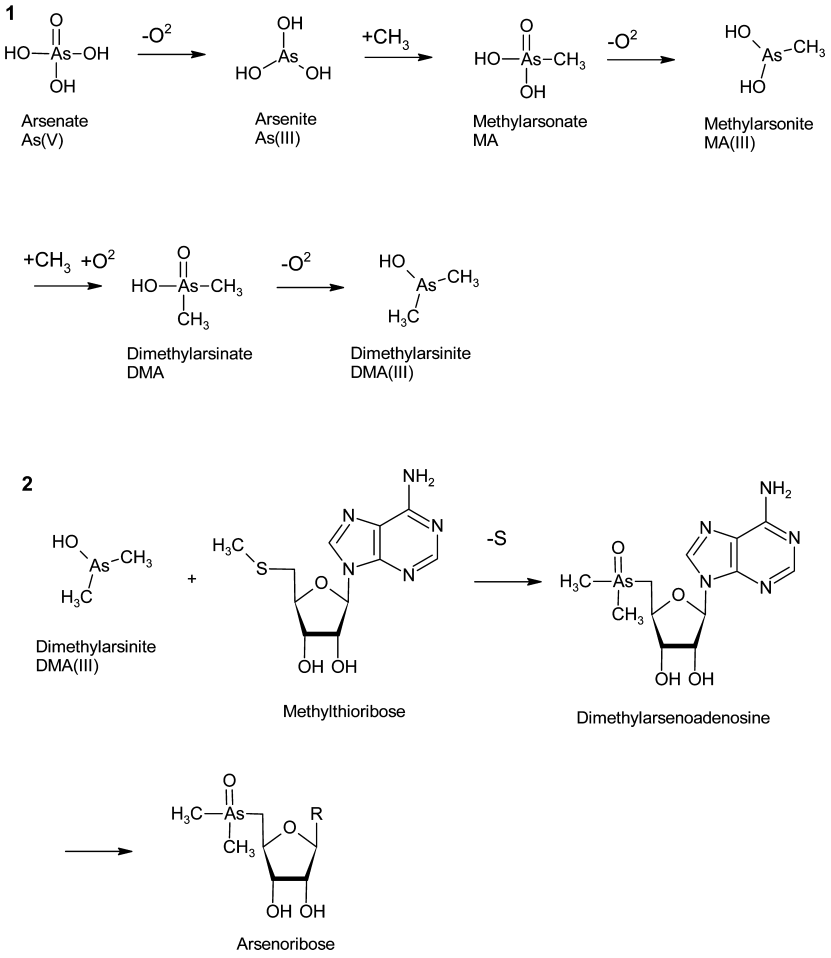

Figure 2. (1) Challenger biomethylation pathway describing the methylation of As(V) by marine primary producers. Adapted from Challenger[71]. (2) Extension of the Challenger pathway[71] to form arsenoribosides in marine primary producers. Adapted from Edmonds and Francesconi.[1]

(a) What arsenic species are found in marine unicellular algae?

(b) Are the arsenic species found in marine unicellular algae similar to those found in marine macro-algae?

(c) Can existing research identify physicochemical, chemical, or biological variables that influence the arsenic species found in marine unicellular algae?

(d) Are the arsenic species found in marine unicellular algae likely to contribute to the formation of AB in marine animals?

■ ARSENIC SPECIES FOUND IN MARINE UNICELLULAR ALGAE

This section of the review synthesizes information on the arsenic species that have been found in unicellular algae reported in the peer-reviewed literature. Within this section, arsenic species are grouped into five groups based upon the major arsenic species found in marine environments—inorganic, methylated, arsenoribosides, thio-arsenic, and metabolized arsenic species. The arsenic species found in marine unicellular algae will also be discussed as to whether they are present in different biochemical cell fractions, i.e., water-soluble (cystolic), lipid-soluble (lipid), and residue (cell membranes and debris) fractions. Arsenic species in these fractions are extracted using various methanol−water (cystolic),[31] chloroform−methanol (lipid)[66] and 1% HNO_3 digestion (residue)[67] extraction procedures. An assessment of the arsenic species in different biochemical cell fractions of unicellular algae is required as this almost certainly influences the ability of arsenic species to be transferred within marine food webs.

Inorganic Arsenic Species. As(V) and As(III) have been found in numerous marine unicellular algal species[59,60,62−65,68,69] in all three major biochemical cell fractions[60,62−64] (Tables 1−3). In cystolic cell fractions, As(V) is the major arsenic species accounting for up to 99% of the total arsenic within the fraction in some studies[68] (Table 1). The presence of As(V) within cystolic fractions of marine unicellular algae is typically associated with environmentally unrealistic As(V) exposures (i.e., milligram per liter concentrations)[59,68,69] and in addition chlorophyte species tended to have greater cystolic As(V) concentrations than heterokontophytes (Table 1).

Both As(V) and As(III) have been identified in lipid fractions of various marine unicellular algal species (Table 2). For most unicellular algae, however, As(V) concentrations are lower in lipid-cell fractions in comparison to concentrations in cystolic fractions[60−64] (Table 2). The only exception to this was when *D. tertiolecta* was exposed to As(V) at a concentration of 50 μg of As L^{-1} in which over 50% of the arsenic in the fraction was found as As(V)[63] (Table 2). Unlike in cystolic fractions, As(III) is regularly identified in lipid fractions and for some species—*D. tertiolecta* and *T. pseudonana*—As(III) concentrations were greater than As(V) concentrations[60,62] (Table 2).

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Table 1. Arsenic Species Present in Water-Soluble Cell Fractions of Various Marine Phytoplankton Species Reported in the Scientific Literature[a]

Algal Species	Arsenic Treatment Concentration + species (μg As L^{-1})	Total As (μg As g^{-1})	Inorganic		Methylated			Arsenoriboside			Other	Source
			As(V) μg g^{-1} (%)	As(III) μg g^{-1} (%)	MA μg g^{-1} (%)	DMA μg g^{-1} (%)	TMA μg g^{-1} (%)	Gly μg g^{-1} (%)	PO_4 μg g^{-1} (%)	OSO_3 μg g^{-1} (%)	DMAE μg g^{-1} (%)	
Chlorophytes												
Chlorella salina	75 As(V)	N.S.	(55)*	(32)*	(2)*	(7)*						Karadjova et al. [65]
C. salina	75 As(III)	N.S.	(2)*	(81)*	(3)*	(9)*						Karadjova et al. [65]
C. salina	75 DMA	N.S.			(2)*	(93)*						Karadjova et al. [65]
Dunaliella salina	100,000 As(V)	62,000	61,800 (>99)		Trace* (<1)	200 (<1)	Trace* (<1)					Yamaoka et al. [68]
D. salina	100,000 As(III)	109,000	108,300 (>99)		100 (<1)	600 (<1)	Trace* (<1)					Yamaoka et al. [68]
Dunaliella tertiolecta	2 As(V) (3 mg PO_4^{3-} L^{-1})	3.84	3.3 (86)			0.28 (8)		0.04 (1)	0.19 (5)			Foster et al. [64]
D. tertiolecta	2 As(V) (1.2 mg PO_4^{3-} L^{-1})	2.66	1.8 (61)		0.03 (1)	0.54 (20)		0.07 (2)	0.18 (7)			Foster et al. [64]
D. tertiolecta	2 As(V) (0.6 mg PO_4^{3-} L^{-1})	2.9	1.6 (54)			0.55 (20)		0.13 (5)	0.57 (20)			Foster et al. [64]
D. tertiolecta	2 As(V) (8 days)	0.26	0.23 (88)			0.02 (8)		0.03 (13)	0.04 (15)		0.01 (4)	Duncan et al. [60]
D. tertiolecta	2 As(V) (14 days)	0.31	0.19 (62)			0.02 (6)		0.05 (16)	0.05 (16)		0.01 (6)	Duncan et al. [60]
D. tertiolecta	2 AB (8 days)	0.35	0.24 (70)			0.03 (8)		0.01 (4)	0.02 (7)		0.02 (5)	Duncan et al. [60]
D. tertiolecta	2 AB (14 days)	0.1	0.06 (60)			0.004 (4)		0.01 (13)	0.02 (15)			Duncan et al. [60]
D. tertiolecta	2 MA (8 days)	0.3	0.23 (76)		0.02 (5)	0.02 (5)		0.01 (4)	0.02 (5)			Duncan et al. [60]
D. tertiolecta	2 MA (14 days)	0.23	0.15 (63)		0.03 (11)	0.03 (9)		0.01 (4)	0.01 (6)			Duncan et al. [60]
D. tertiolecta	2 As(V) (7 days)	1.00	0.52 (46)		0.02 (2)	0.05 (5)		0.33 (29)	0.21 (18)			Duncan et al. [62]
D. tertiolecta	2 As(V) (42 days)	0.10	0.04 (38)	0.03 (25)		0.01 (10)		0.02 (18)	0.01 (9)			Duncan et al. [62]
D. tertiolecta	2 As(V) (Continuous)	2.50	0.70 (28)			0.44 (18)		0.83 (33)	0.53 (21)			Duncan et al. [62]
D. tertiolecta	50 As(V) (3 mg PO_4^{3-} L^{-1})	2.74	2.34 (99)	0.01 (1)								Duncan et al. [63]
D. tertiolecta	2 As(V) (3 mg PO_4^{3-} L^{-1})	0.18	0.12 (93)	0.01 (7)								Duncan et al. [63]
D. tertiolecta	50 As(V) (0.1 mg PO_4^{3-} L^{-1})	0.82	0.52 (66)	0.20 (26)					0.06 (8)			Duncan et al. [63]
D. tertiolecta	2 As(V) (0.1 mg PO_4^{3-} L^{-1})	0.29	0.17 (71)	0.04 (16)					0.03 (13)			Duncan et al. [63]
D. tertiolecta	2 As(V) (operationally sterile)	0.14	0.007 (16)		0.001 (1)	0.002 (4)		0.022 (55)	0.001 (26)			Duncan et al. [61]
D. tertiolecta	2 As(V) (Bacteria exposed)	0.14	0.009 (18)					0.038 (71)	0.005 (11)			Duncan et al. [61]
Ostreococcus tauri	2,221 As(III) (4 days)	N.S.	(76)*	(24)*								Zhang et al. [59]
O. tauri	2,221 As(III) (8 days)	N.S.	(78)*	(20)*		(2)*						Zhang et al. [59]
O. tauri	2,221 As(III) (12 days)	N.S.	(80)*	(18)*		(2)*						Zhang et al. [59]
O. tauri	2,221 As(III) (16 days)	N.S.	(86)*	(13)*		(1)*						Zhang et al. [59]
O. tauri	2,221 As(V) (4 days)	N.S.	(93)*	(7)*								Zhang et al. [59]
O. tauri	2,221 As(V) (8 days)	N.S.	(86)*	(7)*		(7)*						Zhang et al. [59]

