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Formation of Volatile Selenium Species in Synthetic Seawater under Light and Dark Experimental Conditions

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Experiments were performed in the laboratory on synthetic seawater spiked with different selenium species at trace levels to study the formation of volatile selenium compounds under dark or controlled simulated sunlight conditions. Spiking the reaction media with inorganic and organic selenium compounds demonstrated that several volatile selenium species could be formed under these simulated conditions. Selenoamino acids react to produce significant amounts of volatile selenium species in both light and dark conditions. Products formed include dimethyl selenide (DMSe), dimethyl selenyl sulphide (DMSeS) and dimethyl diselenide (DMDSe). Inorganic selenium oxyanions added to the synthetic reaction media did not form volatile species via abiotic reactions despite the presence of strong methylating agents. These results suggest that the formation of stable volatile species from bio-organic selenium compounds can occur via abiotic reactions in the marine photic zone. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Little is known on the subsequent chemical reactivity of natural or anthropogenic metalloid compounds (e.g. of asene, antimony or selenium) in surface marine waters.[1,2] Their reactivity with light-induced activated oxygen species could be an important pathway (via redox processes) which may then affect their biological uptake and transformation, similarly to those observed for iron cycling.[3,4] Trace metals and metalloids are of great interest in coastal areas since they can present either a 'nutrient-like' or a toxic effect, depending on the species present and on their concentrations. The reactivity and stability of these different compounds will control their impact in aquatic ecosystems.[5]

Among the metalloids, selenium is known to present a very narrow range between nutritional needs and toxicological effects.[6] Methylated selenium species are less toxic than their inorganic counterparts. Reduction and further methylation of oxidized selenium species, leading to the release of selenium in the atmosphere, may potentially be understood as a detoxification mechanism.[7]

In surface seawater, photochemistry forms activated species that may in turn generate abiotic redox reactions leading to the derivatization of selenium species. Light was found to activate these processes for tin and mercury compounds.[8,9] The reactivity of selenium via redox reactions in natural waters has only been investigated for heterogeneous processes in the presence of aqueous suspensions of mineral oxides. Selenite was then found to be oxidized, under light radiation and in the presence of titanium oxide, by activated oxygen species.[10] Dimethyl selenide (DMSe) is also oxidized to dimethyl selenoxide by manganese oxide suspensions, with pH-dependent mechanisms.[11]

In natural waters, the formation of organic selenide compounds from inorganic forms is known to derive from biological activity.[12,13] These processes develop after incorporation of inorganic selenium in the biological cells of bacteria or plankton species, and by catalysed reduction and methylation steps. Organic selenide species, such as

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Table 1 Experimental reaction media

Experiment[a]	Composition of the synthetic seawater (SSW)	Experimental conditions
SSW-1	Synthetic seawater (salinity 35)[a]	1 Sample at t = 0
SSW-2		1 Sample at t = 360min (dark) 2 Samples at t = 360min (light)
SSW-3	Synthetic seawater + 1 μg/l as Se selenite (Se^{IV}) and selenate (Se^{VI})[b]	4 Samples (like SSW-2)
SSW-4	Synthetic seawater + 1 μg/l Se^{IV} and Se^{VI} + 5 μM DMSP[c]	4 Samples (like SSW-2)
SSW-5	Synthetic seawater + 1 μg/l Se^{IV} and Se^{VI} + 5 μM Me-l[d]	4 Samples (like SSW-2)
SSW-6	Synthetic seawater + 1 μg/l as Se seleno-methionine	4 Samples (like SSW-2)
SSW-7	Synthetic seawater + 1 μg/l as Se seleno-cystine	4 Samples (like SSW-2)

[a] Marine salts solution + algae extracts (diluted 1/20) + fulvic acids (0.5 mg/l)
[b] From standard solutions of sodium selenite and selenate (pH 2)
[c] DMSP: dimethylsulfoniopropionate
[d] Me-l: iodomethane

organic and amino acids,[14] can then be released in the water as methylated selenium molecules and may partially lead to the formation of volatile compounds.[7,13] Abiotic methylation of selenium, leading to volatile species, may also occur from inorganic selenide–metal cation (M–Se) complexes in the presence of strong carbo-cation donors such as halomethane (CH_3—X) or sulphonium compounds ($(CH_3)S^+$—R_2).[15] The presence of these methylating agents is indicated in productive waters, and favours this hypothesis.[16]

