Applied Organometallic Chemistry (1990) 4 419–437
0268-2605/90/050419-19$09.50

REVIEW

Organometallics in the nearshore marine environment of Australia

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Received 5 March 1990 *Accepted 15 March 1990*

This review draws together published information on the occurrence and biogeochemical cycling of selenium, arsenic and tin in the nearshore marine environment of Australia. The selenium content of marine organisms is well documented but little information is available on the selenium content of waters and sediments. The speciation of selenium in organisms, water and sediments is unknown although it appears that selenium is associated with proteins. The occurrence and speciation of arsenic in marine organisms has been extensively studied, with arsonobetaine being isolated as the probable end-product of arsenic metabolism in marine food chains. However, organisms can produce other organoarsenic compounds, e.g. trimethylarsine oxide, which may be metabolized to toxic end-products. Little is known about the occurrence and speciation of arsenic in waters and sediments. Arsenic(V) is dominant in oxygenated waters, with appreciable quantities of arsenic(III) in some deoxygenated waters.

There are few data for tin in water, sediments or organisms and no data on naturally occurring tin species. Tributyltin has been measured in water, sediment and organisms from areas affected by boating activity.

Keywords: Selenium, arsenic, tin, occurrence, biochemical distribution, speciation, future research directions

INTRODUCTION

Anthropogenic inputs of selenium, arsenic and tin to natural waters have increased during this century due to their release during coal and oil combustion, discharge in wastes or use as antifoulants. The biogeochemical cycling of these elements not only involves inorganic forms but reduced and methylated species as well as other organometallic compounds, e.g. selenoamino-acids, arsenobetaine tributyltin.

The purpose of this review is to draw together published information on the occurrence and biogeochemical cycling of selenium, arsenic and tin in the nearshore marine environment of Australia with particular emphasis on occurrence and speciation. Future research directions will also be discussed.

SELENIUM

Occurrence

Sediment and water

No results for the concentration of selenium in marine waters of Australia have been reported in the literature. Only one study, by Maher,[1] has reported the concentration of the selenium in sediments from Spencer Gulf, South Australia (Table 1). Data on selenium in marine sediments are scarce worldwide but most selenium concentrations lie within the range 0.1–2 mg kg.[2]

Marine organisms

More information is available on selenium concentrations in plants, fish, moluscs and crustaceans (Tables 2–5). In a study of selenium in macroalgae from South Australia,[3] signigicantly lower concentrations of selenium were found in Phaeophyta compared with Rhodophyta and Chlorophyta (excluding *Ulva* sp.). Phaeophyta

Table 1 Selenium in sediments from Spencer Gulf, South Australia

Location	Concentration (mg kg^{-1} dry wt)
Seagrass flat	0.46
Sand flat	0.52
Mangrove	0.60
Estuarine	0.82
Supratidal	1.12

usually contain smaller amounts of amino-acids and proteins than Chlorophyta and Rhodophyta,[4] and as selenium is known to be incorporated in amino-acids and proteins of microalgae[5] and plants,[6,7] lower selenium concentrations in Phaeophyta may be due to fewer sites for binding and storage.

Comparisons of the levels of selenium in fish, crustaceans and molluscs (Tables 3–5) indicate that no animals contain unusually elevated levels of selenium, but that higher selenium concentrations occur in digestive tissues. As organisms were not purged of gut contents before analysis, some of the selenium measured in digestive tissues may be due to residual food present in the gut which may be eventually excreted. Mackay *et al.*[9] have reported that selenium concentrations in muscle tissues of black marlin are correlated to length, girth and weight whilst selenium concentrations in liver tissues are correlated with weight and girth; thus selenium accumulation may be dependent on age. Lyle,[14] in contrast, reported no obvious or consistent relationship between selenium concentrations and length. The available results show that selenium is present at low concentrations in all organisms and preferential accumulation with particular taxa as reported for other elements[15–17] does not appear to occur.

Table 2 Selenium in marine plants

Species	Common name	Location	Tissue	Selenium[a] (mg kg^{-1})	Reference
Chizophora stylosa	Mangrove	Queensland	Leaves	0.063	8
Chlorophyceae		South Australia	Whole plant		3
Ulva sp.				0.053–0.098	
Caulerpa brownii				0.264	
Caulerpa cactoides				0.131–0.187	
Caulerpa flexilis				0.226–0.249	
Enteromorpha sp.				0.166	
Rhodophyceae		South Australia	Whole plant		3
Laurencia filformis				0.160	
Plocamium sp.				0.166–0.199	
Gracilaria sp.				0.153	
Cladurus elatus				0.216	
Phacelocarpus apodus				0.282	
Dictymenia harveyana				0.390–0.434	
Coelarthrum muelleri				0.200	
Areschougia congesta				0.364	
Phaeophyceae		South Australia	Whole plant		3
Sargassum bracteolosum				0.068–0.076	
Ecklonia radiata				0.064–0.071	
Cystophora platylobium				0.110	
Cystophora monitiformis				0.125–0.135	
Cystophora racemosa				0.059	
Cystophora monilifera				0.098	
Cystophora siliquosa				0.014–0.099	
Cystophora subfarcinata				0.065	
Sargassum linearifolium				0.110	
Lobospira bicuspidata				0.108	
Dictyota dichotoma				0.096	

[a] Dry weight.

Table 3 Selenium in marine fish

Species	Common name	Location	Tissue[a]	Selenium (mg kg^{-1})	Reference
Makaira indica cuvier	Black marlin	Cairns, Queensland	M[b]	0.4–4.3	9
			L[b]	1.4–13.5	
Seriola calandi	Yellow-fin bream	Queensland	M[b]	1.5	8
			eye[c]	3.2	
Acanthopagrus australis	Yellow-fin bream	New South Wales	M[d]	0.1–0.8	10
Platycephalus fucus	Dusky flathead	New South Wales	M[d]	0.2	10
Mugil cephalus	Sea mullet	New South Wales	M[d]	0.1–0.3	10
Chrysophris auratus	Snapper	New South Wales	M[d]	0.1–0.6	10
Pomatomus saltatrix	Tailor	New South Wales	M[d]	0.1–0.6	10
Sciaena antarctica	Mulloway	New South Wales	M[d]	0.1–0.4	10
Seriola grandis	Yellow-tail kingfish	New South Wales	M[d]	0.3	10
Arripis tuna	Australia salmon	New South Wales	M[d]	0.3–0.5	10
Thunnus albacares	Yellow-fin tuna	New South Wales	M[d]	0.4–0.7	10
Galeorhinus australis	School shark	Southeast Australia	M[b]	0.2–0.8	11
Mustelus antarcticus	Gummy shark	Southeast Australia	M[b]	0.2–0.5	11
Hemir hamphus australis	Sea garfish	St Vincent's Gulf	M[c]	0.56–0.81	12
			D[c]	1.3–2.0	
Sillaginodes punctatus	Spotted whiting	St Vincent's Gulf	M[c]	1.1–1.7	12
			D[c]	2.0–2.6	12
Arripis georgianus	Tommy rough	St Vincent's Gulf	M[c]	0.72–0.98	12
			D[c]	1.1–1.8	
Callogobius mucosus	Sculptured gobie	St Vincent's Gulf	M[c]	0.4–0.63	12
			D[c]	0.79–1.2	
Notorhynchus cepedignus	Seven-gilled shark	South Australia	?[b]	0.27–0.36	13
Carcharhinus carcharias	White pointer shark	South Australia	?[b]	0.1	13
Alopias vulpinus	Thresher shark	South Australia	?[b]	0.41	13
Furgaleus ventralis	Whiskery shark	South Australia	?[b]	0.40	13
Carcharninus greyi	Bronze whaler shark	South Australia	?[b]	0.3–1.1	13
Carcharhinus carcharias	White pointer shark	Northern Australia	M[b]	0.38–1.1	14
Charcharhinus limbatus	Black-tip shark	Northern Australia	M[b]	0.37–1.0	14
Carcharhinus sorrah	Spot-tail shark	Northern Australia	M[b]	0.40–1.0	14
Carcharhinus fitzroyensis	Sand shark	Northern Australia	M[b]	0.25–0.92	14
Carcharhinus amblyrhynchoides	Graceful shark	Northern Australia	M[b]	0.41–1.6	14
Carcharhinus melanopterus	Black-tip shark	Northern Australia	M[b]	0.28–1.4	14
Carcharhinus cautus	Mangrove shark	Northern Australia	M[b]	0.49–2.1	14
Carcharhinus amboinensis	Java shark	Northern Australia	M[b]	0.39–1.0	14
Carcharhinus macloti	Milk shark	Northern Australia	M[b]	0.48–0.88	14
Carcharhinus dussumieri	Blackspot shark	Northern Australia	M[b]	0.48–3.4	14
Carcharhinus brevipinna	Spinner shark	Northern Australia	M[b]	0.40–0.98	14
Galeocerdo cuvieri	Tiger shark	Northern Australia	M[b]	0.34–0.71	14
Negarpiron acutidens	Lemon shark	Northern Australia	M[b]	0.34–0.40	14
Rhizoprionadon acutus	Milk shark	Northern Australia	M[b]	0.44–1.30	14
Rhizoprionadon taylori	Milk shark	Northern Australia	M[b]	0.32–0.65	14
Sphyrna lewini	Hammerhead shark	Northern Australia	M[b]	0.46–1.50	14
Sphyrna mokarran	Great hammerhead shark	Northern Australia	M[b]	0.33–1.9	14
Sphyrna blochii	Slender/handlebar hammerhead shark	Northern Australia	M[b]	0.61–1.9	14