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Table 1. continued

Algal Species	Arsenic Treatment Concentration + species (μg As L^{-1})	Total As (μg As g^{-1})	Inorganic		Methylated			Arsenoriboside			Other	Source
			As(V) μg g^{-1} (%)	As(III) μg g^{-1} (%)	MA μg g^{-1} (%)	DMA μg g^{-1} (%)	TMA μg g^{-1} (%)	Gly μg g^{-1} (%)	PO_4 μg g^{-1} (%)	OSO_3 μg g^{-1} (%)	DMAE μg g^{-1} (%)	
O. tauri	2,221 As(V) (12 days)	N.S.	(91)*	(6)*		(3)*						Zhang et al. [59]
O. tauri	2,221 As(V) (16 days)	N.S.	(93)*	(5)*		(2)*						Zhang et al. [59]
Polyphysa peniculus	10,000 As(V)	39.8	12.8 (32)	25.1 (63)		1.9 (5)						Cullen et al. [69]
P. peniculus	900 As(V)	48		26.3 (55)		21.7 (45)						Cullen et al. [69]
P. peniculus	10,000 As(III)	49.6	8 (16)	37.7 (76)	3.1 (6)	0.8 (2)						Cullen et al. [69]
P. peniculus	900 As(III)	14.7	1.8 (12)	6.5 (44)	1 (7)	5.4 (37)						Cullen et al. [69]
P. peniculus	10,000 MA	11.8			5.3 (45)	6.5 (55)						Cullen et al. [69]
P. peniculus	900 MA	3			1.4 (47)	1.6 (53)						Cullen et al. [69]
P. peniculus	10,000 DMA	30.3	1.6 (5)		0.6 (2)	28.1 (93)						Cullen et al. [69]
P. peniculus	900 DMA	21.1			0.7 (3)	20.4 (97)						Cullen et al. [69]
Heterokontophytes												
Chaetoceros concavicornis	1000 As(V)	N.S.								(99)*		Edmonds et al. [14]
C. concavicornis	1 As(V)	N.S.							(2)*	(60)*		Edmonds et al. [14]
Heterosigma akashiwo	2 As(V)	N.S.							(84)*			Shibata et al. [75]
Phaeodactylum tricornutum	2 As(V) (3 mg PO_4^{3-} L^{-1})	0.41	0.05 (13)			0.13 (32)		0.03 (6)	0.2 (49)			Foster et al. [64]
P. tricornutum	2 As(V) (1.2 mg PO_4^{3-} L^{-1})	0.48	0.04 (8)		0.003 (1)	0.31 (64)		0.02 (4)	0.11 (23)			Foster et al. [64]
P. tricornutum	2 As(V) (0.6 mg PO_4^{3-} L^{-1})	0.64	0.11 (16)			0.26 (41)		0.04 (7)	0.23 (36)			Foster et al. [64]
Skeletonema costatum	2 As(V)	N.S.							(15)*	(50)*		Shibata et al. [75]
Thalassiosira pseudonana	5 As(V) (7 Days)	1.61	0.13 (9)			0.11 (8)		0.17 (12)	0.18 (12)	0.87 (59)		Duncan et al. [62]
T. pseudonana	5 As(V) (42 Days)	2.11	0.19 (11)			0.18 (11)		0.38 (22)	0.04 (2)	0.93 (54)		Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 7 Days)	0.56	0.14 (30)			0.06 (13)		0.09 (18)	0.02 (4)	0.16 (35)		Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 42 Days)	0.62	0.09 (18)			0.06 (14)		0.08 (17)	0.06 (12)	0.18 (39)		Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 7 Days No Nutrients)	1.01	0.19 (22)			0.10 (11)		0.10 (12)		0.46 (55)		Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 42 Days No Nutrients)	0.34						0.04 (14)		0.24 (86)		Duncan et al. [62]

[a]Concentrations of species are presented as absolute concentrations (μg of As g^{-1}) or as proportions of the total arsenic content within the cell fraction (%) or both depending on the data present in the relevant publication. Values marked with * are estimates as actual values were not published. N.S. indicates data not published in study. Batch cultures unless indicated.

In all studies, across all unicellular algae species investigated, inorganic arsenic species—As(V) or As(III)—accounted for in excess of 95% of the arsenic within residue cell fractions (Table 3). The significance of inorganic arsenic present in residue cell fractions is uncertain as it is difficult to determine the extent of "biologically active" residual arsenic. It has been demonstrated that As(V) has the ability to bind extracellularly to *D. tertiolecta* cells, whereas MA and AB were not found to bind extracellularly,[60] which suggests that some inorganic arsenic associated with unicellular algae is adsorbed rather than absorbed. The significance of this arsenic "sink" is uncertain but warrants further investigation.

Methylated Arsenic Species. Unicellular algae have been implicated as a key source of methylated arsenic species DMA and MA in aquatic ecosystems.[70] The production of DMA and MA has been hypothesized to form part of a detoxification pathway for incorporated As(V).[71] Despite DMA and MA being produced by unicellular algae these have not been found

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Table 2. Arsenic Species Present in Lipid-Soluble Cell Fractions of Various Marine Phytoplankton Species Reported in the Scientific Literature[a]

