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REVIEW

Characteristics of selenium in Australian marine biota

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The occurrence, distribution and speciation of selenium in Australian marine biota is discussed. Biochemical pathways for the accumulation of selenium by marine organisms are also postulated. Comparison of the levels of selenium in macro-algae, fish, crustaceans and molluscs indicates that preferential accumulation of selenium by particular taxa does not occur. Phaeophyta have significantly lower selenium concentrations than Rhodophyta and Chlorophyta. Fish have lower selenium contents in muscle tissues than molluscs and crustaceans. Marine animals with different dietary intake (planktonic vs herbivorous vs carnivorous) are not observed to have significantly different levels of selenium ($P > 0.05$). Selenium in all the organisms studied was predominantly associated with free amino-acids or protein residues and was not present as characterizable inorganic selenium species (SeO_3^{2-}, SeO_4^{2-}). These results indicate that selenium is probably only incorporated into biota for specific biochemical purposes with any excess selenium being excreted or eliminated.

Keywords: Selenium, biota, marine, Australia, environment

INTRODUCTION

Anthropogenic inputs of selenium to the marine environment have increased in recent years and selenium is now considered to be a potential marine pollutant.[2] Selenium is of interest because it is not only classified as an essential element for marine animals[3,4] but is also toxic at elevated levels.[5,6] The biogeochemical cycling of this element is also unusual because it involves both inorganic forms and organometallic compounds such as selenoamino-acids.[7-9]

OCCURRENCE

Published measurements of selenium in Australian marine organisms are given in Table 1. Comparison of levels of selenium in macro-algae, fish, crustaceans and molluscs show that selenium is present at low concentrations in all organisms, but preferential accumulation with particular taxa, as reported for arsenic, tin and vanadium,[10-12] does not occur.

Significantly lower concentrations of selenium ($P > 0.05$) are found in Phaeophyta relative to Chlorophyta (excluding *Ulva* sp.) and Rhodophyta (see Fig. 1). Similar findings have been reported for macro-algae collected from coastal areas of Japan[13] and from Kimmeridge Bay, England.[14] A possible explanation for this observation is that Phaeophyta usually contain smaller amounts of amino-acids and proteins than Chlorophyta and Rhodophyta.[15] Selenium is thought to be incorporated into the amino-acids and proteins of these macro-algae in much the same way as it is known to be incorporated into micro-algae[7,9] and plants.[16,17] Lower selenium concentrations in Phaeophyta may therefore be due to the relatively lower concentrations of sulphur-containing amino-acids for binding and storage.

Examining the available data for selenium concentrations in muscle tissue of marine animals (Fig. 2) it is apparent that fish (excluding Black Marlin[18]) contain lower concentrations of selenium than other marine organisms: 86% of fish analysed had selenium concentrations below 0.5 mg kg^{-1}, whereas only 49% of molluscs and 50% of crustaceans analysed had selenium concentrations under 0.5 mg kg^{-1}. Higher selenium concentrations are normally found in digestive and liver tissues (Table 1). As the gut contents of organisms were not purged before most analyses, some of the selenium measured in digestive tissues may be due to residual food present in the gut which would otherwise be eliminated. The

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Table 1 Selenium in Australian marine organisms

Class	Location	Tissue[a]	Selenium (mg kg^{-1})	Reference
Macro-algae				
	Queensland	Leaves[b]	0.063	55
	South Australia			
Phaeophyceae		Whole plant[b]	0.014–0.135	33
Rhodophyceae		Whole plant[b]	0.153–0.434	33
Chlorophyceae		Whole plant[b]	0.053–0.264	33
Molluscs	Queensland	M[b]	2.6	55
	South Australia	M[b]	0.7–2.6	56
		D[b]	1.1–2.7	56
		?[c]	0.04–6.4	57
	New South Wales	?[c]	ND–0.4	21
Crustaceans	Queensland	M[b]	1.9–2.2	55
	South Australia	M[b]	1.8–5.6	56
		D[b]	3–3.5	56
		Soft tissue[b]	1.6–2.7	56
		?[c]	0.1–0.44	57
		?[c]	0.4–1.6	21
Fish	Queensland	M[c]	0.4–4.3	18
		L[c]	1.4–13.5	18
		M[c]	1.5	55
		Eye[c]	3.2	55
	South Australia	M[b]	0.4–1.7	56
		D[b]	0.79–2.6	56
		?[c]	0.1–0.41	57
	New South Wales	M[d]	0.1–0.8	58
		M[c]	ND–0.5	21
		L[c]	0.2–20	21
		M[c]	0.07–1.17	59
		M[c]	0.05–0.72	20
		M[c]	0.15–0.85	30
	South-eastern Australia	M[c]	0.2–0.8	60
	Northern Australia	M[c]	0.25–3.4	29