[a] M, muscle; L, liver; D, digestive tissue; ?, unknown tissue. [b] Wet weight. [c] Dry weight. [d] Unspecified (dry or wet weight).

Maher[18] re-examined the selenium concentrations in organisms from St Vincent's Gulf, South Australia, by considering the diet of some of the marine animals [Table 6(a)]. The total selenium in animals in each diet group was not significantly different ($P<0.05$), indicating that the route of

Table 4 Selenium in marine molluscs

Species	Common name	Location	Tissue[a]	Selenium (mg kg^{-1})	Reference
Saccostrea cucculláta	Oyster	Queensland	M[c]	2.6	8
Mytilus edulius planulatus	Mussel	St Vincent's Gulf	M[c]	0.7–1.5	12
		St Vincent's Gulf	D[c]	1.1–2.3	12
Pecten alba	King scallop	St Vincent's Gulf	M[c]	1.6–2.5	12
		St Vincent's Gulf	D[c]	1.4–27	12
Sepioteuthis australis	Southern calamary squid	St Vincent's Gulf	M[c]	0.9–2.6	12
Pinna bicolor	Razor fish	South Australia	?[d]	0.56–6.4	13
Haliotis ruber	Black-lip abalone	South Australia	?[d]	0.04–0.07	13

[a] M, muscle; D, digestive tissue; ?, unknown tissue. [b] Wet weight. [c] Dry weight.

uptake of selenium may not be playing an important role in the accumulation/retention of selenium. It was pointed out, however, that the differences in selenium content in each diet group may have been obscured because of unknown differences in animal ages. Trace metal levels in general are known to be dependent on the age of an organism.[19,20]

Selenium has been reported to modify the accumulation of trace elements and the physiological effects exerted by some elements, e.g. arsenic, cadmium and mercury.[2] The protective effect of selenium against mercury is of particular interest. Published literature[21] suggests a correlation between mercury and selenium concentrations. Lyle,[14] however, measured selenium and mercury concentrations in 18 species of shark from Northern Australian waters and found no significant correlation between selenium and mercury concentrations. When other available data for selenium and mercury concentrations in Australian marine organisms are plotted (Fig. 1), no significant correlation of selenium and mercury except in black marlin liver is observed. No linear relationship between selenium and mercury concentration was observed in any tissues.

Distribution

Maher[3,18,22] used a sequential extraction scheme to identify some of the properties of the selenium compounds present in marine macroalgae and

Table 5 Selenium in marine crustaceans

Species	Common name	Location	Tissue[a]	Selenium (mg kg^{-1})	Reference
Penaeus merguiensis	Banana prawn	Queensland	M[c]	2.2	8
Penaeus monodon	Panda prawn	Queensland	M[c]	1.9	8
Penaeus latisulcatus	Western king	St Vincent's Gulf	M[c]	3.7–5.6	12
Jasus novae hollandiae	Southern rock lobster	St Vincent's Gulf	M[c]	2.5–2.9	12
			D[c]	3.0–3.5	
Crangon novae zelandiae	New Zealand snapping prawn	St Vincent's Gulf	M[c]	3.4–3.9	12
Helograpsus sp.		St Vincent's Gulf	M[c]	1.8–3.3	12
			Soft tissue[c]	1.6–2.7	12
Schizophrys aspera	Red Sea toad	St Vincent's Gulf	M[c]	3.0–3.6	12
			Soft tissue[c]	2.6–3.2	12
Jasus novae hollandiae	Southern rock lobster	South Australia	?[b]	0.10–0.44	13

[a] M, muscle; D, digestive system. [b] Wet weight. [c] Dry weight.

Table 6 Distribution of selenium in marine animals
(a) Relationship to diet[a]

Diet species	Total selenium[c] (mg kg^{-1})	Inorganic selenium (mg kg^{-1})	Selenium (%)		
			$CH_3OH/CHCl_3$	CH_3CH_2OH/H_2O	Residue
Plankton					
Mytilus edulis planulatus	1.1	N.D.	2	8	86
Pecten alba	2.1	N.D.	2	10	84
Pinna bicolor	1.9	N.D.	3	14	83
Equilchlamys bifrons	2.3	N.D.	1	15	77
Mean ± SD	1.8±0.5	–	2±0.8	12±3	83±4
Herbivores					
Haliotis ruber	2.2	N.D.	1	10	84
Hyporhamphus melanochir	0.03	N.D.	2	13	80
Helograpsus haswellianus	1.9	N.D.	1	18	78
Schizophyrs aspera	3.2	N.D.	1	11	77
Mean ± SD	2±1	—	1.3±0.5	13±3	78±3
Carnivores					
Sepioteuthis australis	2.4	N.D.	2	5	82
Silliganodes punctatus	1.3	N.D.	3	8	79
Jasus novae hollandiae	2.6	N.D.	1	17	81
Crangon novae zelandiae	3.6	N.D.	1	11	85
Portunus pelagicus	3.8	N.D.	1	12	79
Penaeus latisulcatus	5.1	N.D.	3	10	75
Mean ± SD	3±1	—	2±1	11±4	80±4

[a] Ref. 18. [b] N.D., <0.001 mg kg^{-1}. [c] Dry weight.