Algal Species	Arsenic Treatment Concentration + species μg As L^{-1}	Total Arsenic μg As g^{-1}	Inorganic		Methylated		Arsenoriboside			Other		Source
			As(V) μg g^{-1} (%)	As(III) μg g^{-1} (%)	MA μg g^{-1} (%)	DMA μg g^{-1} (%)	Gly μg g^{-1} (%)	PO_4 μg g^{-1} (%)	OSO_3 μg g^{-1} (%)	DMAE μg g^{-1} (%)	DMAA μg g^{-1} (%)	
Chlorophytes												
Dunaliella tertiolecta	2 As(V) (3 mg PO_4^{3-} L^{-1})	3.95	0.33 (8)			0.82 (21)	2.7 (69)					Foster et al. [64]
D. tertiolecta	2 As(V) (1.2 mg PO_4^{3-} L^{-1})	4.92	0.38 (8)			1.00 (21)	3.4 (69)					Foster et al. [64]
D. tertiolecta	2 As(V) (0.6 mg PO_4^{3-} L^{-1})	3.77	0.58 (15)			0.83 (22)	2.2 (58)					Foster et al. [64]
D. tertiolecta	2 As(V) (8 days)	1.42	0.04 (3)	0.28 (20)	0.04 (3)	0.13 (9)	0.1 (7)	0.01 (1)		0.81 (58)		Duncan et al. [60]
D. tertiolecta	2 As(V) (14 days)	1.6	0.03 (2)	0.36 (23)	0.06 (4)	0.22 (14)	0.12 (7)	0.02 (1)		0.80 (51)		Duncan et al. [60]
D. tertiolecta	2 AB (8 days)	1.09	0.03 (3)	0.26 (24)		0.07 (7)	0.12 (12)	0.02 (1)		0.59 (56)		Duncan et al. [60]
D. tertiolecta	2 AB (14 days)	0.89	0.02 (2)	0.09 (11)		0.04 (4)	0.03 (3)			0.73 (84)		Duncan et al. [60]
D. tertiolecta	2 MA (8 days)	1.07	0.03 (3)	0.08 (8)		0.03 (3)	0.03 (3)			0.91 (86)		Duncan et al. [60]
D. tertiolecta	2 MA (14 days)	1.04	0.03 (3)	0.14 (13)		0.06 (5)	0.04 (4)			0.65 (63)		Duncan et al. [60]
D. tertiolecta	2 As(V) (7 days)	3.02	0.04 (2)				2.41 (98)					Duncan et al. [62]
D. tertiolecta	2 As(V) (42 days)	1.11	0.02 (2)				1.00 (98)					Duncan et al. [62]
D. tertiolecta	2 As(V) (Continuous)	0.34	0.02 (5)				0.31 (76)	0.01 (3)				Duncan et al. [62]
D. tertiolecta	50 As(V) (3 mg PO_4^{3-} L^{-1})	3.08	1.22 (56)	0.11 (5)			0.56 (26)	0.28 (13)				Duncan et al. [63]
D. tertiolecta	2 As(V) (3 mg PO_4^{3-} L^{-1})	0.71	0.09 (18)				0.23 (44)	0.20 (38)				Duncan et al. [63]
D. tertiolecta	50 As(V) (0.1 mg PO_4^{3-} L^{-1})	3.62	0.18 (8)				2.12 (92)					Duncan et al. [63]
D. tertiolecta	2 As(V) (0.1 mg PO_4^{3-} L^{-1})	0.56	0.04 (10)				0.31 (84)	0.02 (6)				Duncan et al. [63]
D. tertiolecta	2 As(V) (Operationally sterile)	0.02	0.005 (17)		0.004 (15)		0.006 (31)	0.004 (17)				Duncan et al. [61]
D. tertiolecta	2 As(V) (Bacteria exposed)	0.02					0.004 (31)	0.007 (55)		0.001 (11)		Duncan et al. [61]
Heterokontophytes												
Phaeodactylum tricornutum	2 As(V) (3 mg PO_4^{3-} L^{-1})	0.09	0.04 (46)				0.05 (54)					Foster et al. [64]
P. tricornutum	2 As(V)	0.04	0.02				0.02					Foster et al. [64]
	(1.2 mg PO_4^{3-} L^{-1})		(45)				(55)					
P. tricornutum	2 As(V) (0.6 mg PO_4^{3-} L^{-1})	0.20	0.07 (33)				0.13 (67)					Foster et al. [64]
Thalassiosira pseudonana	5 As(V) (7 Days)	4.30	0.69 (20)	0.19 (5)	0.02 (1)	0.56 (16)	0.72 (21)	0.37 (11)	0.95 (27)			Duncan et al. [62]
T. pseudonana	5 As(V) (42 Days)	4.07	0.32 (8)	0.43 (10)	0.03 (1)	0.52 (13)	1.14 (28)	0.15 (4)	0.93 (23)		0.51 (13)	Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 7 Days)	1.62	0.25 (18)	0.12 (9)	0.01 (1)	0.25 (18)	0.28 (20)	0.06 (4)	0.41 (30)			Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 42 Days)	5.60	0.03 (1)	0.88 (16)	0.02 (1)	1.23 (22)	1.60 (29)	0.86 (16)	0.88 (16)			Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 7 Days No Nutrients)	1.83	0.46 (32)	0.09 (6)		0.20 (14)	0.25 (17)	0.01 (1)	0.38 (27)	0.04 (3)		Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 42 Days No Nutrients)	1.51	0.02 (2)	0.31 (25)		0.48 (39)	0.31 (25)	0.02 (2)	0.09 (7)			Duncan et al. [62]

[a]Concentrations of species are presented as absolute concentrations (μg of As g^{-1}) or as proportions of the total arsenic content in the cell fraction (%) or both depending on the data present in the relevant publication. Batch cultures unless indicated.

in unicellular algae as major arsenic species (Tables 1-3). In cystolic cell fractions, chlorophyte species contained less than 20% of the total arsenic as DMA, whereas heterokontophytes, particularly *P. tricornutum* contained between 30 and 60% of the total arsenic in the fraction as DMA[64] (Table 1). DMA concentrations that accounted for greater than 60% only

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Table 3. Arsenic Species Present as Residue-Bound Arsenic in Various Phytoplankton Species Reported in the Scientific Literature[a]

Phytoplankton	Arsenic Treatment Concentration + species μg As L^{-1}	Total Arsenic μg As g^{-1}	Inorganic		Methylated		Ribose	Source
			As(V) μg g^{-1} (%)	As(III) μg g^{-1} (%)	MA μg g^{-1} (%)	DMA μg g^{-1} (%)	PO_4 μg g^{-1} (%)	
Chlorophytes								
Dunaliella tertiolecta	2 As(V) (3 mg PO_4^{3-} L^{-1})	6.18	5.9 (96)	0.26 (3.7)		0.02 (0.3)		Foster et al. [64]
D. tertiolecta	2 As(V) (1.2 mg PO_4^{3-} L^{-1})	5.24	5 (94)	0.2 (5.8)		0.04 (0.2)		Foster et al. [64]
D. tertiolecta	2 As(V) (0.6 mg PO_4^{3-} L^{-1})	5.36	5.2 (98)	0.16 (2)				Foster et al. [64]
D. tertiolecta	2 As(V) (8 days)	2.09	1.97 (85)	0.13 (6)			0.03 (3)	Duncan et al. [60]
D. tertiolecta	2 As(V) (14 days)	1.2	0.99 (83)	0.13 (11)		0.01 (1)		Duncan et al. [60]
D. tertiolecta	2 AB (8 days)	1.21	1.04 (80)	0.06 (4)			0.04 (3)	Duncan et al. [60]
D. tertiolecta	2 AB (14 days)	1.98	1.81 (91)	0.13 (6)		0.06 (3)		Duncan et al. [60]
D. tertiolecta	2 MA (8 days)	0.41	0.27 (63)	0.06 (13)	0.01 (2)			Duncan et al. [60]
D. tertiolecta	2 MA (14 days)	1.52	1.23 (80)	0.06 (4)	0.02 (1)	0.04 (2)	0.1 (6)	Duncan et al. [60]
D. tertiolecta	2 As(V) (7 days)	5.58	5.89 (99)	0.03 (<1)	0.01 (<1)			Duncan et al. [62]
D. tertiolecta	2 As(V) (42 days)	6.20	5.65 (99)	0.14 (<1)	0.01 (<1)			Duncan et al. [62]
D. tertiolecta	2 As(V) (Continuous)	3.76	2.35 (67)	0.91 (26)	0.06 (1)	0.14 (3)		Duncan et al. [62]
D. tertiolecta	50 As(V) (3 mg PO_4^{3-} L^{-1})	2.43	2.62 (108)	0.09 (4)				Duncan et al. [63]
D. tertiolecta	2 As(V) (3 mg PO_4^{3-} L^{-1})	0.54	0.46 (86)	0.06 (11)				Duncan et al. [63]
D. tertiolecta	50 As(V) (0.1 mg PO_4^{3-} L^{-1})	5.44	4.38 (81)	0.48 (9)	0.02 (<1)			Duncan et al. [63]
D. tertiolecta	2 As(V) (0.1 mg PO_4^{3-} L^{-1})	2.51	2.13 (85)	0.09 (4)				Duncan et al. [63]
D. tertiolecta	2 As(V) (Operationally sterile)	1.29	0.8 (62)	0.14 (11)				Duncan et al. [61]
D. tertiolecta	2 As(V) (Bacteria exposed)	0.65	0.29 (45)	0.13 (20)				Duncan et al. [61]
Heterokontophytes								
Phaeodactylum	2 As(V)	1.07	1.00	0.05		0.02		Foster et al. [64]
tricornutum	(3 mg PO_4^{3-} L^{-1})		(94)	(5)		(2)		
P. tricornutum	2 As(V) (1.2 mg PO_4^{3-} L^{-1})	0.91	0.80 (88)	0.07 (8)		0.04 (4)		Foster et al. [64]
P. tricornutum	2 As(V) (0.6 mg PO_4^{3-} L^{-1})	1.08	1.00 (94)	0.07 (5)		0.01 (1)		Foster et al. [64]
Thalassiosira pseudonana	5 As(V) (7 Days)	4.18	4.01 (96)	0.16 (4)	0.04 (1)			Duncan et al. [62]
T. pseudonana	5 As(V) (42 Days)	2.02	2.18 (108)	0.17 (9)	0.02 (1)			Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 7 Days)	0.45	0.43 (97)					Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 42 Days)	1.69	1.74 (104)	0.10 (6)	0.01 (1)			Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 7 Days No Nutrients)	0.79	0.73 (92)	0.06 (8)				Duncan et al. [62]
T. pseudonana	5 As(V) (Continuous 42 Days No Nutrients)	4.19	4.98 (119)	0.13 (3)				Duncan et al. [62]