The volatile methylated selenium species may then represent the 'end products' of selenium speciation reactions in the aquatic environment, due to their good stability with respect to oxidation and hydrolysis.[5] Their escape into the atmosphere prevents them from any further internal recycling.[13] The main volatile compounds identified to date in

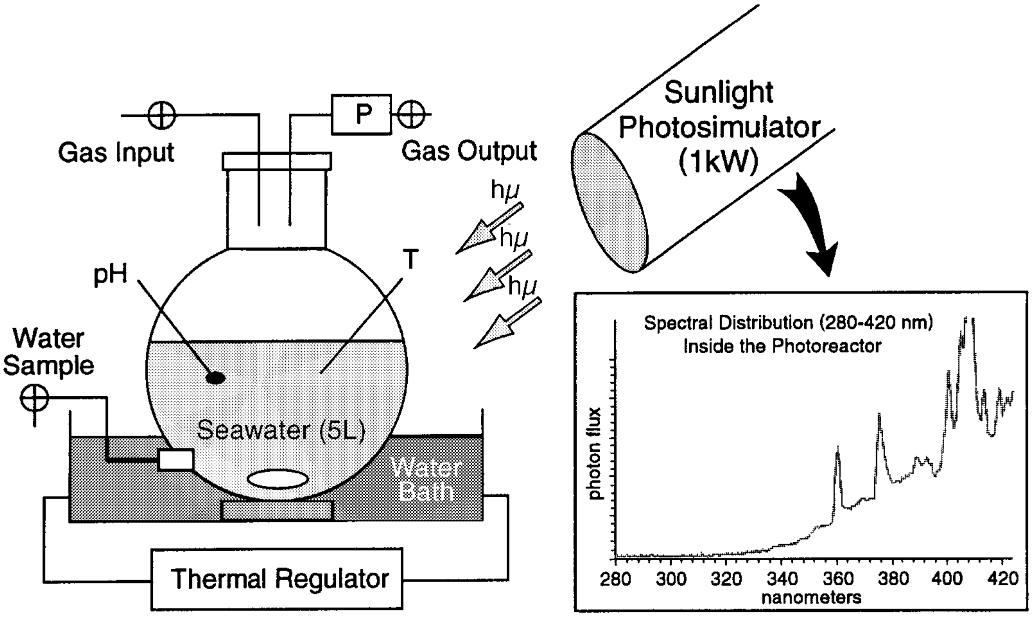

Figure 1 Experimental reactor used for the dark or light irradiation conditions. Working conditions: $T_{water} = 20 \pm 0.1$ °C, $P = 1.0 \pm 0.1$ atm, pH = 8.1 ± 0.1; sunlight simulator at 2.5 m distance and 45 ° incidence.

natural waters are dimethyl selenide (DMSe), dimethyl diselenide (DMDSe) and dimethylselenyl sulphide (DMSeS).[12,17–19]

In the present work, we have studied the role and impact of abiotic chemical processes on the reactivity and the mobility of selenium in coastal marine waters during simulated dark and sunlight experimental conditions.

MATERIALS AND METHODS

Synthetic seawater (SSW)

Synthetic seawaters were prepared from Millipore Milli-Q salts solution (salinity 35) according to Lyman and Fleming[20] using analytical-grade salts (NaCl, $MgCl_2$, Na_2SO_4, $CaCl_2$, KCl, $NaHCO_3$, KBr, H_3BO_3, $SrCl_2$ and NaF; Aldrich). The prepared solution was spiked with 0.5 mg l^{-1} of reference fulvic acids (Contech) and 50 ml l^{-1} of liquid extracts obtained from clean laboratory algal cultures filtered on 0.22 μm cellulose acetate filters (Ifremer Centre, Arcachon). These extracts were obtained after two weeks of final-stage growth (Conway medium, 5 l) of common *Isochrisis Galbana* algal culture (E. His, Ifremer, personal communication). The final stage of development was determined after daily cell counting (Coulter, Ifremer Arcachon) and monitoring of tryptophan-like fluorescence after filtration at 0.45 μm (excitation 280 nm / emission 350 nm;). After complete development of the algal density, the maximum of tryptophan-like fluorescence was obtained just before the decay stage. The Conway medium (5 l) was then filtered, stored in opaque 250 ml polyethylene bottles (Nalgene) and frozen at −20 °C. Synthetic seawater (SSW) is seawater reconstituted by mixing the different components (artificial seawater + humic acid solution + algal exudates) to give a fluorescence spectrum similar to that obtained in Arcachon Bay seawater for different excitation wavelengths (280, 313 and 340 nm). The synthetic seawater was prepared 3 h before the experiments in order to allow complete homogenization of the solution by continuous mixing and thermoregulation. A series of synthetic seawater solutions were prepared. Two synthetic seawater media were prepared to be used as blank experiments without any addition of selenium species (SSW-1 and SSW-2). Volatile selenium species analysis were only performed on SSW-2. All other SSW media were spiked with selenium species and were analysed for volatile selenium species (SSW-3 to SSW-7) (Table 1).