(b) Extraction of selenium

Tissue	Selenium (%)		
	$CH_3OH/CHCl_3$	CH_3CH_2OH/H_2O	Tris/HCl
Penaeus latisulcatus	5±2	19±5	72±4
Pecten alba	3±1	20±6	80±5
Sepioteuthis australis	2±1	14±3	78±7
Hemir hamphus australis	4±1	17±4	76±3

Table 7 Selenium associated with biochemical fractions of marine macroalgae

Alga	Selenium (%)				
	Lipids/lipoproteins	Amino acids	Organic acids/sugars	Proteins	Residue
Chlorophyceae					
Caulerpa flexilis	N.D.[a]	23	1	62	3
Caulerpa cactoides	N.D.	31	2	56	N.D.
Phaeophyceae					
Cystophora siliquosa	N.D.	7	5	61	13
Cystophora moniliformis	N.D.	11	2	58	16
Rhodophyceae					
Cladurus elatus	N.D.	21	1	73	N.D.
Phacelocarpus apodus	N.D.	14	1	70	10

[a] N.D., not detectable

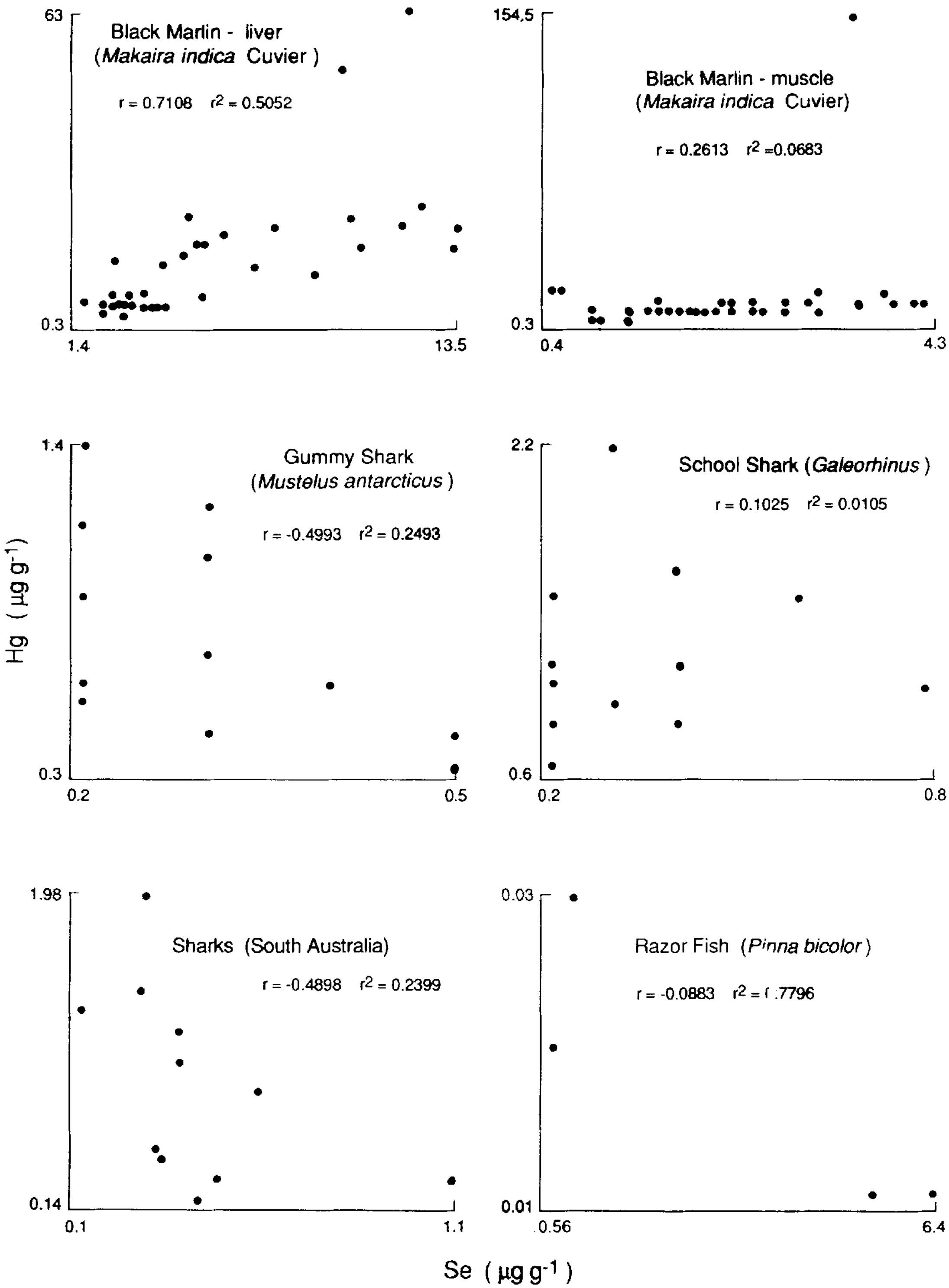

Figure 1 Relationship of selenium and mercury in marine animals.

animals. In marine macroalgae, selenium is predominantly associated with amino-acids and proteins in all algal classes (Table 7). In marine animals [Table 6(a)], most of the selenium is associated with the non-extractable protein residue. This non-extractable selenium could, however, be extracted by using a Tris buffer solution [Table 6(b)]. The addition of ethanol to the buffer extracts to precipitate protein also quantitatively precipitated selenium suggesting that a large fraction of selenium in the muscle tissues of marine animals may be associated with proteins.

The non-preferential accumulation of selenium in taxa and the dietary independence of selenium chemical form suggests that selenium is incorporated only for specific roles, e.g. into selenoproteins such as gluthathionine peroxidase,[23] with excess selenium being excreted.[24]

Speciation

Maher[3, 18, 22] attempted to extract inorganic selenium from marine tissues with hydrochloric acid followed by reduction to hydrogen selenide using sodium tetrahydroborate. Selenium in all tissues was not present as characterizable inorganic selenium species (SeO_3^{2-}, SeO_4^{2-}). Inorganic selenium species ionically complexed by tissues should have been released by acid extraction and some may have been lost by volatilization. Selenium incorporated into selenoamino-acids would not have been released by the extraction procedure employed.

Other studies

Ahsanullah and co-workers[25, 26] have investigated the adverse effect of selenium on two marine invertebrates (*Cyclaspsis usitate* and *Notocallista* sp.) and an amphipod (*Allorchestes compressa*). Their results indicate that juveniles may be more affected by increased selenium levels than adults. Localized increases of selenium in estuaries with restricted circulation may be detrimental to organisms.

Future research directions

Data are required for the selenium content of waters, sediment and biota of nearshore Australian marine environments so that the biogeochemical cycling of selenium can be understood and the effects of localized inputs of selenium predicted.

It has been suggested[27] that selenium is dissolved from riverine particles entering estuaries. It is necessary to determine if indeed selenium is conservative in estuarine environments. Selenium bound to sediment and considered unavailable to some organisms may be released and become bioavailable.

Little is known about the speciation of selenium in organisms, water and sediments. It appears that selenium is associated with proteins; however, these need to be isolated and characterized before the biochemical pathways of selenium utilization can be postulated. Studies must be performed at elevated selenium levels to determine if the biochemical utilization of selenium is different at such concentrations. Organisms may have mechanisms for dealing with elevated selenium levels by excretion or they may accumulate selenium at harmful levels or in forms that are detrimental to other organisms.

Organisms analysed for selenium should also be analysed for mercury and other elements (e.g. arsenic, cadmium) to determine whether selenium does influence the accumulation of other trace elements.