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Table 3. continued

[a]Concentrations of species are presented as absolute concentrations (μg of As g^{-1}) or as proportions of the total arsenic content within the cell fraction (%) or both depending on the data present in the relevant publication. Batch cultures unless indicated.

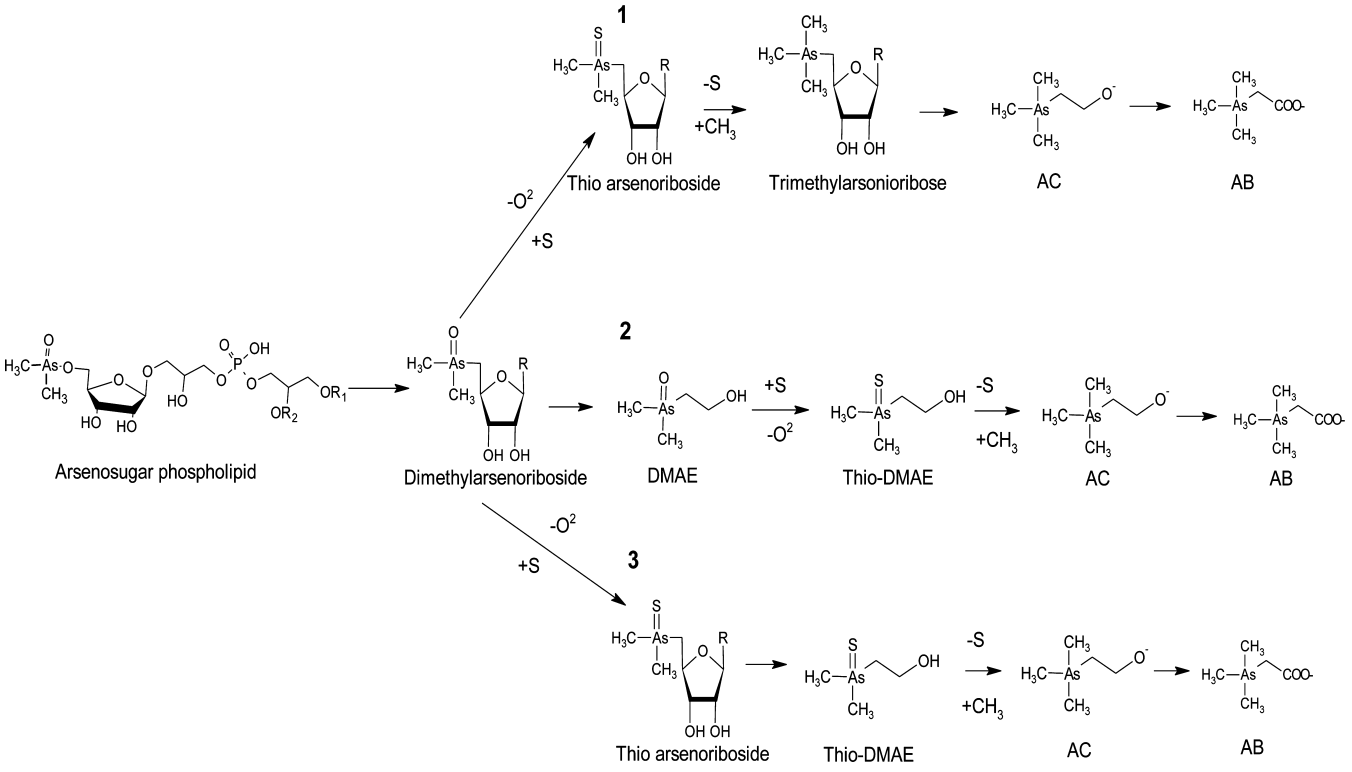

Figure 3. Potential pathways for the formation of AB from arsenoribosides: via (1) thio-arsenoribosides/trimethylarsonioribose, (2) DMAE, and (3) thio-arsenoribosides/thio-DMAE Adapted from Foster et al.[7]

occurred when unicellular algae were exposed to DMA rather than As(V) (Table 1). MA was only found in cystolic cell fractions of unicellular algae sporadically and in low concentrations, with the exception being when exposed to high MA concentrations[69] (Table 1). Trimethylarsine (TMA) was only detected in one study[68] and only at trace concentrations (Table 1).

DMA and MA are usually not major arsenic species in lipid-soluble cell fractions in the unicellular algal species reviewed here (Table 2). DMA accounted for between 3 and 39% of the total arsenic within lipid-cell fractions across all of the unicellular algae species, with concentrations in *T. pseudonana* (13−39%) generally higher than those in *D. tertiolecta* (3−22%) (Table 2). The arsenic species present in lipid-soluble cell fractions are from hydrolyzed lipid extracts as the analytical techniques suitable for the separation and characterization of intact arsenolipids were developed after or while the bulk of these studies were being performed.[34,49,51−53,72,87] Recent research has shown that arsenic hydrocarbons in fish oil contain DMA moieties,[51] which suggests that DMA present in lipid-soluble extracts may be from the degradation of arsenic hydrocarbons, a process which may be variable across different unicellular algal species. As was the case for cystolic fractions, MA was only detected sporadically and at low concentrations in lipid-soluble cell fractions (Table 2). DMA and MA were both only found sporadically in residue cell fractions, accounting for only trace concentrations in all unicellular algae species studied (Table 3).

Arsenoribosides. Arsenoribosides are, with few exceptions, the major water-soluble arsenic species present in marine macro-algae, accounting for in excess of 90% of the total arsenic content in some species.[18−23] Due to the cellular similarities between unicellular and multicellular algae,[73] it has been hypothesized that both groups of organisms would have similar arsenic species. *C. concavicornis*,[14] *D. tertiolecta*,[60−64] *H. akashiwo*,[74] *P. tricornutum*,[64] *S. costatum*,[74] and *T. pseudonana*[62] all contained arsenoribosides in cystolic cell fractions in appreciable concentrations (Table 1). The specific arsenoriboside species differed with algal phyla, with chlorophytes generally containing Gly- and PO_4-ribosides,[60,62−64] while heterokontophytes contained Gly-, PO_4-, and OSO_3-ribosides.[14,64,74] In addition, the concentration of inorganic arsenic species in cystolic cell fractions is greater than that of arsenoribosides for chlorophyte species, whereas the reverse is true for heterokontophytes (Table 1). PO_4-riboside is the most sporadically found arsenoriboside species with large variations reported for a number of algal species.[60,62−64] Across the relevant studies, it is clear that PO_4- riboside concentrations were highest in "young" batch cultures (<7 days) or cultures containing high nutrient concentrations, while low PO_4-riboside concentrations were reported in old and nutrient-limited cultures (Table 1).

Arsenoribosides were more prominent in lipid-cell fractions than in cystolic fractions in all the unicellular algal species reviewed in the literature (Table 2). *D. tertiolecta*, the only chlorophyte species where data are available, contained Gly-

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and PO_4-ribosides, with Gly-ribosde the major species and PO_4-ribosides more prominent under high nutrient conditions[62−64] (Table 2). The heterokontophyte species *P. tricornutum* contained only Gly-riboside,[64] whereas *T. pseudonana* contained Gly-ribosde, OSO_3-riboside, and PO_4-riboside, with concentrations of PO_4-riboside again correlated with nutrient availability.[62] It had long been hypothesized that arsenoribosides are formed in marine primary producers via an extension of the Challenger pathway[71] as illustrated in Figure 2 which are free species in the cytosol. Recently, however, it has been proposed that arsenoribosides may also be formed from the degradation of arsenolipids as arsenic phospholipids have been shown to contain arsenoriboside moieties[34] (Figure 3). The prominence of arsenoriboside species in the lipid-soluble cell fractions of marine unicellular algae is significant as it provides strong evidence to support the hypothesis that arsenoribosides in the cytosol are arsenolipid degradation. Further research on the formation and prominence of arsenolipid species in marine unicellular algae are essential to understand the role of arsenoriboisdes in marine arsenic cycling. Arsenoribosides have only been detected sporadically and in trace concentrations in residual cell fractions across all unicellular algae species studied in the literature.