[a] Abbreviations: M, muscle; L, liver; D, digestive tissue; ?, unknown tissue. [b] Dry weight. [c] Wet weight. [d] Unspecified (dry or wet weight). ND, not detectable.

liver is an organ of detoxification and probably indicates active excretion of selenium.

The effect of diet on selenium concentrations in some marine animals has been examined (Table 2). The total selenium concentration in animals in each diet group was not significantly different, indicating that the dietary source of selenium is not playing an important role in its accumulation/retention. However, differences in selenium content in each diet group may have been obscured because difference in animal ages, sex, habitat or prevailing physicochemical conditions were not documented. Trace metal levels in general are known to be dependent on these factors.[19]

Mackay *et al.*[18] have reported that selenium concentrations in muscle tissues of Black Marlin are correlated with length, girth and weight, while selenium concentrations in liver tissues are correlated with weight and girth. Other studies have found no obvious or consistent relationship

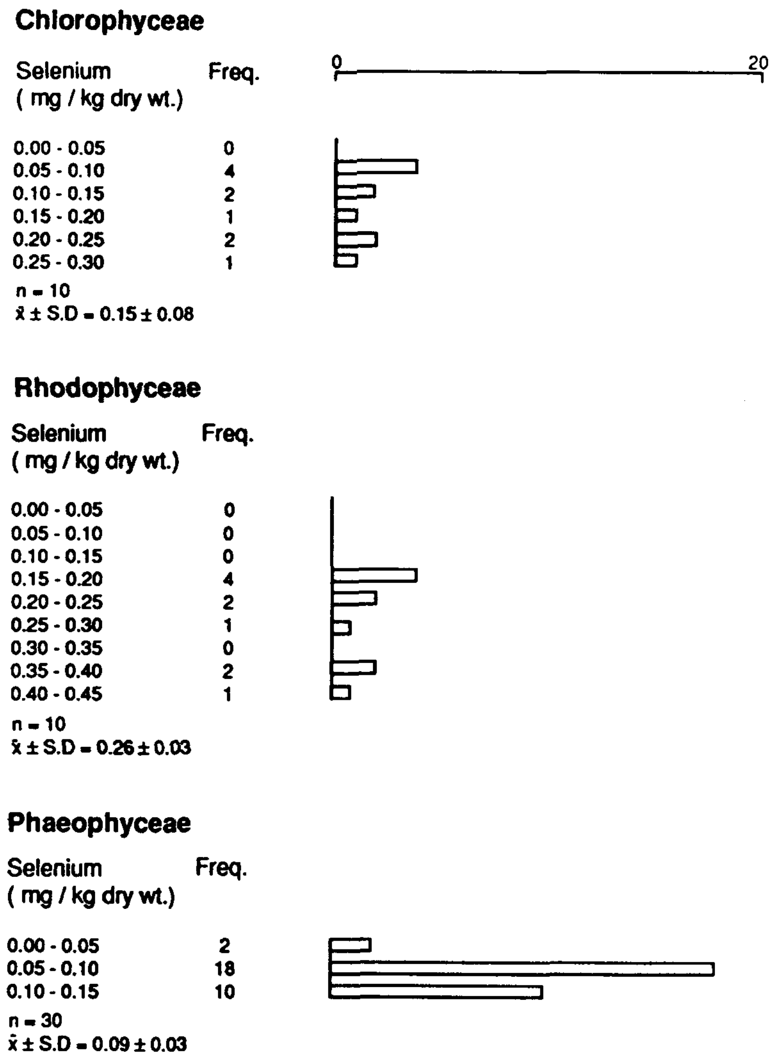

Figure 1 Selenium concentrations in marine macro-algae.

between selenium concentration and length, girth or weight for sharks or fish.[20,21] It is unlikely that the accumulation of selenium is a function of age.