ARSENIC

Occurrence

Water and sediment

Few published studies of arsenic in Australian marine water samples are available (Table 8). In general, dissolved arsenic concentrations are between 1 and 2 μg litre^{-1}, similar to those found in non-polluted coastal and oceanic waters.[36-39] Levels in excess of 2 μg litre^{-1} are indicative of anthropogenic input. Contaminated marine wastes have been reported to arise from acid waste disposal (Burnie/Penguin, Tasmania[28,33]), and from the operation of an electrolytic zinc refinery.[35] In the latter case, arsenic concentration in the estuarine waters near the refinery was 6 μg litre^{-1} in common with other trace metal contaminants. The concentration decreased both upstream and downstream of the refinery.

Even fewer studies have looked at arsenic in marine sediments[28,35,40] and the available results are shown in Table 9. Davies[40] examined the distribution of arsenic in shelf sediments and found elevated arsenic concentrations in sediments between Port Kembla and Newcastle

Table 8 Arsenic in marine waters

Location	As(III)	Total arsenic[a] (μg litre^{-1})	Reference
Burnie/Penguin, Tasmania			
1970	—	1–30	28
1971	—	1–3	
Derwent Estuary, Tasmania	—	<1–6	29
South Australia	0.013–0.055	1.1–1.61	30
Yarra River	0.07–0.66	0.51–2.37	31
Bass Strait	0.01–0.17	0.88–1.44	32
Port Hacking	0.1–0.27	0.97–2.4	73
Derwent River Estuary	—	0.1–6.1	33
Derwent River Estuary	—	0.4–4.3	34
Northwest coast,Tasmania	—	<1–170	35

[a] In some papers this may corespond to As(V).

Table 9 Arsenic in marine sediments

Location	Arsenic[a] (mg kg^{-1})	Reference
Continental shelf, Southeast Australia	10–180	40
Burnie/Penguin, Tasmania		
1970	<16–70	28
1971	<16–190	
Northwest coast, Tasmania	<13–116	35

[a] Dry weight.

(NSW) and a general increase in arsenic seaward. He could not elucidate the source of arsenic in continental shelf sediments.

Marine organisms

Arsenic measurements in marine plants of Australia are given in Table 10. An enrichment of total arsenic in Phaeophyta relative to Rhodophyta and Chlorophyta is apparent when arsenic concentrations in algae from the same site are compared. Similar findings have been reported for macroalgae from sites in North America, Canada and Britain.[42–44] Arsenic levels in Phaeophyta are also similar to those found in Phaeophyta from other parts of the world.[43,45,46] The significant differences in each algal taxonomic class will be due to metabolic or age differences. Maher and Clarke[41] collected juvenile macroalgal specimens (less than four months old) from the intertidal zone of Port Stanvac, St Vincent's Gulf. Again elevated arsenic concentrations were found in Phaeophyta specimens relative to other classes, suggesting that the differences in arsenic accumulation are due to metabolic rather than age differences.

Arsenic concentrations measured in marine animals are reported in Tables 11, 12 and 13. In general, arsenic concentrations are higher in the muscle tissues of crustaceans and molluscs than in the muscle tissue of fish. This in agreement with the observations of other workers.[49,50]

Digestive tissues contained higher arsenic concentrations than muscle tissue, but as organisms were not purged before analysis, some of the arsenic measured may have been due to residual food, in the gut eg. macroalgae, which would eventually be excreted.

Maher[47] investigated the accumulation of arsenic in the marine food chain in relation to diet (Table 14). The total arsenic concentrations of animals in each diet group were not significantly different. ($P<0.05$). Differences in arsenic concentration due to diet may have been obscured, as animals were collected from different areas and the concentration of arsenic may only reflect the environmental supply of arsenic. The concentrations found may also be influenced by the age of the animals, as trace metal levels in general are dependent on the age of the organisms.[19,20,51]

Distribution

Maher[52,55] has looked at the distribution of arsenic in marine animals in relationship to diet and in marine macroalgae. Most of the arsenic in marine animals [Table 14(a)] was in a methanol–water-soluble form (70–98%). Lipid-soluble arsenic was present in all tisues but the proportion varied (0.5–15%) depending on the species and diet. Lipid-soluble arsenic was significantly higher ($P > 0.999$) in plankton feeders (14 ± 1%) relative to herbivores (8 ± 3%) and carnivores (4 ± 3%). Plankton feeders also contained higher concentrations of unextractable arsenic (10 ± 1%) relative to herbivores and carnivores (2 ± 2%). Studies of arsenic in marine crustaceans from coastal waters around Japan showed similar results.[53] In marine macroalgae [Table 14(b)], most of the arsenic was again present in a methanol-soluble forms (70–85%), with a small proportion of the arsenic in lipid-soluble forms (7–10%). When extracts were subjected to ion-exchange chromatography, the arsenic compounds were eluted with soluble sugars. Degradation of fractions by hydrolysis with 1M

Table 10 Arsenic in marine plants

Species	Common name	Location	Arsenic (mg kg^{-1})	Reference
Ruppia sp.	Seagrass	South Australia	22–1000[b]	13
Zostera mucronata	Seagrass	South Australia	17–160[b]	13
Posidonia australis	Seagrass	South Australia	21–33[b]	13
Rhodophyceae		South Australia		41
Phacelocarpus adopus			26.2[a]	
Dictymenia harveyana			17.6[a]	
Gigartina sp.			20.1[a]	
Coelarthrum muelleri			31.3[a]	
Areschougia congesta			24.5[a]	
Laurencia sp.			15.3[a]	
Plocamium sp.			15.9–16.2[a]	
Gracilaria			12.5[a]	
Porophyra lucasii			12.5[a]	
Chlorophyceae		South Australia		41
Ulva			8.8–11.6[a]	
Caulerpa brownii			8.7[a]	
Caulerpa cactoides			16.3[a]	
Caulerpa flexilis			12.0[a]	
Caulerpa obscura			6.3[a]	
Caulerpa scalpelliformis			13.4[a]	
Enteromorpha sp.			9.6–10[a]	
Phaeophyceae		South Australia		41
Petalonia fascia			21.3[a]	
Scytosiphon lometaria			36.6[a]	
Ectocarpus sp.			29.8[a]	
Cystophora monilifera			35.3–42.2[a]	
Cystophora moniliformis			65.3–123[a]	
Cystophora subfacinata			37.3–54.9[a]	
Cystophora platylobium			179[a]	
Cystophora racemosa			83.8[a]	
Cystophora siliquosa			61.3[a]	
Ecklonia radiata			49.6–84.7[a]	
Sargassum bracteolosum			62–125[a]	
Sargassum linearifolium			58.4[a]	
Lobospira bicuspidata			29.4[a]	
Dictyota dichotoma			26.3[a]	
	Green algae	Great Barrier Reef	4–21[a]	16
	Mixed diatoms	Great Barrier Reef	9[a]	16

[a] Dry weight. [b] Wet weight.