Thioarsenic Species. Thio-arsenic species refer to arsenic species in which sulfur (S) groups replace oxygen (O) at the functional group on arsenic.[36,37,75] Thio-arsenoribosides were originally isolated from the gut tissue of marine herbivores[37] and have now been isolated from live[36] and decomposing macro-algal tissue[27] and have subsequently been proposed as a key intermediate in arsenic species formation pathways (Figure 3). In addition to thio-arsenoribosides, thio-DMAE has also been found in live[8] and decomposing[76] algal tissue and also in the gut tissues of some marine herbivores[8] and is also a proposed intermediate in the formation of AB[8,11,] (Figure 3). Since thio-arsenoribosides and thio-DMAE have been identified in live and decomposing macro-algae, it is also likely that they are present in unicellular algae. No studies within the peer-reviewed literature have extracted thio-arsenic species from unicellular algae (Tables 1−3), although due to the relatively limited number of studies on the topic the presence of thio-arsenoribosides in marine unicellular algae cannot be confirmed or denied at this stage.

Metabolized Arsenic Species. Metabolised arsenic species refers to arsenic species that are commonly found in marine animals such as DMAE, DMAA, TMAO, TMAP, AC, and AB.[1,10,14,31] It had been hypothesized that unicellular algae produce AB or the precursors to AB (e.g., DMAE, DMAA, TMAO, and AC).[60,77] In all of the peer-reviewed studies undertaken to date, AB has not been detected in any unicellular algae (Tables 1−3). Based on the limited data available it would appear unlikely that AB is produced by marine unicellular algae, and in addition *D. tertiolecta* did not accumulate AB when exposed to it in culture,[60] which suggests that it is a foreign arsenic species to marine unicellular algae. Intermediate arsenic species in the formation of AB such as DMAA and DMAE (Figure 1) have, however, been identified in laboratory cultured unicellular algae[60] (Tables 1-2). DMAE was identified as the major arsenic species in lipid fractions of *D. tertiolecta* in one study[60] while DMAE and DMAA were also found at low concentrations in the lipids and cytosol of *D. tertiolecta*[60−62] and *T. pseudonana*,[62] respectively. Although DMAE and DMAA have been found with some degree of regularity in unicellular algae, it is uncertain as to whether they have been actively biosynthesised as DMAE and DMAA are also arsenoriboside degradation products.[24−27,76,78,79] In the study in which DMAE was the major lipid arsenic species, *D. tertiolecta* was cultured under harsh environmental conditions,[60] while other cultures containing DMAE and DMAA were either old or nutrient-starved (Tables 1 and 2). The common link between all unicellular algal cultures that contained DMAE and DMAA is that the proportion of dead cell material is likely to be high, which could explain the presence of these precursors. Irrespective of whether DMAE or DMAA are actively produced by marine unicellular algae or not, they represent an alternate source of these arsenic species within marine ecosystems, which has implications for our understanding of AB production pathways in marine ecosystems.

COMPARISONS BETWEEN ARSENIC SPECIES DISTRIBUTIONS IN MARINE UNICELLULAR AND MACRO-ALGAE

Although limited data exist with regard to the arsenic species found in marine unicellular algae, considerable research has investigated the arsenic species in macro-algae,[18−22,24−26,32−39] which are biochemically similar at a cellular level to unicellular algae.[73] It has been hypothesized that the distributions of arsenic species present in marine unicellular algae will mirror those in macro-algae due to these similarities.[73] This section will compare the findings presented in the previous sections to the arsenic species typically found in marine macro-algae to highlight any similarities or major differences between the organisms in an attempt to better understand the role of unicellular algae in marine arsenic cycling.

Inorganic Arsenic Species in Marine Macro-algae. Inorganic arsenic, primarily As(V), has been found in considerable proportions in the cystolic fractions of various marine macroalgal species including the following: *Cystoseira barbata* (49−98%),[80,81] *Fucus* sp. (45−54%),[82] *Halopteris platycena* (61%),[10] *Hizikia fusiforme* (46−80%),[83] *Lobophora* sp. (34%),[19] *Phyllospora comosa* (37%),[10] *Sargassum fulvellum* (54%),[84] and *Sargassum* sp. (62%),[19] (all heterokontophytes); *Ceramium* sp. (75%),[81] *Champa viridis* (63%),[19] *Laurencia* sp. (40−43%),[18,19] *Martenisa fragilis* (29%),[19] and *Polisyphonia* sp. (80%)[81] (all rhodophytes); *Caulerpa cactoides* (37%),[18] *Cladophera subsimplex* (74%),[18] *Codium vermilara* (29%),[85] *Rhizoclonium implexium* (61%),[18] and *Ulva lactuca* (35%)[19] (all chlorophytes). The proportion of arsenic found as inorganic species in marine macro-algae are similar to those described earlier for unicellular marine algae (Table 1) which suggests that both groups of organisms can contribute significant As(V) concentrations within marine food webs.

From the limited data on the presence of inorganic arsenic species in marine unicellular algae, it appears that chlorophyte species generally contained higher cystolic As(V) concentrations than heterokontophyte species (Table 1). In addition, high As(V) concentrations in cystolic cell fractions of marine unicellular algae typically occurred under high As(V) exposures (Table 1). High As(V) concentrations in the cystolic cell fractions of marine macro-algae were found in species representing the chlorophyte, heterokontophyte, and rhodophyte classes,[10,18,19,80−85] which suggests that cystolic As(V) is common in marine algae irrespective of phyla. The inorganic arsenic content (As(III) + As(V)) in the macro-algae *Fucus* sp. was found to increase from 14−16% to 45−54% when exposed to increased As(V) concentrations,[82] which mirrors studies reported earlier for unicellular algae[59,63,65,68,69] (Table 1). *Fucus*

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serratus was also found to contain increased cystolic As(V) concentrations when exposed to As(V) concentrations of 50−100 μg of As L^{-1}.[86] Similarly, the chlorophytes *Cladophora* sp. and *Chara* sp. both contained elevated cystolic As(V) concentrations when collected from an arsenic-rich environment in Chile.[87] The observation that both marine unicellular algae and macro-algae have the ability to accumulate high inorganic arsenic concentrations when exposed to elevated arsenic concentrations is concerning and demonstrates that both algal groups have the potential to transfer inorganic arsenic to higher marine organisms which could potentially affect the health of humans via ingestion of inorganic arsenic-contaminated seafood products.

Relatively few studies have detailed hydrolyzed lipid-soluble arsenic species in marine macro-algae.[17,18] The limited data on hydrolyzed lipid-soluble arsenic species in marine macro-algae have not found inorganic arsenic to be a major constituent, which supports data described earlier for unicellular algae.[60−64] Inorganic arsenic species have, however, been found to be the major arsenic species in residual cell fractions of marine macro-algae,[18,33,88] which mirrors the observations presented earlier for various marine unicellular algae species.[60−64] As is the case for unicellular algae the biological significance of inorganic arsenic within residue cell fractions of marine macro-algae is uncertain and requires future research.

Methylated Arsenic Species in Marine Macro-algae. Methylated arsenic species such as DMA and MA were minor arsenic species in the cystolic cell fractions of the marine unicellular algae species surveyed in this review (Table 1). In the majority of marine macro-algal species studied in the literature, DMA and MA were also minor constituents of cystolic cell fractions.[8,18,19,32,35,80,81,84,85,87,89−92] There were, however, some exceptions to this as species such as *Myelophycus simplex*,[84] *Amphiroa anceps*, *Codium lucasii*, *Padina fraseri*, *Laurencia* sp., and *Ulva lactuca*[19] all contained higher proportions of simple methylated species compared to the unicellular algal species described previously (Table 1). In addition *Fucus serratus* was found to contain high DMA and MA concentrations when exposed to As(V) at 50−100 μg of As L^{-1}.[86] The production of methylated arsenic species by marine primary producers has been long described as a detoxification mechanism for inorganic arsenic.[3,70,71,86,93] DMA and MA were found in high concentrations and proportions typically when algae were exposed to high arsenic concentrations,[59,65,68,69,86] which thus supports the notion that the production of DMA and MA is a As(V) detoxification mechanism at high As concentrations.