RELATIONSHIP WITH OTHER ELEMENTS

Published findings[22] suggest that mercury and selenium concentrations may be correlated in some marine organisms. Selenium may protect against the toxic effect of mercury.[23-28] A significant correlation between selenium and mercury in Black Marlin livers has been found.[18] However, no significant correlations of selenium and mercury concentrations in sharks from northern Australian waters[29] and Snapper from New South Wales coastal waters[30] have been found.

When other available data for selenium and mercury concentrations in Australian marine organisms are examined (Table 3), no significant correlation between selenium and mercury is observed.

Selenium has also been reported to influence the uptake of cadmium[31] and arsenic.[32] Selenium and cadmium in Black Marlin livers are found to

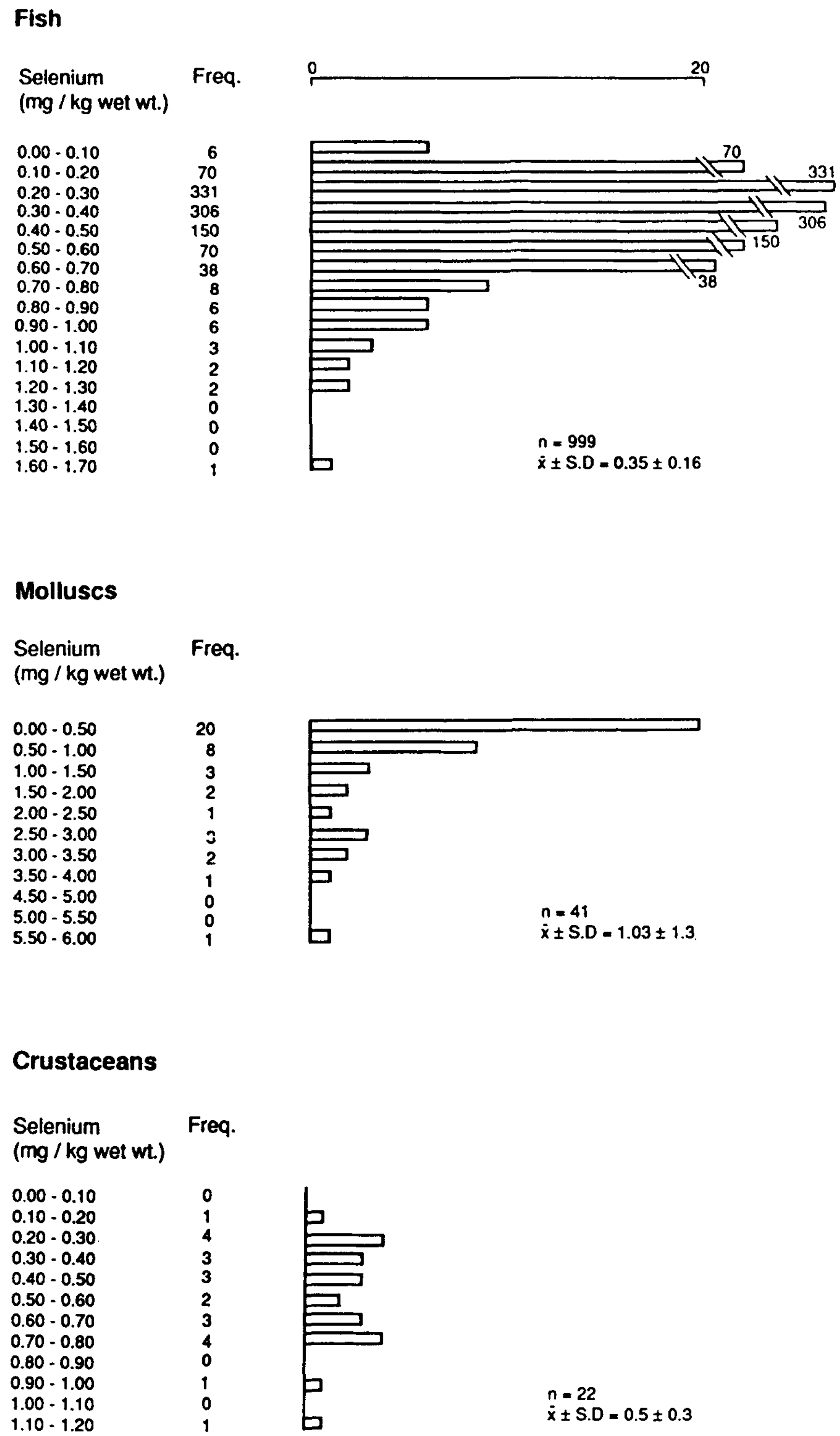

Figure 2 Selenium concentrations in marine muscle tissues.