Table 11 Arsenic in marine fish

Species	Common name	Location	Tissue[a]	Arsenic (mg kg^{-1})	Reference
Hemir hamphus australis	Sea garfish	South Australia	M[b]	0.82–8.4	47
			D[b]	3.4–12.0	
Sillaginodes punctatus	Spotted whiting	South Australia	M[b]	8.6–13.8	47
		South Australia	D[b]	10.2–22.8	47
Arripis georgianus	Tommy rough	South Australia	M[b]	3–7.2	47
			D[b]	1.8–5.8	
Callogobius mucosus	Sculptured gobic	South Australia	M[b]	1–3.6	47
			D[b]	0.6–4.4	
Notorhynchus cepedianus	Seven-gilled shark	South Australia	?[c]	19.8–22.4	13
Heterodontus portus jacksoni	Port Jackson shark	South Australia	?[c]	12–15	13
Carcharhinus carcharias	White pointer shark	South Australia	?[c]	10.1	13
Alopias vulpinus	Thresher shark	South Australia	?[c]	10.6	13
Halaelurus analis	Spotted cat shark	South Australia	?[c]	100	13
Furgaleus ventralis	Whiskery shark	South Australia	?[c]	36.1	13
Carcharhinus greyi	Bronze whaler shark	South Australia	?[c]	13.2–50.3	13
Sphyrna zygaena	Hammerhead shark	South Australia	?[c]	50	13
Deania calcea	Dorian Gray dogfish	South Australia	?[c]	30	13
Rexea solandri	Gem fish	South Australia	?[c]	0.5–1.6	13
Anthias pichellus	Orange perch	South Australia	?[c]	14	13
Platycephalus fuscus	Dusky flathead	South Australia	?[c]	0.5–9.0	13
Platycephalus bassensis	Sand flathead	South Australia	?[c]	1–12	13
Pterygotrigla polyommata	Sharp-beaked gurnard	South Australia	?[c]	1.5–5.0	13
Chelidonichethys kumu	Red gurnard	South Australia	?[c]	4–5	13
Neosebastes thetidis	Thetis fish	South Australia	?[c]	1.9–2.8	13
Upeneichthys lineatus	Red mullet	South Australia	?[c]	7–25	13
Sillaginodes punctatus	Spotted whiting	South Australia	?[c]	10–44	13
Sillago schomburgkii	Yellow-finned whiting	South Australia	?[c]	5–8	13
Argyrosomus hololepdotus	Mulloway	South Australia	?[c]	0.5–1.0	13
Plagiogeneion macrolepis	Ruby fish	South Australia	?[c]	1.6–2.0	13
Chrysophyrs auratus	Snapper	South Australia	?[c]	2.5–18	13
Acanthopagrus butcheri	Black bream	South Australia	?[c]	1.5–15	13
Ostorhinchus conwaii	Knife jaw	South Australia	?[c]	12	13
Nemadactylus macropoterus	Jackass fish	South Australia	?[c]	30–150	13
Squatina australis	Angel shark	South Australia	?[c]	25–100	13
Trygonorhina fasciata	Fiddler ray	South Australia	?[c]	1–15	13
Myliobatis australis	Eagle ray	South Australia	?[c]	94	13
Sardinops sagax	Pilchard	South Australia	?[c]	6.2	13
Hyporhamphus melanochir	Garfish	South Australia	?[c]	4–7	13
Pseudorhombus arsius	Large-toothed flounder	South Australia	?[c]	9	13
Pseudorhombus jenynsii	Small-toothed flounder	South Australia	?[c]	2–12	13

[a] M, muscle; D, digestive system; ?, unknown tissue. [b] Dry weight. [c] Wet weight. [d] Not known whether wet or dry weight.

sodium hydroxide released 50–60% of arsenic as dimethylarsenic. Arsenic sugars have been isolated from *Ecklonia radiata*[54] and it is likely that the methylated arsenic compounds found are degradation products of arsenosugars.

Speciation

Water

Maher[30] measured the arsenite/arsenate concentrations in South Australian coastal waters. Only a small percentage of arsenic was present as arsenite (1.2 – 4.3%), as expected from thermodynamic considerations which indicate that arsenic should exist as arsenate.[56] The arsenite found was attributed to biological activity.[37,38]

Butler and Smith[31] and Smith *et al.*[73] examined arsenic species in oxygen-depleted marine waters. Seawater in two deep holes of the Yarra River estuary were isolated by a surface flow of freshwater, and the sub-halocline waters were oxygen-deficient ($<20\,\mu$g atm litre^{-1}). In the latter

Table 11 Continued

Species	Common name	Location	Tissue[a]	Arsenic (mg kg $^{-1}$)	Reference
Rhombosolea tapirina	Greenback flounder	South Australia	?[c]	<0.5–8.0	13
Cyttus australis	Silver dory	South Australia	?[c]	2.6–2.8	13
Macrorhamphosidae	Bellows fish	South Australia	?[c]	6.2	13
Liza argentea	Jumping mullet	South Australia	?[c]	2	13
Aldrichetta forsteri	Yellow-eye mullet	South Australia	?[c]	0.25–5.0	13
Australuszza sphyraena	Snook	South Australia	?[c]	0.2–2.0	13
Polyprion oxygeneios	Hapuka	South Australia	?[c]	1	13
Trachurus declivis	Horse mackerel	South Australia	?[c]	2–8	13
Caranx georgianus	Trevally	South Australia	?[c]	1–5	13
Arripus trutta	Australian salmon	South Australia	?[c]	1	13
Arripus georgianus	Tommy rough	South Australia	?[c]	3	13
Pelates sexlineatus	Striped perch	South Australia	?[c]	5	13
Pseudaphyritis uruilli	Congolli	South Australia	?[c]	8	13
Torquigener pleurogramma	Banded toadfish	South Australia	?[c]	12–15	13
Allomycterus pilatus	Porcupine fish	South Australia	?[c]	1	13
Aracana ornata	Ornate cowfish	South Australia	?[c]	6	13
Scobinichthys granulatus	Rough leatherjacket	South Australia	?[c]	12	13
Monacanthidae	Leatherjacket	South Australia	?[c]	10–12	13
Galeorhinus australis	School shark	Southeast Australia	M[c]	5–23	11
Mustelus antarcticus	Gummy shark	Southeast Australia	M[c]	7–30	11
Makaira indica cuvier	Black marlin	Cairn's Queensland	M[c]	0.1–1.65	9
			liver[c]	0.25–2.15	
Acanthopagrus australis	Yellow-fin bream	New South Wales	M[d]	0.1–2.4	10
Platycephalus fuscus	Dusky flathead	New South Wales	M[d]	0.1–0.4	10
Musil cephalus	Sea mullet	New South Wales	M[d]	0.1–3.8	10
Chrysophiris auratus	Snapper	New South Wales	M[d]	0.4–4.4	10
Pomatomus satratrix	Tailor	New South Wales	M[d]	0.2–1.4	10
Sciaena antarctica	Mulloway	New South Wales	M[d]	<2.3	10
Seriola grandis	Yellow-tail kingfish	New South Wales	M[d]	0.4–1.0	10
Arripus tuna	Australian salmon	New South Wales	M[d]	0.1–0.5	10
Thunnus albacares	Yellow-fin tuna	New South Wales	M[d]	0.2–2.2	10

[a] M, muscle; D, digestive system; ?, unknown tissue. [b] Dry weight. [c] Wet weight. [d] Not known whether wet or dry weight.

instance, seawaters of South West Arm. Port Hacking (NSW) were thermally stratified. At the time of sampling, low oxygen conditions ($<100\,\mu$g atm litre^{-1}) prevailed in the bottom waters. From both studies, arsenic input from anoxic sediments was inferred. Against thermodynamic predictions, arsenic(V) was the major species emanating from the sediments and only in one bottom water sample in the Yarra estuary did arsenic(III) account for 50% of the dissolved inorganic arsenic. The higher oxidation state of arsenic also predominates under very similar conditions of oxygen depletion in Saanich Inlet.[57]

Brockbank *et al.*[58] investigated the photochemical decomposition of arsenic species in natural waters. In seawater, it was shown that arsenite will eventually be oxidized to arsenate, whereas any methylated arsenic species (e.g. monomethylarsenic acid or dimethylarsinic acid) will be unaffected because of their refractory nature.