DMA is not a major arsenic species in lipid-soluble cell fractions of the marine unicellular algae described in this review (Table 2); however, *Ulva rigida* (33%), *Cladophoropsis herpestica* (51%), *Rhizoclonium implexium* (57%), and *Cladophera subsimplex* (44%) were found to contain considerable DMA concentrations in lipid-soluble cell fractions.[18] In addition marine macro-algae species such as *Undaria pinnatifida*,[34] *Hizikia fusiformis*,[34] and *Saccharina latissima*[88] have been found to contain arsenic hydrocarbons which have been shown to contain DMA moieties.[51] Consequently, it is not surprising that DMA is a major arsenic species in hydrolyzed lipid extracts of marine macro-algae, and as a result future research needs to investigate the arsenolipid species produced by marine unicellular algae to establish if all algae produce arsenic hydrocarbons or whether this trait is specific to macro-algae.

Arsenoribosides in Marine Macro-algae. Arsenoribosides were first isolated from marine macro-algae,[22] and subsequently arsenoribosides have been widely reported in marine macro-algae (see refs 6−10, 18−21, 23−27, 30, 35, 76, 78, 80, 81, 84−87, 89, 91, 92, and 94−96). In some macro-algal species, arsenoribosides have been found to account for between 85 and 100% of the cystolic arsenic, e.g., *Ecklonia radiata*,[7,19,26,76,78] *Corallina officinalis*,[19] *Padina fraseri*,[19] and *Caulerpa flexilis*,[18] whereas in other macroalgal species arsenoriboside concentrations are lower than cystolic inorganic and methylated arsenic concentrations, e.g., *Laurenica* sp.,[18,19] *Rhizoclonium implexium*,[18] *Cladophera subsimplex*,[18] *Sargassum* sp., *Lobophora* sp., *Champa viridis*, and *Ulva lactuca*.[19] In addition it has been found that different arsenoriboside species are present in different macro-algae phyla.[19] Generally chlorophyte species have been shown to contain Gly- and PO_4-ribosides[18,19,80,85,89] and rhodophytes have been shown to contain Gly- and PO_4-ribosides plus in some cases SO_3- and OSO_3-ribosides,[80,91] while heterokontophytes have been shown to contain all four arsenoriboside species on occasions.[81,84,90] In unicellular algae, chlorophyte species (*Dunaliella* sp.) have been shown to produce Gly- and PO_4-ribosides,[60−64] which is similar to chlorophyte macro-algae species,[18,19,80,85,89] while unicellular heterokontophyte species[14,62,64,74] produced the same arsenoriboside species as their macro-algae cousins.[81,84,90.] Although comparisons between unicellular and macro-algae are limited due to the sparse data on unicellular algae, it appears that similar processes govern the production of arsenoribosides in both unicellular and macro-algae. This means that the pathways that describe the formation of AB in marine animals from arsenoribosides (Figure 2) are applicable for both macro-algae and unicellular algae, which is significant given that unicellular algae are a considerable food source in marine ecosystems.

Arsenoribosides were also found to be major arsenic species in the hydrolyzed lipid fractions of marine macro-algae.[18] In a range of macro-algae species Gly-riboside was found to be a major arsenic species in hydrolyzed lipid fractions[18] which is again similar to unicellular algae reported in the literature.[60,62−64] Recently, arsenosugar phospholipids have been identified in marine macro-algae[34,88] which are almost certainly the source of these arsenoribosides in hydrolyzed lipid fractions. Considerable arsenic concentrations have been measured in lipid fractions of both unicellular[60,62−64] and macro-algae[18,34,88] (Table 2), and thus arsenosugar phospholipids have the potential to be a major arsenic species in all marine algae. Research investigating the formation and environmental relevance of arsenosugar phospholipids needs to continue for all marine algae to establish their role in marine arsenic cycling.

Metabolized and Thioarsenic Species in Marine Macro-algae. AB has been detected as a minor arsenic species in a number of marine macro-algae species including the following: *Corallina officinalis*,[18] *Ulva rigida*,[18,81,89] *Cladophoropsis herpestica*,[18] *Hormosira banksii*,[8] *Phyllophora antarctica*,[35] *Cladophora prolifera*,[85] *Enteromorpha* sp.,[81,85] *Codium effusum*, *Codium vermilara*, *Halopteris filicina*, *Halopteris scoparia*, *Alsidium corallinum*, *Jania rubens*,[85] *Laminaria ochroleuca*, *Laminaria saccharina*,[89] *Cystoseira barbata*,[80] *Ceramium* sp., *Gelidium* sp., *Fucus virsoides*, and *Padina pavonica*.[81] Although AB has been widely identified in marine macro-algae, it is uncertain as to whether the algae itself or associated epiphytes are the source of AB.[11] High AB concentrations have been found either in red macro-algae in which animal epiphytes

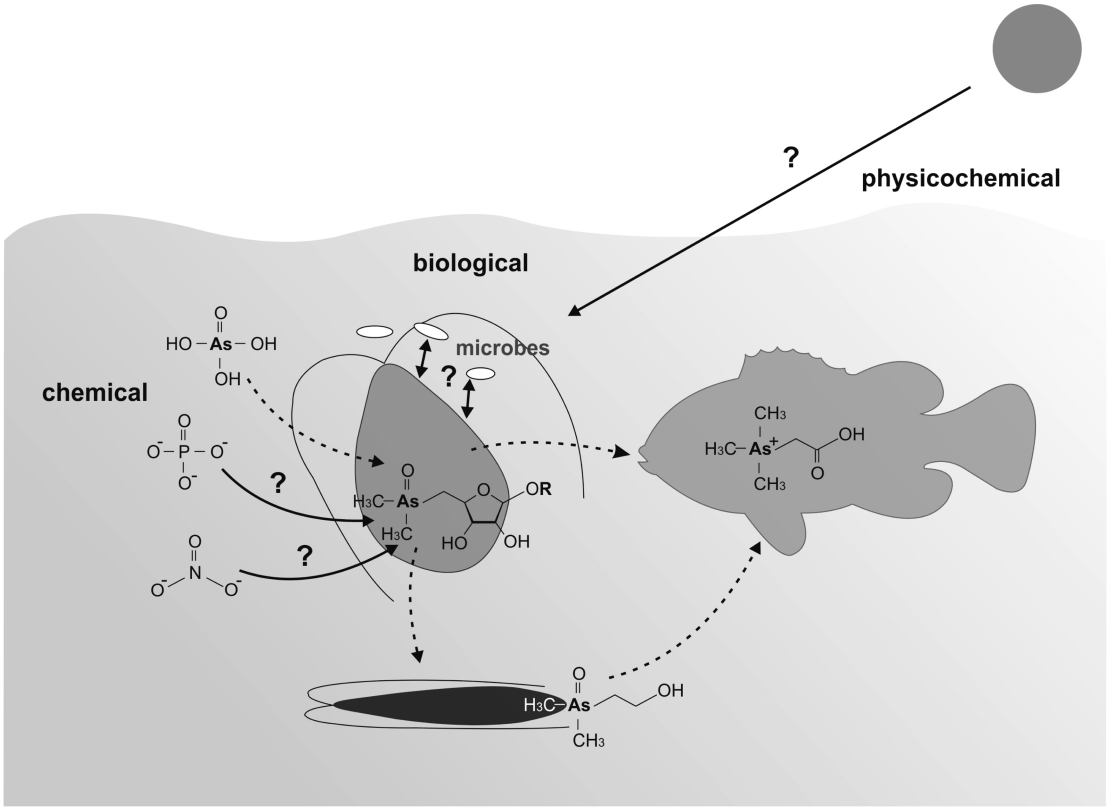

Figure 4. Conceptual diagram of the role of phytoplankton in influencing the production of arsenic species such as AB in higher marine organisms.

are typically hard to remove[11] or on algal samples in which epiphytes have not been removed. No unicellular algae species studied in the literature produced AB (Tables 1−3), and unicellular algae do not contain epiphytic organisms. If AB is produced by marine algae, then based on the data from the previous sections, it would be expected that unicellular and macro-algae would both produce AB. Consequently, the lack of AB in unicellular algae points to the likelihood that epiphytic organisms are the source of AB in marine macro-algae.