Photoreactor set-up

The photochemical experiments were performed in a large silica-bore Pyrex photoreactor (6 l, wavelength cut-off >300 nm) (Fig 1). Continuous agitation was provided with an ovoid Teflon-coated magnetic stirrer and thermal regulation was controlled by a thermoregulated water bath (Huber). The temperature and pH of the seawater were monitored continuously with two probes immersed in the reaction media (Jenco). The photoreactor was gas-tight and pressure-controlled. Water and gas samples could be sampled continuously by two outlets located at the base and at the top of the reactor. Experiments in the presence of natural simulated light flux were performed with a large 1-kW sunlight photosimulator (Applied Photophysics) positioned at an angle of 45 ° and at 2.5 m from the horizontal line (Fig 1) passing through the centre of the photoreactor. The light flux in the photoreactor (300–500 nm) was calibrated with a ferric oxalate actinometer and the global lamp-flux stability was monitored with a thermopile light sensor (Applied Photophysics).

Experimental procedures

All experiments were performed in a dark room under similar thermodynamic conditions, giving a temperature of 20.0 ± 1.0 °C as recorded in the photoreactor, a pH of 8.1 ± 0.1 for the seawater and an atmospheric pressure of 1.0 ± 0.1 atm. For all experiments, 5 l of seawater was prepared in a dark environment, transferred to the photoreactor (which had been previously rinsed with the sample), mixed and thermoregulated. Just before exposure to the simulated sunlight commenced, two samples were collected, respectively, for the dark incubation (kept under the same experimental conditions) and for the initial point of the experimental study ($t = 0$). The irradiations were performed during 6 h to reproduce a diurnal time scale. The initial volume of seawater was adjusted in order to obtain a final volume presenting similar irradiation conditions (V(final) >3.5 l). The reproducibility of the whole experimental procedure was monitored by measurement of the H_2O_2 concentration during the different experiments.[21] Reproducibility of the kinetics of H_2O_2 production was within than 10% on the same body of synthetic seawater (SSW-1 and SSW-2) submitted to the photon flux.[22,23]

Selenium spiking conditions

Ultra pure reagents and Millipore Milli-Q water were used to prepare the different solutions for the experiments. Sodium selenite and sodium selenate (Merck) were used for the preparation of inorganic selenium standard aqueous solutions (pH 2). Standard solutions from crystallized DL-selenomethionine (Se-Met; Sigma–Aldrich) and DL-selenocystine (Se-Cys; Sigma–Aldrich) were prepared a few minutes before the experiments, to prevent degradation. Stock solutions of iodomethane (MeI; Merck) and potassium dimethyl sulphoniopropionate (DMSP; Research Plus) were also freshly prepared before use.

Selenium compounds were added to obtain a final concentration of $1\,\mu g\,l^{-1}$ as Se (12.7 nM) in the synthetic seawater (SSW) in order to study the effects of abiotic processes on selenium speciation at trace concentrations. Selenoamino acids forms represent the major pool of non-volatile dissolved organic selenium in productive surface marine waters.[14] However, their reactivity in natural waters is still unknown. As a consequence, two different experiments were performed after spiking the SSW media with either Se-Met or Se-Cys in order to also obtain a final concentration of Se of $1\,\mu g\,l^{-1}$ similarly to the inorganic Se spiking experiments.

Methylating agents, such as MeI and DMSP, were added separately to obtain a concentration of $5\,\mu$M in the SSW medium spiked with inorganic Se.