Marine organisms

Flanjak[48] and Maher[47] have reported that the concentrations of inorganic arsenic (N.D. – 0.87 mg kg^{-1}) in a large number of fish, crustaceans and molluscs are insignificant when compared with total arsenic concentrations (0.6–91 mg kg^{-1}). Marine macroalgae, however, can contain an appreciable quantity of inorganic arsenic, 0.9–7.3 mg kg^{-1},[47] and this may be due to the ability of algal lipids to complex inorganic arsenic.[59] Edmonds and Francesconi have isolated a number of naturally occurring organoarsenic compounds from Australian marine organisms,

Table 12 Arsenic in crustacea

Species	Common name	Location	Tissue[a]	Arsenic (mg kg^{-1})	Reference
Penaeus latisulcatus	Western king prawn	South Australia	M[b]	11.4–23.1	47
Jasus novae hollandiae	Southern rock lobster	South Australia	M[b]	46–91	47
Crangon novae zelandiae	New Zealand snapping prawn	South Australia	M[b]	7.1–13.2	47
Helograpsus sp.		South Australia	M[b]	17.4–26.3	47
			Soft tissue[b]	25.7–58	47
Schizophrys aspera	Red Sea toad	South Australia	M[b]	15.1–28.4	47
			Soft tissue[b]	22.3–47	
Portunus pelagicus	Blue swimmer crab	South Australia	M[b]	48	47
Panaeus latisulcatus	Western king prawn	South Australia	?[c]	12–50	13
Jasus novae hollandiae	Southern rock lobster		?[c]	11.2–52	13
Ibacus incisus	Moreton Bay bug	South Australia	?[c]	30–40	13
Portunus pelagicus	Blue swimmer crab	South Australia	?[c]	25–39	13
Metapenaeus macleayi	School prawn	New South Wales	?[c]	3.5–5.1[e]	48
Penaeus plebjus	King prawn	New South Wales	?[c]	2.8–14.6[e]	48
Hymenopenaeus sibogae	Royal red prawn	New South Wales	?[c]	N.D.–5.1[d,e]	48
Portunus pelagicus	Blue swimmer crab	New South Wales	?[c]	1.2–5.9[e]	48
Scylla serrata	Mud crab	New South Wales	?[c]	N.D.–4[d,e]	48
Jasus verreauxii	Eastern common crayfish	New South Wales	?[c]	11.9–54.1[e]	48

[a] M, muscle tissue; ?, unknown tissue. [b] Dry weight. [c] Wet weight. [d] N.D., not detectable. [e] Organic arsenic.

including arsenic-containing ribofuranosides from the macroalga *Ecklonia radiata*,[54] an arsenic-containing sugar sulphate from the kidney of the giant clam *Tridacna maxima*,[60] trimethylarsine oxide [$(CH_3)_3AsO$] from the estuary catfish *Cnidoglanis macrocephalus*[61] and arsenobetaine from the western rock lobster *Panulirus longipes cygnus* George,[62] school whiting *Sillago bassensis*[61] and the estuary catfish.[61] Whitfield[63] also identified trimethylarsine as a degradation product in prawns.

Dimethyloxarsylethanol has been isolated from anaerobically incubated *Ecklonia radiata*[64] and is thought to be the likely precursor for the formation of arsenobetaine.

Edmonds and Francesconi[65] have synthesized their published work (Fig. 2) and suggested a possible route for the formation of arsenobetaine from arsenate, the predominant form of dissolved arsenic in seawater.[37, 38]

Arsenobetaine is widely distributed in marine animals at different trophic levels[66] and is probably the end-product of arsenic metabolism in the marine food chain.

Edmonds and Francesconi[61] administered sodium arsenate to school whiting and estuary catfish and found trimethylarsine oxide accumlated in their tissues. The isolation of this naturally occurring compound from catfish, and the demonstration that some organisms can produce it, indicate that other organoarsenic compounds may be present in marine organisms, although arsenobetaine may be the major component.

Future research directions

Information is required on the arsenic species in marine waters to determine how organisms in Australian waters have evolved stragegies for dealing with arsenic uptake. The role of coral in arsenic cycling in phosphate-deficient tropical waters is of particular interest. How does coral discriminate between arsenic and phosphate during uptake? If arsenic is taken up, is it accumulated or is it released in other forms? The prevailing arsenic/phosphate ratios in coastal waters need to be measured as these ratios may be a key element in determining the rate of uptake of arsenic. The physiological significance of lipid- and water-soluble arsenic compounds and their relationship and interconvertibility in marine organisms needs to be determined. It remains to be established whether arsenobetaine is synthesized from other compounds (e.g. macroalgae arsenosugars) and passed up the food chain or whether organisms at different trophic levels have the ability to synthesize arsonobetaine. The existence of trimethylarsenic oxide, which may be converted to the toxic trimethylarsine, leads to a concern that other unidentified arsenic compounds may exist in marine organisms which have undesirable effects.

As arsenic may be released from sediments in oxygen-depleted environments,[66] estimates of riverine and atmospheric inputs of arsenic and an understanding of arsenic cycling in sediments is required. Adsorption processes and the role of microbes in determining arsenic speciation need to be studied, especially in estuaries, to assess the potential remobilization of arsenic from sediments. Organisms may be able to detoxify or eliminate arsenic at naturally occurring levels, but what happens at elevated arsenic levels is uncertain.

TIN

Occurrence

General

The major concern for organometallic species of tin in the aquatic environment has been for alkyltin species, principally tributyltin (TBT). This

Table 13 Arsenic in molluscs

Species	Common name	Location	Tissue[a]	Arsenic (mg kg^{-1})	Reference
Mytilus edulis planulatus	Mussel	South Australia	M[b]	12.6–22	47
		South Australia	V[b]	25–47	47
Pecten alba	King scallop	South Australia	M[b]	23.3–30	47
			V[b]	40–72	47
Sepioteuthis australis	Southern calamary squid	South Australia	M[b]	3.9–8.8	47
Pinna bicolor	Razor fish	South Australia	M[b]	51	47
Equilchlamys bifrons	Queen scallop	South Australia	M[b]	60	47
Haliotis ruber	Black-lip abalone	South Australia	M[b]	22	47
Sepia apam	Cuttlefish	South Australia	?[c]	42–82	13
Sepioteuthis australis	Southern calamary squid	South Australia	?[c]	18	13
Nototodarus gouldi	Gould's squid	South Australia	?[c]	20	13
Electroma georgiana	Butterfly shell	South Australia	?[c]	7	13
Pinna bicolor	Razor fish	South Australia	?[c]	12–21	13
Grassostrea gigas	Pacific oyster	South Australia	?[c]	1.5–8.6	13
Equichlamys bifrons	Queen scallop	South Australia	?[c]	18	13
Trichomya hirsuta	Hairy mussel	South Australia	?[c]	5.2–8	13
Katelysia sp.	Cockle	South Australia	?[c]	30	13
Semele exigua	Cockle	South Australia	?[c]	10	13
Haliotis ruber	Black-lip abalone	South Australia	?[c]	1.2–6.2	13
Elminius modestus	Mangrove barnacle	South Australia	?[c]	5–22	13
Saccostrea sp.	Rock oyster	Great Barrier Reef	?[b]	58	16
Hippopus hippopus	Giant clam	Great Barrier Reef	Kidney[b]	481–561	16
			Gonad[b]	21	16
			Digestive tract[b]	65	16
			Zoxanthellae[b]	15–16	16
Tridacna maxima	Giant clam	Great Barrier Reef	Kidney[b]	953–1004	16
			Zoxanthellae[b]	33	16
			Abductor muscle[b]	12–25	16
Tridacna derasa	Giant clam	Great Barrier Reef	Kidney[b]	454–1025	16
			Gonad[b]	22	16
			Digestive tract[b]	26	16
			Abductor muscle[b]	11.6–12.3	16
			Gills[b]	5.2–24.8	16
Pictada margaritifora	Mother of pearl		?[b]	70	16
Lambis lambis	Spider strom		?[b]	15	16
Didemnum ternatanum			?[b]	371–226	16

[a] M, muscle; V, viscera; ?, unknown tissue. [b] Dry weight. [c] Wet weight.