In earlier sections it was highlighted that DMAE is at times a major arsenic species in unicellular algae cultures, particularly in lipid-cell fractions[60] (Tables 1 and 2). DMAE has been detected in macro-algae in some studies;[97] however, often it is not present.[6−10,18−21,23−27,30,34,35,76,78,80,81,84−87,89,91,94−96] DMAE has, however, been widely detected in decomposing marine macro-algae[24−27,76,78,79] and has subsequently been designated a major arsenoriboside degradation product. As will be discussed further in the next section, one of the key limitations with existing research on the arsenic species produced by marine unicellular algae is that live and dead cells are difficult to separate.[62] Consequently, the arsenic species found in marine unicellular algae have the potential to be a combination of live and dead cell material thus potentially explaining why arsenic species such as DMAE and DMAA are often detected while they are not found in macro-algae.

Thio-arsenic species such as thio-arsenoribosides and thio-DMAE have been found in both live[8,36,98] and decomposing[27,76] macro-algal tissue and in the gut tissues of marine herbivores.[7,8,37,99] These arsenic species have been hypothesized to be key intermediates in the formation of AB in marine animals.[8,11] Because these arsenic species have not been found in marine unicellular algae to date, it makes comparisons between the two groups of organisms impossible. Further assessment of the prominence of thio-arsenic species in all marine algae is required to properly determine the significance of these arsenic species in the cycling of arsenic in marine systems.

INFLUENCE OF PHYSICOCHEMICAL, CHEMICAL, OR BIOLOGICAL VARIABLES ON THE ARSENIC SPECIES FOUND IN MARINE UNICELLULAR ALGAE?

The previous sections have highlighted the wide variety of arsenic species found in marine unicellular and macro-algae. Additionally, the previous sections have highlighted similarities between unicellular and macro-algae such as the presence of inorganic arsenic and arsenoribosides and differences such as the presence of AB in macro-algae but not in unicellular algae and alternatively the presence of DMAE in unicellular algae cultures but not live macro-algae. Despite the similarities between unicellular and macro-algae, there is one major difference in studies between the two groups of organisms which is that studies on marine macro-algae can be successfully carried out in the field, whereas studies investigating the arsenic species found in and produced by unicellular algae generally need to be performed under laboratory conditions. Although laboratory-based experiments can be sophisticated and a good representation of marine environments, a number of abiotic and biotic variables need to be taken into account as they have the potential to influence the production of arsenic species (Figure 4). The following sections of this review will therefore discuss how abiotic and biotic variables could influence the arsenic species found in cultures.

Physicochemical Variables. Physicochemical variables such as temperature,[100] light intensity and photoperiod,[58,101,102]

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Table 4. Algal Culture Regimes and Environmental Conditions Employed within Arsenic Cycling Studies Collated from the Scientific Literature[a]

study	algae cultured	culture type	growth medium	temp (°C)	incubation period (days)	light intensity (μmol of photons m^{-1} s^{-1})	photoperiod (light:dark)	culture sterility
Cullen et al.[69]	*P. peniculus*	batch	Shepards'[122]	20	7	60	16:8	axenic conditions
Shibata et al.[74]	*H. akashiwo*; *S. costatum*	batch	Guillard f2[124]	20	14	184	24:0	axenic conditions
Edmonds et al.[14]	*C. concavicornis*	batch	Artificial seawater[125]	20	4	N.S.	N.S.	axenic conditions
Yamaoka et al.[68]	*D. salina*	batch	Fe-EDTA; KNO_3 and KH_2PO_4 added (mg L^{-1} range)	23	7	83	24:0	operationally sterile
Foster et al.[64]	*D. tertiolecta*; *P. tricornutum*	batch	Guillard f2[124] 0.6−3 mg L^{-1} PO_4^{3-}	21	7	75	12:12	axenic conditions
Karadjova et al.[65]	*C. salina*	batch	Guillard f2[124]	20	3	25	12:12	N.S.
Duncan et al.[60]	*D. tertiolecta*	batch	Guillard f2[124]	33	8−14	170	16:8	axenic conditions
Duncan et al.[62]	*D. tertiolecta*; *T. pseudonana*	batch; continuous	Guillard f2;[124] autoclaved seawater	20−25	4−42	110	12:12	operationally sterile
Duncan et al.[63]	*D. tertiolecta*	batch	Guillard f2[124] 0.1−3 mg L^{-1} PO_4^{3-}	20−25	7	110	12:12	operationally sterile
Zhang et al.[59]	*O. tauri*	batch	Keller[123]	20−22	4−16	280	16:8	N.S.
Duncan et al.[61]	*D. tertiolecta*	batch	Guillard f2[124] 0.1 mg L^{-1} PO_4^{3-}	20−25	7	110	12:12	operationally sterile; microbial inoculated

[a]N.S. = information not published in study.

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salinity[103] and pH[104] play key roles in influencing growth and cellular processes in unicellular algae.[58,105−107] Changes to growth patterns and alterations to various cellular processes have the ability to influence the production of arsenic species in marine unicellular algae. Research investigating the effect of physicochemical variables on the production of arsenic species by marine unicellular algae is limited when compared to other variables such as arsenic and nutrient exposure. The majority of studies investigating arsenic species production by marine unicellular algae have utilized very similar culture conditions utilizing temperatures of 20−23 °C, light intensities of 60−100 μmol of photons m^{-1} s^{-1}, and light exposure periods of between 12 and 16 h of illumination (Table 4). One study, however, cultured *D. tertiolecta* at temperatures of 30−35 °C and light intensities of 170−200 μmol of photons m^{-1} s^{-1} under a 16:8 light:dark photoperiod,[60] which are harsher conditions than those used in other studies[14,59,60,62−65,69,74,108,109] (Table 4). Under these conditions *D. tertiolecta* was found to produce DMAE in hydrolyzed lipid extracts,[60] whereas Gly-riboside is commonly found under more benign environmental conditions.[62−64] Environmental variables such as light exposure and temperature are at a conceptual level a particularly important experimental consideration as they are known to regulate the lipid composition in unicellular and macro-algae, with "harsh" conditions inducing the production of storage lipids (e.g., hydrocarbons and fatty acids) whereas structural lipids (e.g., phospholipids) are more prominent under more benign environmental conditions.[110−113] In some marine unicellular algae species (e.g., *Dunaliella*) over 50% of the total arsenic content has been shown to be lipid-soluble,[60,62,64] and as shown for macroalgae,[34,88] it is likely that a variety of arsenolipid species can be produced by marine unicellular algae. Consequently, environmentally induced changes to the lipid composition of unicellular algae could alter arsenic accumulation and arsenic species production, which could have major ramifications for the cycling of arsenic and needs to be taken into account when designing laboratory-based experiments.

Chemical Variables. The chemical composition of the surrounding environment can alter the arsenic species produced by marine unicellular and macro-algae via two key processes. First, within the peer-reviewed literature, marine unicellular algae have been exposed to arsenic concentrations that range from 2 μg of As L^{-1}[60−64] to 100 mg L^{-1}.[68] At environmentally realistic arsenic concentrations (2 μg of As L^{-1}) unicellular algae have been shown to produce arsenoribosides,[14,60−64,74] while excessive arsenic concentrations (i.e., milligrams of arsenic per liter concentrations) inorganic arsenic species were the major arsenic species found.[59,65,68,69] This suggests that unicellular algae alter the production of arsenic species depending on the arsenic concentration they are exposed to. It is likely that under high arsenic concentrations many arsenic detoxification mechanisms are overwhelmed, explaining why the arsenic species produced are dissimilar to those produced under ambient arsenic concentrations.

Marine unicellular algae have also been exposed to a wide range of nutrient concentrations when exposed to arsenic.[14,59−65,68,69,74] Elements such as nitrogen (N), phosphorus (P), iron (Fe), and silicon (Si) are essential for the growth and cellular metabolism of unicellular algae[106,114−116] and can all be growth-limiting factors. Since variable N, P, Fe, and Si concentrations can alter growth in marine unicellular algae, it is reasonable to assume they may also influence the production of arsenic species given that biogeochemical cycles are linked. Preliminary research has suggested that the arsenic species produced by unicellular algae differs with variable nutrient concentrations in the surrounding environment.[62−64] *D. tertiolecta* was found to increase its cystolic DMA concentrations under decreased phosphate (PO_4^{3-}) concentrations,[64] and increase its cystolic and lipid-soluble PO_4-riboside concentrations under increased PO_4^{3-} concentrations,[60,62,63] while *T. pseudonana* also contained increased cystolic and lipid-soluble PO_4-riboside concentrations under increased PO_4^{3-} concentrations.[62]

Most studies that have investigated the role of nutrient availability on the production of arsenic species have investigated PO_4^{3-} availability.[62−64] PO_4^{3-} and As(V) have an intricate relationship, with primary producers and microorganisms known to accumulate arsenic via PO_4^{3-} uptake pathways[117,118] due to structural similarities between the compounds.[3,119,120] Although the relationship between PO_4^{3-} and As(V) uptake has been established,[3,120,121] it is uncertain as to how PO_4^{3-} availability influences the production of arsenic species in marine unicellular algae. Some studies have demonstrated that variable PO_4^{3-} exposure altered the production of arsenic species such as PO_4-riboside,[62,63] whereas other studies found no effects of variable PO_4^{3-} exposure on the production of arsenic species.[64] Within the literature most studies have utilized nutrient concentrations in the milligrams per liter concentration range[14,59,60,64,65,69,74,108,109,122−125] (Table 4), which far exceeds concentrations of essential nutrients such as N, P, Fe, and Si in the natural environment.[55] Due to the likelihood that nutrient availability influences the production of arsenic species by unicellular algae both directly and indirectly, future research must attempt to culture organisms at nutrient concentrations that are an appropriate representation of marine environments to ensure that data produced are as environmentally relevant as possible.