Table 2 Distribution of selenium in marine animals—relationship to diet

(a) St Vincents Gulf

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

(b) Fish from Australian coastal waters

Diet/species	Food	Selenium ($mg\ kg^{-1}$ wet wt)	
		Range	Mean ± SD
Herbivorous			
Hyporhamphus australis	Seagrass epiphytes	0.11–0.16	0.13 ± 0.03
Girella tricuspidta	algae, seagrass	0.21–0.32	0.28 ± 0.05
Omnivorous			
Nemadactylus macropterus	Algae, molluscs, crustaceans,	0.43–1.00	0.66 ± 0.18
Arripis trutta	worms, seagrass epiphytes	0.3–0.5	0.38 ± 0.16
Mugil cephalus		0.1–0.3	0.14 ± 0.7
Carnivorous			
Squatina australis	Fish, molluscs, worms, crustaceans	0.13–0.67	0.37 ± 0.12
Squatina tergocellata		0.15–0.43	0.32 ± 0.07
Sillago ciliata		0.26–0.49	0.37 ± 0.07
Zenopsis nebulosus		0.25–0.73	0.43 ± 0.11
Platycephalus richardsoni		0.30–0.62	0.47 ± 0.08
Arripus georgianus		0.14–0.19	0.17 ± 0.03
Sillaginodes punctata		0.2–0.34	0.3 ± 0.08
Callogobius mucosus		0.1–0.13	0.05 ± 0.01

SD, Standard deviation; ND, not detectable.

Table 3 Correlation of selenium with mercury, arsenic and cadmium in some Australian marine organisms

Organism	Correlation factor		
	Se–Hg	Se–As	Se–Cd
Sharks	−0.5353	0.6418*	0.0190
Cheilodactylus fucus (Red Morwong)	−0.0552	−0.0208	
Pinna bicolor (Razor Fish)		0.5606	−0.9878*
Halitois ruber (Black Tip Abalone)		0.4699	0.2887
Jasus novaehollandiae (Rock Lobster)		0.4544	
Galeohinus australis (School Shark)	0.1025	0.2354	0.2599
Mustelus antarcticus (Gummy Shark)	−0.6260	0.1598	−0.1145

* Significant correlation [critical value (two-tail, 0.05)] = ∓0.5740.

be correlated.[18] Selenium and cadmium, and selenium and arsenic, concentrations in most other Australian marine organisms are not significantly correlated (Table 3).

DISTRIBUTION

Some of the characteristics of the selenium compounds present in marine organisms have been identified by use of a sequential extraction scheme which separates chemical species found in the tissues into different biochemical fractions.[33-35] Selenium in macro-algae is predominantly associated with amino-acids and proteins in all algal classes (Table 4).

In marine animals most of the selenium is associated with protein residues (Table 2). The addition of ethanol to the buffer extracts of proteins to precipitate protein was also found to precipitate selenium quantitatively, suggesting that a large fraction of selenium in the muscle tissues of marine animals may be associated with proteins.

SPECIATION

An attempt has been made by our laboratories[33-35] 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-}).

BIOCHEMICAL TRANSFORMATIONS OF SELENIUM

Algae

The possible biochemical transformations of selenium in algae and plants are shown in Fig. 3. Direct evidence for the presence of selenium in combined and free analogues of sulphur-containing amino-acids has come from the selenium uptake studies performed by Wrench[7] and Bottino *et al.*[9] The compounds identified are shown in bold type in Fig. 3. It should be noted that these studies were performed at elevated

Table 4 Selenium associated with biochemical fractions of marine macro-algae

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

[a] ND, not detectable.