Table 14 Distribution of arsenic in marine organisms
(a) Marine animals

Species	Total arsenic (mg kg^{-1})	Arsenic (%)			
		Inorganic	$CH_3OH/CHCl_3$	CH_3OH/H_2O	Residue
Plankton diet					
Mytilus edulis planulatus	20.1	1.0	14	72	9
Pecten alba	39	0.8	12	74	14
Pinna bicolor	51	0.6	15	70	8
Equilchlamys bifrons	60	0.4	13	76	7
Mean ± SD	42.5 ± 17.2	0.7 ± 0.3	14 ± 1	73 ± 3	10 ± 3
Herbivores*					
Haliotis ruber	22	0.8	12	85	—
Hyporhampus melanochir	8.6	0.7	7	81	5
Helograpsus haswellianus	22.8	1.1	5	95	1
Schizophyrs aspera	20.1	1.0	7	86	2
Mean ± SD	18.4 ± 6.6	0.9 ± 0.2	8 ± 3	87 ± 6	2 ± 2
Carnivores					
Sepioteuthis australia	6.9	0.7	8	82	6
Sillaginodes punctatus	9.8	1.2	4	94	2
Jasus novae hollandiae	67	0.7	1	97	—
Crangon novae zelandiae	8.4	1.0	1	96	1
Portunus pelagicus	48	0.4	7	91	2
Penaeus latisulcatus	21	0.5	0.5	98	1
Mean ± SD	27 ± 25	0.8 ± 0.3	4 ± 3	96 ± 6	2 ± 2

* Omnivorous but mainly herbivorous

(b) Macroalgae

Species	Total arsenic[a] (mg kg^{-1})	Arsenic (%)			
		Inorganic	$CH_3OH/CHCl_3$	CH_3OH/H_2O	Residue
Sargassum bracteolosum	79	1.7	7	85	—
Ecklonia radiata	90	3.6	4	82	9
Cystophora moniliformis	114	3.1	6	76	11
Dictyota bicuspidata	35	1.1	10	70	14

[a] *Dry weight.*

interest parallels worldwide concern over the usage of TBT in marine antifouling paints, and the impact of TBT release on bivalves, and in particular on oyster culture, which in Eastern Australia is a multimillion dollar industry. The use of TBT-based paints is now banned in most states of Australia, but only on vessels under 25 m in length. Prior to banning, considerable data had been accumulated on the concentrations of TBT and its degradation products in waters, sediments and biota and these provided the evidence for regulatory action.

In additon to its use in marine antifouling paints, TBT is also used as an algicide in cooling water circuits in concentrations as high as 10 μg Sn litre^{-1}. In NSW, waste waters from this source are discharged at sea after primary treatment only; however, given the discharged volumes, it does not represent a major environmental problem.

Dialkyltins are used as heat stabilizers in PVC plastics, and also as catalysts in the production of polyurethanes and some silicone elastomers. The extent to which aqueous wastes containing these species reach nearshore waters is unknown.

Water

There are similarly few data for inorganic tin in Australian coastal waters, although overseas results have shown high concentrations present in sewage sludge.[67] In seawater, tin(IV) is the dominant valency state, and, in either this or the

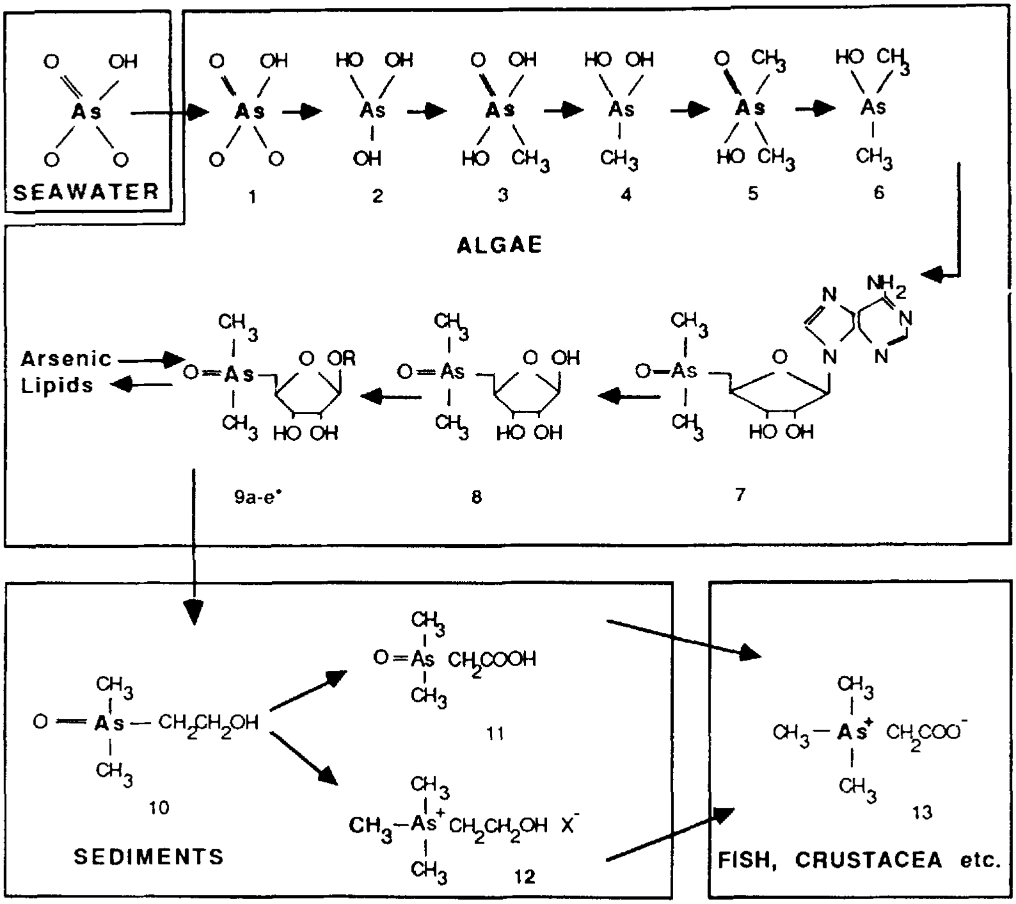

Figure 2 Proposed scheme for transformations of arsenic compounds in the marine environment[65] 9: Arseno sugars; 10: Dimethyloxarsylethanol; 13: Arsenobetaine

divalent state, tin is not considered an environmental hazard in water, although in sediments the potential for biogenic methylation can result in compounds which are toxic to some aquatic biota.[68]

Marine organisms

There appears to be no significant accumulation of tin by coastal marine organisms because the concentrations in the water column are so low. In estuaries the situation is different, especially where the tidal flushing is poor, or where the tin concentration is elevated because of boating activity.