All the different reagents were added to the SSW media 10 min before initiating the experiment, in order to obtain a complete homogenization of the reaction medium. All the experimental conditions are summarized in Table 1.

Determination of volatile selenium species

For each experiment performed with synthetic seawater (SSW), four aliquots of 320 ± 10 ml were collected and analysed for volatile selenium species with quartz furnace atomic absorption spectrometry (QF–AAS) detection (PE 5000, Perkin-Elmer) and cryofocusing. Four samples were obtained during each experiment: one at $t = 0$, which is the initial point; one under dark incubation ($t = 360$ min); and two under light radiation ($t = 360$ min). All the sample treatment and analysis procedures are described in detail elsewhere.[18,19] The samples were collected and transferred to the purge-and-trap vessel using an on-line Teflon-capped Pyrex bottle and helium overpressure to avoid any loss of dissolved gas in the ambient air. The samples were then purged for 1 h with pure helium gas (L'Air Liquide) and the volatile species were cryofocused onto a packed column (silanized Chromosorb WHP 60/80-mesh with 10% SP2100; Supelco) immersed in liquid nitrogen. The packed columns were sealed with Teflon caps and stored in liquid nitrogen. Volatile selenium compounds were desorbed for chromatographic separation and QF–AAS detection within one week.

Pure DMSe and DMDSe solutions (99%; Strem) were used to prepare standard solutions to calibrate the analytical system. Calibration was performed by spiking DMSe and DMDSe standard solutions in 300 ml of Milli-Q water and following the analytical procedure. The detection limits under these experimental conditions were 10 pM for both DMSe and DMDSe as Se. Unknown volatile compounds were calibrated versus DMSe or DMDSe sensitivity according to their retention times and expected chemical forms. Methane selenol (MeSeH) and an unknown compound ('U') respectively eluted just before DMSe and DMDSe, and were therefore calibrated against these two respective standard compounds. The reproducibility of such procedures, characterised as relative standard deviation (RSD) was less than 15%.[18]

RESULTS AND DISCUSSION

The results are displayed in Table 2.

One blank experiment, to provide a control for production of volatile selenium species, was performed with SSW alone and the results were used as a reference (SSW-2). No volatile selenium compounds were detectable during this experiment (concentration <10 pM; see Fig. 2). Three examples of chromatograms are displayed in Fig. 2, showing the different volatile selenium species detected in different experimental media. One peak appears in all the chromatograms and was attributed to flame combustion emission (fce). This peak could correspond to a selenium-containing compound such as hydrogen selenide (H_2Se), considering the relatively good selectivity of QF–AAS detection. However, Pécheyran *et al.*[18] demonstrated, using atomic fluorescence spectrometry for the detection, that an interference with a carbon-containing compound such as CO_2 is certainly responsible for the fce peak.

Table 2 Formation and relative yields of volatile selenium species in the dark or under irradiation conditions

Experiment abbreviations	Volatile Se species	Δ(Vol Se)[a] Dark (%)	Δ(Vol Se) Light (%)	Type of chemical mechanisms
SSW-2	Traces	<0.3	<0.3	n.d.
SSW-3	Traces	<0.3	<0.3	n.d.
SSW-4	Traces	<0.3	<0.3	n.d.
SSW-5	Traces	<0.3	<0.3	n.d.
SSW-6	DMSe	2.6	1.4	Selenol / thiol
	DMSeS	4.6	28.8	Catalytic oxidation
	DMDSe	41.5	33.2	
SSW-7	MeSeH	1.1	0.3	Selenol / thiol
	DMSeS	3.3	2.3	Catalytic oxidation
	DMDSe	2.4	0.8	

[a] Δ(Vol Se), chemical yield of volatile compounds as a percentage of spiked Se under light or dark condition.

Addition of inorganic selenium species

Synthetic media containing only inorganic species (SSW-3 to SSW-5) did not yield any volatile species, as shown in Fig. 2. When the inorganic selenium species were added in presence of a methylating agent (Table 1), the determination of volatile selenium species did not show any evidence of production of methylated species under irradiation or in the dark. Traces were occasionally observed, but they were not significantly greater than those obtained with the SSW media alone and could correspond to potential artefacts. In Fig. 2, the small peak does not correspond to a known volatile selenium compound and was not present in other samples. We therefore suppose it to be an analytical artifact. On the other hand, this small peak could correspond to DMSe, but its calculated concentration was below the detection limit of the method (10 pM for a 300-ml sample).