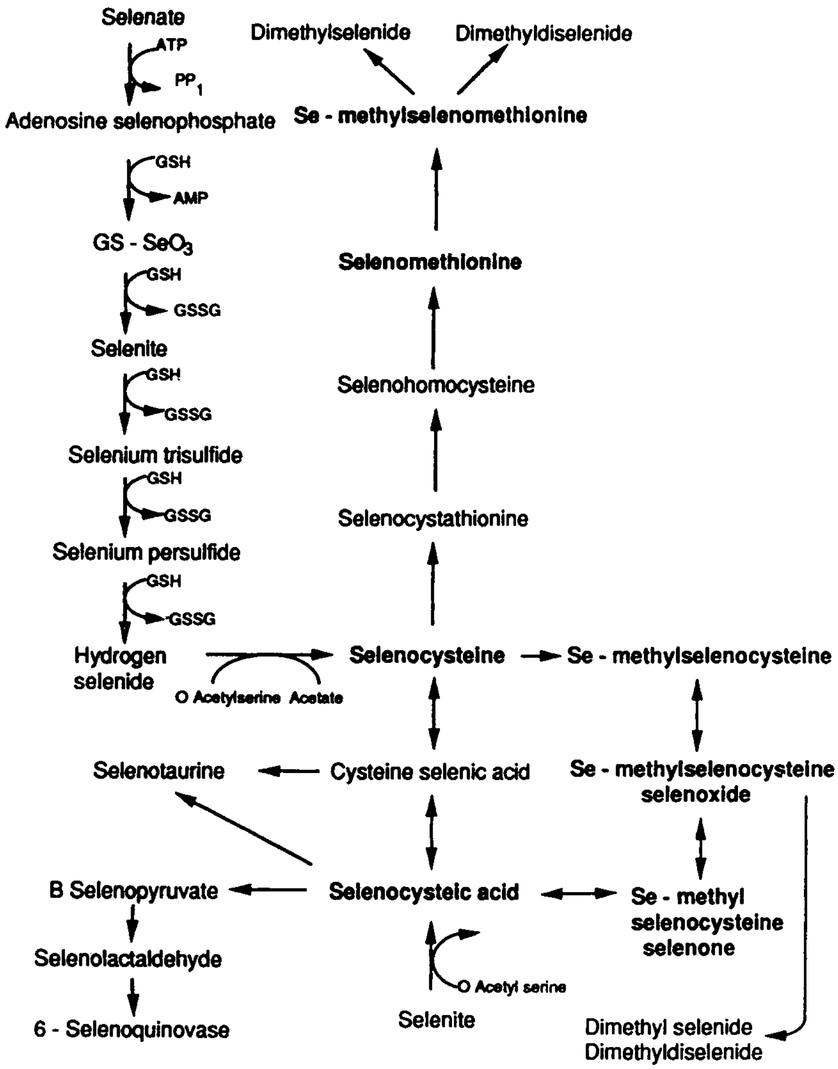

Figure 3 Selenium metabolism in marine algae and plants.

selenium concentrations and that algae may have different biochemical mechanisms for dealing with lower, naturally occurring selenium levels. The production of selenoamino-acids and proteins is however a general phenomenon of terrestrial plants involving chloroplasts.[36,37] It is likely that marine algae and plants will also synthesize these compounds.

The study of Gennity *et al.*[38] indicated that inorganic selenium and non-sulphur analogues may also exist in marine alga. In their experiments, the green alga, *Dunaliella primolecta*, and the red alga, *Porphyridium crunentum*, were grown in anoxic cultures in the presence of selenium. They found that selenium, instead of being metabolically incorporated, was probably non-covalently bound to lipids. They also determined that when inorganic selenium was added it became bound to algal lipids during lipid extraction. Therefore, the release of bound selenium and reassociation with lipids may be an artefact of their isolation procedure.

Animals

Studies of the uptake of selenium in controlled environments have shown that zooplankton, molluscs and crustaceans can accumulate selenium either from seawater or food. In experiments involving the uptake of inorganic selenium from the water column, most of the selenium absorbed by organisms was accumulated in the exoskelton