Gastropods have been shown to be sensitive indicators of TBT as indicated by the incidence of imposex, the development of male sexual characteristics in female animals. Evidence for imposex has been demonstrated in two Australian species of gastropod, *Thais orbiter* and *Morula marginalba*;[69] however, laboratory experiments are still being carried out to determine, the TBT concentrations needed to induce imposex.

Data are available for TBT and its degradation products for a range of bivalves (Table 15). In NSW, the major impact has been on oysters and in particular the local delicacy, the Sydney rock oyster, *Saccostrea commercialis*. Bioaccumulation of TBT to over 100 ng Sn g^{-1} was measured in species from the upper Georges River NSW, but typical values for oysters growing in well-flushed areas were below 7 ng Sn g^{-1}.[70] Samples of the Pacific oyster, *Crassostrea gigas*, accumulated more TBT than Sydney rock oysters growing in the same leases, due possibly to the faster rate at which they pump water.

A range of investigations on the impact of TBT on the Sydney rock oyster has been undertaken,[71] including an examination of the mechanism of TBT uptake, synergistic effects of copper and

Table 15 Tributyltin in Australian aquatic biota

Species	Common name	Site	TBT (ng Sn g^{-1}, fresh wt)
Saccostrea commercialis	Sydney rock oyster	Upper Georges River, New South Wales	40–128
		Lower Georges River, New South Wales	15–44
		Coba Bay, Hawkesbury River, New South Wales	7
		Sand Brook Inlet, Hawkesbury River, New South Wales	350
		Wallis Lake, New South Wales	2
		Botany Bay, New South Wales	15
Crassostrea gigas	Pacific oyster	Upper Georges River, New South Wales	175
Ostrea angasi	Mud oyster	Port Phillip Bay, Victoria	<1
Mytilus edulis	Mussel	Mussel farm, Cockburn Sound, Western Australia	18
		As above, near slipway	166
		Port Phillip Bay, Victoria	<1–3
Pecten alba	Commercial scallop	Port Phillip Bay, Victoria	3–16

TBT, the distribution of copper and TBT within an oyster, and the effects on oyster bioaccumulation of removal of the source of TBT in an estuary. These will be the subject of future publications.

Accumulation of TBT by mussels and scallops has also been identified. Typical results for scallops are below 15 ng Sn g^{-1}. These species grow subtidally and may be removed from surface film enrichment which has greater impact on intertidal dwelling oysters. Mussels are usually grown on lines both subtidally and intertidally. Concentrations over 300 ng Sn g^{-1} have been found in samples growing near marinas; however, typical tissue concentrations elsewhere were below 30 ng Sn g^{-1} fresh wt.

Speciation

Water

Early data for the total tin concentration in coastal seawater show concentrations in the range 0.02–3 μg Sn litre^{-1}.[15,72] Analyses of Australian coastal waters by Florence and Farrar[74] using anodic stripping voltammetry found a mean concentration of 0.58 μg Sn litre^{-1} in seawater samples from near Sydney and Brisbane, and similar concentrations in estuarine waters. These concentrations will be almost entirely inorganic tin; however, valency-state speciation was not determined.

The first data on TBT in Australian waters were obtained at the CSIRO Centre for Advanced Analytical Chemistry, by Batley and co-workers in 1989.[70,75] As part of a survey carried out in collaboration with the NSW State Pollution Control Commission, measurements were made on samples from Sydney Harbour (NSW) and the nearby Georges River estuary. This laboratory remains the only Australian laboratory currently with the facilities and expertise for TBT analyses at ng litre^{-1} concentrations. Whilst initially their methodology used capillary column gas chromatography of the extracted butyltin hydrides, better precision and detection limits were obtained using a modification of the method of Donard *et al.*[76,77] In this method, the tin hydrides are trapped on a chomatographic column at liquid nitrogen temperature, and are then thermally desorbed and in the presence of hydrogen are atomized in an electrically heated quartz furnace, with detection of the successively eluting tin species by atomic absorption spectrometry. Subsequently, in collaboration with agencies in other states, results have been obtained for a range of other waters and these are shown in Table 16.

Results show TBT concentrations in open waters to be below 10 ng Sn litre^{-1}, increasing to around 40 ng Sn litre^{-1} in the presence of boating activity and up to 150 ng Sn litre^{-1} near marinas or other areas of high boat density. These are not inconsistent with overseas data. Recent banning in most states of Australia of the use of

Table 16 Tributyltin in Australian waters

Site	Description	TBT (ng Sn litre^{-1})
Georges River, New South Wales	Oyster growing area	8–40
Kogarah Bay, New South Wales	Near slipway	100
Garden Island, New South Wales	Naval dockyard	190
Rushcutters Bay, New South Wales	Large marina	112–220
Manly, Queensland[a]	Enclosed area, near marina	109
Swan Bay, Queensland[a]	Fish sanctuary	14
Southport, Queensland[a]	Near marina	45
Great Keppel Island, Queensland[a]	Uncontaminated area	1
Lakes Entrance, Victoria[b]	Port of Melbourne Authority slipway	249
Clifton Springs, Port Phillip Bay, Victoria[b]	Shellfish farming area	23
Mornington, Port Phillip Bay, Victoria	Shellfish farming area	3
South Australia	Marina site	187
South Australia	Swimming beach	<1

[a] Data from Division of Fisheries and Wetlands Management, Queensland Department of Primary Industries. [b] Data from Victorian Environment Protection Authority.

TBT-based antifouling paints on vessels under 25 m in length has already led to a decline in dissolved TBT concentrations away from the sites of larger vessels.

The degradation products of TBT, dibutyltin and monobutyltin, are present in most waters, but at concentrations well below that of TBT. There is no evidence for any independent source of these compounds.

Sediments

The low solubility of TBT in water results in its ultimate accumulation in bottom sediments. In the vicinity of slipways, very high sediment TBT concentrations (2–40 ng Sn kg^{-1} dry wt) have been measured. These data are possibly biased by the presence of paint flakes from hydroblasted hulls. In sandy sediments, as expected, concentrations are low, whilst in silty deposits typical concentrations near 50 mg Sn kg^{-1} are found. Despite reports that the half-life for TBT in estuarine sediments is of the order of months,[78] we have found TBT to depths of 15 cm in undisturbed Sydney Harbour sediments, which supports the findings of De Mora *et al.*,[79] from studies in Auckland, New Zealand, of a half-life of 1.85 years.

Future research directions

The banning of TBT-based paints will result in much of the TBT research being redirected to examine the biological effects of alternative paint additives. In the interim a monitoring programme has been established to follow the expected recovery of the shellfish industry. Concern for the long-term impact of TBT in dredged sediments seems ill-founded even though the half-life may be higher than originally anticipated.

Although both biotic and abiotic routes exist for the methylation of inorganic tin formed by TBT degradation, or of inorganic tin from other anthropogenic sources, there have been no measurements of its extent in Australian waters of sediments, nor is there yet sufficient evidence to suggest that methyltin species are likely to represent an environmental threat.[68] There are indeed few data on inorganic tin in Australian coastal sediments, and a knowledge of this and the toxicity of any methylated species present would be of value.

It is likely that TBT-based paints will continue to be used on vessels over 25 m in length, and hence there will be a need for a continuing assessment of the impact of such activities on sensitive aquatic biota such as, for example, gastropods.

The need for more rigorous constraints on the painting of such vessels in port, including drydocking and the containment and treatment of wastes, will need to be examined, depending on the results of ecotoxicological investigations.

Acknowledgments The assistance of E Butler, P Kailola, A Ivanocici and J D Smith in providing information is greatly appreciated.

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