Under these experimental conditions, the minimum significantly detectable yield of volatile selenium production was estimated to be 0.3%. If it is supposed that abiotic methylation is occurring, the yields from it would be very low under such

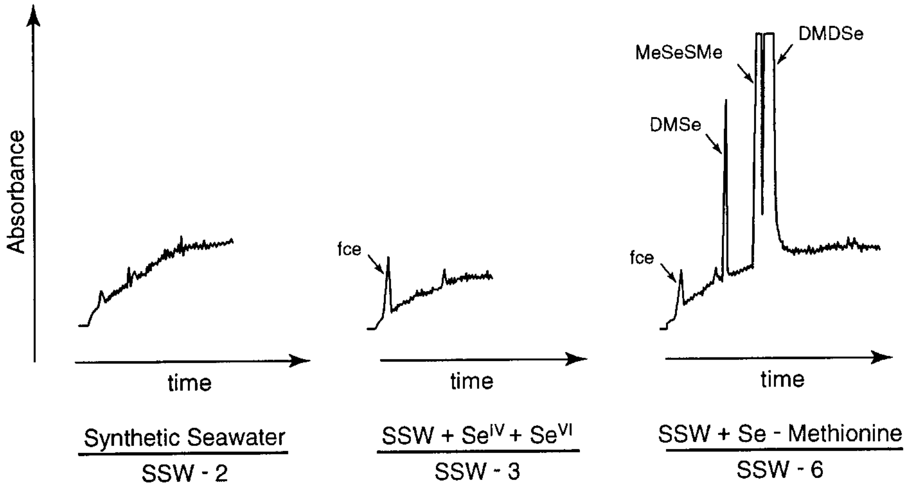

Figure 2 Typical chromatograms obtained for the volatile selenium species formed under the different experimental conditions: results obtained with purge-and-trap – gas chromatography – quartz furnace atomic absorption spectrometry. The first peak is assumed to be a flame combustion emission (fce) signal since the system was operated without D2 background correction.

simulated environmental conditions. Similar results have been obtained with tin. Inorganic tin methylation yields reported under similar irradiation conditions were found to be less than 0.2% (0.001–0.18%).[8]

Addition of organic selenium species

Volatile selenium species were only detected with SSW-6 and SSW-7 experimental conditions, when organic selenium species were added to the medium. Significant yields of selenium species were evident under both dark and light conditions for the seawater medium spiked with Se-Met. Much lower yields were obtained in the case of the medium spiked with Se-Cys. The highest yields were usually obtained under dark controlled conditions.

The volatile selenium species detected after the irradiation experiments demonstrated that volatile selenium species could only be formed significantly when SSWs were supplemented with selenoamino acids. In this case only, several species such as dimethyl selenide (DMSe), dimethyl diselenide (DMDSe) and an unknown Se compound, eluting just before the DMDSe (referred in the text as unknown, U) were detected. These species were identified on the basis of the selectivity of the atomic absorption detector and of their retention time compared with synthetic standards. A typical chromatogram is displayed in Fig. 2.

Chasteen[25] reported the occurrence of a selenium species which exhibited an order of elution similar to that for compound U in this work (just before DMDSe). This species was identified by gas chromatography with mass spectrometry detection to be dimethylselenyl sulphide (DMSeS) and to have an apparent boiling point of 132 °C deduced from its retention time. The chromatographic technique used here also produced a quasi-linear relationship for low-molecular-weight compounds between their boiling points and their retention times.[19] Using this relationship similarly to Amouroux *et al.*,[19] it was easy to confirm that the retention time of compound U exactly matched the boiling point of DMSeS. Considering that no split of the DMDSe peak occurred when different amounts of standard solution were spiked, it is reasonable to assume that U is really present in the sample and corresponds to DMSeS.

On the contrary to what has been observed with inorganic selenium addition, a very high production of volatile compounds (50–65% yield) was observed under both dark and irradiated conditions, but with very different yields.