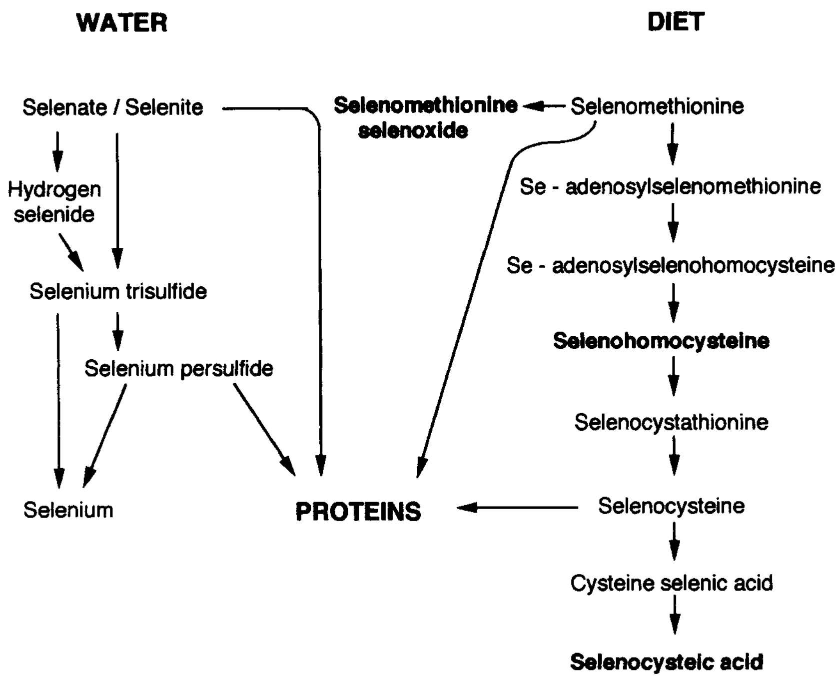

Figure 4 Selenium metabolism in marine animals.

or shells.[39] A large percentage (60–90%) of selenium was subsequently lost through moults,[2] suggesting that a non-metabolic sorption process was involved in the uptake and binding of selenium from water. Selenium absorbed from water is then lost relatively quickly.[2] An exception was the accumulation of selenium from water by the zooplankton, *Meganyctiphanes norvegica*, where selenium was incorporated into internal organs and surface adsorption did not appear to be important.[40] Accumulation of selenium from water cannot be neglected as studies with mussels and shrimps[2] have shown that, over time, selenium is translocated from the exoskeleton to muscle and viscera. Selenium taken up through food is retained for longer periods, unless it is excreted or translocated to exoskeletons from the visceral mass.[39]

Several studies have isolated selenium in protein extracts from the muscle and liver tissues of marine animals[13, 35, 42–44] but have not identified the chemical forms of selenium present. Selenium compounds in some marine fish have also been found to be associated with lipid material,[45] and have properties similar to lipoproteins.[46]

Possible biochemical transformations of selenium in marine animals are shown in Fig. 4. If selenium is following sulphur pathways, it is likely that selenomethionine in the diet is converted to selenocysteine, as occurs in terrestrial organisms.

No conclusive evidence exists for the production or storage of selenoamino acids in marine (or terrestrial) animals. Wrench[8] has isolated selenocysteic acid, selenomethionine, selenoxide and selenohomocysteine from oysters fed radiolabelled selenium (bold type in Fig. 4). Again these may not be naturally occurring compounds but artefacts of the high dosage of selenium used. Selenium-dependent glutathione peroxidase (GHS-peroxidase) has been isolated from the Black Sea Bass *Centropristis striata*,[43] indicating that some selenium may be present in marine animals as selenocysteine. Selenocysteine is a normal component of glutathione peroxidase.[47] Alternatively, selenium may be in a non-protein moiety tightly held to proteins but not covalently bound. For example, it has been shown that selenium can readily form selenotrisulphides with thiols such as cysteine, glutathione, etc.[48, 49] These can then be incorporated and stabilized within protein structures.[50] Chemical isolation of these types of compounds during extraction will prove difficult as destablization results in the precipitation of elemental selenium.[49]

The non-preferential accumulation of selenium in taxa, and dietary independence of selenium, suggest that selenium is only metabolized by marine organisms for specific roles such as in the glutathione peroxidase pathway[43] with excess selenium being excreted.[51] Selenium's role as an essential element for the growth of marine organisms, such as algae,[52,4] can therefore only be speculated on.

When organisms are supplied with large amounts of selenium, it may travel along sulphur metabolic pathways, but when supplied at lower levels, selenium may follow its own metabolic pathways. This original hypothesis by Schwarz[54] still needs to be verified.

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