Biological Variables. Two major biological considerations need to be taken into account when performing laboratory studies aimed at determining the arsenic species produced by marine unicellular algae. Bacteria and other microorganisms form various symbiotic[126−129] and antagonistic[130,131] relationships with unicellular algae. Most existing research has utilized so-called "sterile" or "axenic" unicellular algae cultures[14,60−64,68,74] (Table 4) to ensure observed processes are of algal origin, although recent research has demonstrated that "sterile" cultures are unlikely to be sterile.[61,132] This loss of microbial diversity within laboratory cultures has the potential to result in atypical arsenic species being produced as algal−microbial interactions are likely to be critical in the production of certain arsenic species. A solution to this issue is, however, not straightforward given that the creation of truly sterile cultures may be impossible[61,132] and simulating algal−microbial interactions in cultures is difficult as it is inherently difficut to maintain "representative" microbial communities under laboratory conditions.[127,129,133] Until culturing techniques have improved to the point at which "representative" communities can be kept in culture, many of algal−microbial interactions will remain unknown but still need to be considered when discussing findings from laboratory-based studies.

As described earlier it is difficult to establish the arsenic species produced by marine unicellular algae *in situ*. Consequently, all studies within the published literature that have investigated arsenic species production by marine phytoplankton have utilized readily culturable spe-

cies.[14,59,60,64,65,69,74,108,109] Over 5,000 species of marine unicellular algae have currently been described, with countless more yet to be discovered.[134] The major reason that countless species remain undiscovered is that current culture techniques are incapable of culturing the bulk of unicellular algae present in the world's oceans.[127,129,133] As a result, it could be questioned whether the arsenic species produced by these algal species are applicable to the thousands of other unicellular algal species that exist throughout the globe or whether their ability to be easily cultured makes them unique in terms of how they cycle arsenic (Table 4). Establishing the arsenic species in a wider variety of marine unicellular algal species is thus an important avenue for future research as it will help determine the relevance of existing data and also provide a greater perspective of the influence of phytoplankton in marine arsenic cycling.

CONTRIBUTION OF THE ARSENIC SPECIES FOUND IN MARINE UNICELLULAR ALGAE TO THE FORMATION OF AB IN HIGHER MARINE ORGANISMS

Since the identification of AB in marine organisms[135] much research has been conducted to determine how AB is formed in marine organisms.[24,30,48,77] The identification of arsenoribosides in marine algae[22,23] followed by the detection of various AB intermediates[24] in both marine algae and animals led to the generation of arsenic transformation pathways which connect As(V) → arsenoribosides → AB in marine ecosystems (Figures 2 and 3). Although most of these pathways have been hypothesized from sound experimental data, the contribution of unicellular algae to these pathways had not been assessed despite their importance in marine ecosystems.

It had been hypothesized that unicellular algae could contribute to the formation of AB in marine organisms through two pathways which include (1) the further metabolism of arsenoribosides from unicellular algae to AB in gut tissues of marine animals or (2) AB or AB precursors being present in unicellular algae which is directly transferred to marine animals via ingestion. This review has highlighted that many of the arsenic species found in marine unicellular algae (e.g., arsenoribosides, As(V), and DMA) are found in proportions similar to those found in marine macro-algae,[6−10,18−21,23−27,30,35,76,78,80,81,84−87,89,91,92,94−96] which suggests that similar processes govern the production of arsenic species in all marine algae. Unicellular algae are a major food source for many marine filter feeders[136] (e.g., oysters, mussels, and clams) which have been found to contain high AB concentrations.[6,8,137−139] These observations support the pathway identified in Figure 3 and give credence to the idea that unicellular algae contribute to the formation of AB in marine organisms as a result of the further metabolism of ingested arsenoribosides provided by the algae.

From this review it is also apparent that AB precursors such as DMAE are produced by unicellular algae,[60] although due to limitations in laboratory-based research, it is uncertain as to whether these species are actively produced or are instead arsenoriboside degradation products. Irrespective of this it is likely that unicellular algae may also contribute to the formation of AB in marine animals via the arsenic species produced as degradation products as cells decompose and decay. Many organisms within benthic marine environments are detritivores[140] (e.g., various polychaete, gastropod, and crustacean species) and have been found to contain high AB concentrations.[42,141] Within these environments, unicellular algae can account for a considerable proportion of the detritus, particularly after bloom events.[142,143] Unicellular algae appear, therefore, to be able to influence the production of AB via two means which is the further metabolism of arsenoribosides from live cells and/or DMAE from dead cells. In addition, although thio-arsenic species (e.g., thio-arsenoribosides and thio-DMAE) have not been detected in unicellular algae, it is probable that these arsenic species are present in unicellular algal-based detritus and as a result could also be a significant contributor to the formation of AB in higher marine organisms.

Although marine unicellular algae are likely to contribute to the formation of AB in higher marine organisms, this review has outlined that they are also likely to influence the arsenic species present in higher marine organisms by other means. First, various studies on unicellular algae demonstrated that inorganic arsenic is a common arsenic species[59,60,62−65,68,69] and in addition the concentration of inorganic arsenic has been found to increase when excessive As or nutrient (N and P) concentrations are present in the system.[59,61,62,64,69] Instances of wide scale pollution and eutrophication of marine environments will almost certainly become more common as global populations continue to increase, which has the potential to result in unicellular algae contributing greater inorganic arsenic contents to marine food webs which could have negative health implications for those who utilize marine organisms as protein sources. Furthermore, some marine unicellular algal species, e.g., *Dunaliella* sp.,[60,62−64] have been found to contain higher concentrations of lipid-soluble arsenic when compared to marine macro-algae.[18,20,33,34,88] Although a range of arsenolipid species have been identified in recent years,[34,49,51,53,72,88,144] it is uncertain what arsenolipid species exist in marine unicellular algae and how arsenolipids are metabolized within marine food webs. Given that some unicellular algae have high lipid arsenic contents, it is possible that they play a significant role in the cycling of lipid arsenic species in marine ecosystems which may significantly alter our perceptions regarding the cycling of arsenic in marine ecosystems.

Future research on marine unicellular algae should thus be focused on determining the arsenic species, including thio-species, found in a wider variety of unicellular algae to establish if the conclusions generated in this review are representative of the wider range of algal species that inhabit the world's oceans. Furthermore, research should be undertaken to further assess the role of environmental variability (i.e., temperature, light exposure, and nutrient and As availability) on the production of arsenic species by unicellular algae to determine whether or not these organisms could contribute increased concentrations of toxic arsenic species such as As(V) to marine food webs under altered environmental conditions. On a similar note, research should also be undertaken to establish the arsenolipid species present in marine unicellular algae, how and if the production of arsenolipid species are altered by environmental variability, and whether arsenolipids are transferred within marine food webs as is the case with water-soluble arsenic species. Finally, research or technological advances that are able to measure the arsenic species in unicellular algae *in situ* would also be advantageous and would be able to remove some of the variability related with the culturing of unicellular algae for research studies.

In conclusion, marine unicellular algae contain a wide variety of arsenic species that are distributed in a similar manner to their macro-algae cousins. Unicellular algae are thus likely to

contribute to the formation of AB in higher marine organisms via the further metabolism of arsenoribosides from live cells and DMAE from unicellular algal detritus. Future research establishing how environmental variability can influence the production of arsenic species by marine unicellular algae and what effect this has on arsenic cycling within marine food webs is essential to clarify the role of these organisms in marine arsenic cycling which represents one of the missing links in marine arsenic biogeochemical research.

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