High production of DMDSe were evident together with a significant signal for the compound identified as DMSeS, and with traces of DMSe for addition of either Se-Met or Se-Cys. The highest yield of DMSeS was observed under irradiation conditions (28.8% yield) compared with the dark controls (4.8%). In contrast, the DMDSe production decreased in the presence of light (33.2%) compared with dark incubations (41.5%). Low yields of DMSe production were observed in both dark (2.6%) and light (1.4%) incubation experiments.

Obtaining high yields of DMDSe could have been expected since Se-Met spikes in soils has led to the production of significant amounts of volatile selenium species, mainly as DMDSe,[24] but authors could not then distinguish whether the formation pathway was due to microbial activity or simple chemical reactivity in the soil matrix.[24] Formation of DMSeS from our experiment is also in accordance with previous pioneering work on volatile selenium compounds in the environment. As mentioned before, it has been identified after its formation from microbial culture amended with inorganic selenium species.[25] This compound had also been reported previously to be dimethylselenone and was found to occur in various aquatic environments.[26,27] For the purpose of this work, we evaluated the reactivity of selenoamino acids without investigating any isomeric selectivity in the potential chemical reaction yield or rate.

Reactivity of selenomethionine in seawater

Results obtained after spiking the seawater medium with selenoamino acids suggest that the DMDSe yield observed could be chemically formed from Se-Met [DL-$CH_3Se(CH_2)_2CH(NH_2)COOH$] degradation by potential release of the CH_3Se group via cleavage or hydrolysis pathways (SSW-6).

This pathway could be counterbalanced by simultaneous photochemically assisted production of DMSeS. DMSeS was also produced in the dark, but in lower yields. Chemical formation of the Se–Se bond in such a complex medium cannot be simply explained but could relate to sulphide autooxidation reaction types, as reviewed by Hoffman.[28] Formation of DMSeS may also be related with the production of organic sulphide or thiol compounds originating from algal extracts and

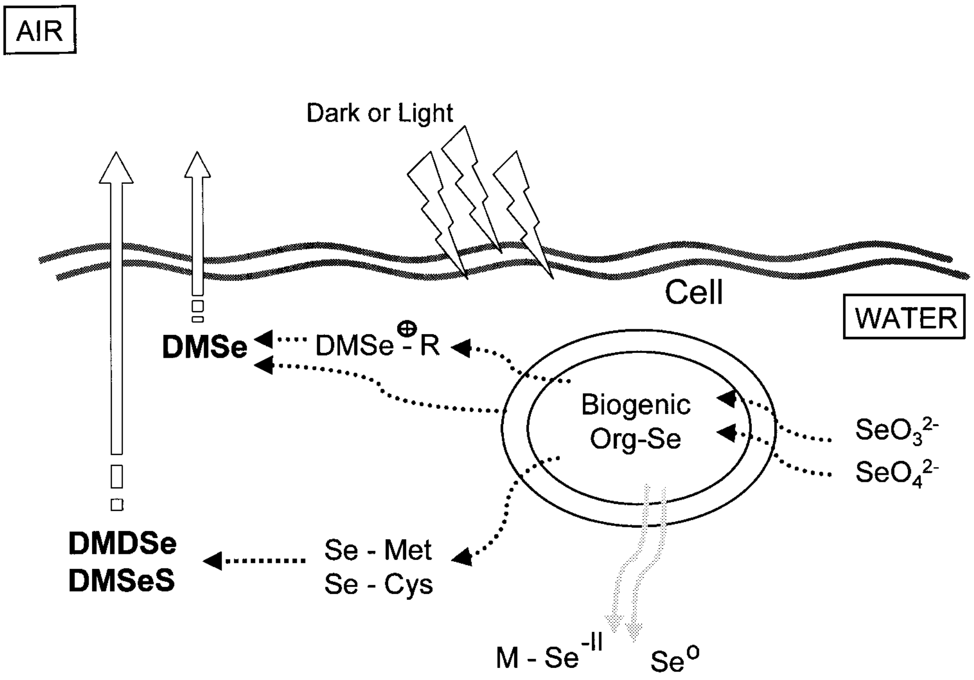

Figure 3 Possible chemical cycling of selenium in marine surface waters (adapted from Ref. 13).

organic selenide or selenol species reacting together.

Organic selenide and diselenide compounds studied for their photochemical reactivity were found to produce alkylselenyl radical intermediates (RSe) and to be involved in homolytic substitution reactions of the alkylated group.[29,30]

H_2O_2 is usually produced in seawater under irradiation conditions.[31] The direct oxidation of selenide and selenol via H_2O_2 nucleophilic attack could take place to form RSeSeR, RSeSR or R_2SeO, similarly to observations for sulphide compounds.[28,32] Potential pathways of formation of volatile selenium compounds in the presence of light are therefore given as in Eqns [1] and [2].

$$2RSeH + H_2O_2 \rightarrow RSeSeR + 2H_2O \qquad (1)$$

$$RSeH + RSH + H_2O_2 \rightarrow RSeSR + 2H_2O \qquad (2)$$

Finally, another competing process may be involved, taking into account the results obtained from incubation in the dark. In SSW-6 medium, experiments in the dark produced a large yield of DMDSe. Consequently, the formation of volatile selenium compounds in the dark could originate from catalytic auto-oxidation (Eqn [3]).

$$2RSeH + O_2 \rightarrow RSeSeR + H_2O_2 \qquad (3)$$

Reactivity of selenocystine in seawater

Se-Cys [DL-$(SeCH_2CH(NH_2)COOH)_2$] (βA) is the commercially available oxidized form of selenocysteine (RSeH) (βB) due to the high instability of the latter. An unexpectedly low production of volatile selenium compounds (3–7% yield) was measured (SSW-7) from βA. Selenium species generated include DMDSe, DMSeS. MeSeH was previously identified by the same technique after generation from DMDSe in the presence of concentrated hydrochloric acid and sodium borohydride.[33] The results also demonstrated that MeSeH sensitivity was nearly identical to that of DMSe, which was therefore used to estimate MeSeH concentrations in the samples.

Higher yields of volatile species were obtained in the dark than in light conditions (SSW-7). Production yields of 1.1, 3.3 and 2.4% for MeSeH, DMSeS and DMDSe under dark conditions are significantly higher than those obtained in the presence of light, with production yields of 0.3, 2.3 and 0.8% respectively. These results suggest that no direct photochemical pathways can be associated with the production of volatile selenium species. The lower reactivity of Se-Cys compared with selenocysteine under oxidizing conditions may explain these results.

Implications for selenium biogeochemical cycle

The large variety of dissolved selenium species in both inorganic and organic forms, together with the large range of stable redox states (−II, O, IV, VI) of this element, contributes to its complex reactivity and speciation in marine waters.

Several processes may participate significantly in the biogeochemical cycling of selenium in euphotic surface seawaters. Naturally occurring abiotic methylation pathways with inorganic selenium species appear to have negligible impact in the production of volatile selenium species. Selenoamino acids, such as Se-Met and Se-Cys, were found to be very reactive under both dark and light conditions. Under simulated light or dark conditions, both compounds lead to the significant formation of volatile selenium forms such as DMDSe, DMSeS, DMSe and MeSeH.

Experiments using seleno-amino acids demonstrated that DMDSe and DMSeS were produced under both light and dark conditions. However, the major volatile selenium compound encountered in fresh and marine waters is DMSe. These observations suggest then that similarly to DMS, DMSe could have a specific precursor, possibly in the form of a dimethylselenonium compound [$(CH_3)_2Se^+R$], as mentioned by Cooke and Bruland[13] (Fig. 3). More recently, it was shown that euryhaline microalgae were able to produce large amounts of DMSe when inorganic selenium was spiked into the culture. The potential precursor of DMSe present in the intracellular medium was certainly a dimethylselenonium species.[34] The release of this compound by marine algae followed by enzymic cleavage could therefore explain the predominance of DMSe in the oceanic environment.[17,35] In the same cultures, DMDSe and DMSeS were also produced significantly and Se-Met was present in the cell fraction.[34] Our results could therefore explain the production of these volatile selenium compounds (i.e. DMDSe, DMSeS) through abiotic reactions after the release of Se-Met into the extracellular medium. This hypothesis allows us to complete the chemical cycle of selenium in surface marine waters, as shown in Fig. 3.

Finally, similarly to selenite stability, organoselenide compounds display a long lifetime versus oxidation in surface seawater.[2] This signifies that complementary photochemical and biological processes leading to volatile species will be important pathways for the removal or organoselenide compounds from surface waters. This efficient removal from surface oceans definitely contributes to a major part of the atmospheric transfer and global cycle of selenium.[35]

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