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The Methylation of Metals and Metalloids in Aquatic Systems

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1. Introduction

This chapter will focus on the formation processes and fate of the more common methylated metals and metalloids in the aquatic environment, focusing on both the ocean and freshwater ecosystems. In addition to the formation of the methylated compounds, the biotic and abiotic degradation of these compounds in the natural environment will also be discussed. The formation pathways and the microbes responsible for environmental methylation of different elements will be examined in detail with the focus on the organometallic or organic metalloid compounds of Hg, As, Sb and Se. Methylated compounds of other metal(loids)s will also be discussed. Such compounds are defined here as those in which the attachment of the organic moiety to the metal/metalloid ion is directly through a carbon-metal bond. Most of these bonds are covalent, especially for the metals and metalloids which have filled d and f orbitals [1]. There is an ever growing field of organometallic chemistry related to the use of manufactured transition metal compounds as catalysts or in organic production synthesis, or for other uses (e.g. alkylated Pb and butylated Sn compounds). These compounds will not be discussed in detail.

Most of the compounds that will be discussed contain one or more methyl group attached to the metal or metalloid atom (Table 1). Methylated halogens are formed in the environment but their formation and fate will not be included in this chapter. Methylation of transition metals does not occur under environmental conditions. In terms of the Periodic Table this chapter will focus on Groups 12-16, but will not directly discuss the major elements of Groups 14-16 (C, N, O, Si, P and S). Organometallic compounds with other alkyl groups (ethylated, butylated or phenyl-metal compounds) in the environment are mostly added as a result of human activity [1]. Most of these methylated compounds are formed biotically in the environment by microorganisms but abiotic pathways of methylation by methyl donor

reactions within the aquatic system will also be discussed. Methylation within cells is a fundamental biochemical process and can be carried out by a number of biochemical pathways. It appears, however, that the mechanisms of methylation of metals and metalloids are carried out by one of three pathways, involving either: S-adenosylmethionine, methylcobalamin or N-methyltetrahydrofolate (Figure 1) [1].

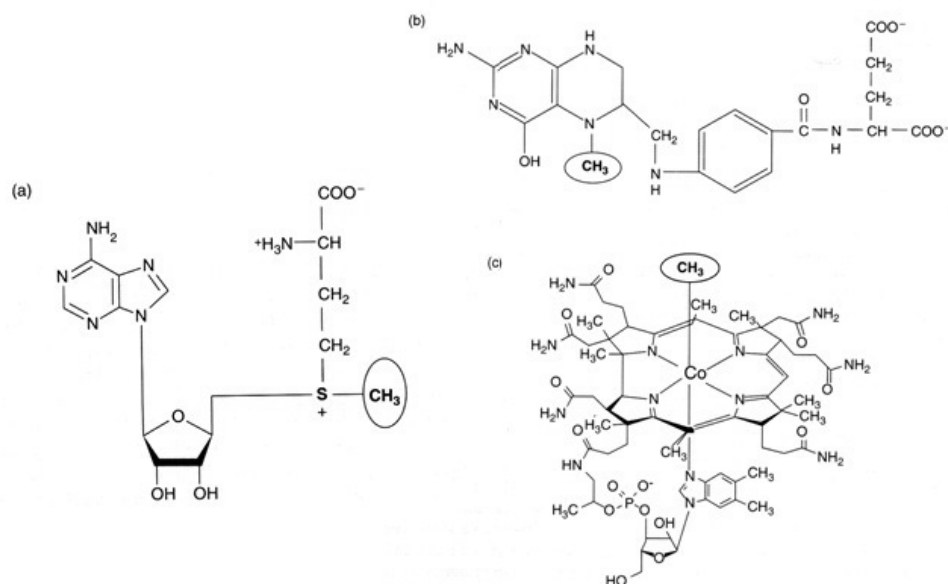


Figure 1. The primary methylating enzymes for metals and metalloids in organisms: a) SAM, b) tetrahydrofolate and c) methylcobalamin.

For example, methylation of Hg by sulfate-reducing and iron-reducing bacteria [2, 3] involves methylcobalamin, or related Co-containing enzymes. As ionic Hg (Hg^{II}) is the form that is methylated, methylation requires a methyl *carbanion* (CH_3^-), with methylation via a $\text{S}_\text{N}2$ reaction, and this process is not possible via the other methylation pathways. In contrast, the methyl group given up by S-adenosylmethionine (SAM) and N-methyltetrahydrofolate is a *carbocation* (CH_3^+). Thus there are fundamental differences in the potential methylating biochemicals and the pathways by which they react with metals and metalloids. For example, the so-called “Challenger” pathway of methylation of As by SAM requires that initially the As^{V} is reduced to As^{III} and then methylated [4, 5]. The methylated product is oxidized to the As^{V} state during the methylation step and must be further reduced before addition of more methyl groups. Methylation of Se appears to follow a similar mechanism. In contrast, the methylation of Sn and other cations is thought to involve mainly the cobalamin pathway, in a similar fashion to Hg, with these elements being methylated while in their most oxidized form. There is no concrete evidence for the methylation of reduced Hg (Hg^{I} or Hg^0) in the environment [2]. This is probably a result of the unstable nature of Hg^{I} in the environment and the chemical nature of Hg^0 . As a dissolved gas in most environmental aquatic systems it is not accumulated to any significant degree by microorganisms [6], or other organisms, unless it is oxidized upon uptake. So, therefore while Hg^0

could likely be methylated by SAM, methylation of Hg^{II} by other pathways appears to be more efficient.

Element	Methylated species	Element	Methylated species
As	$(\text{CH}_3)_4\text{As}_2$, $(\text{CH}_3)_3\text{As}$, $(\text{CH}_3)_3\text{AsO}$, $(\text{CH}_3)_2\text{AsH}$, CH_3AsH_2 , $\text{CH}_3\text{AsO}(\text{OH})_2$, $\text{CH}_3\text{AsO}(\text{OH})$	Sb	$(\text{CH}_3)_3\text{Sb}$, $(\text{CH}_3)_3\text{SbO}$, $(\text{CH}_3)_2\text{SbH}$, CH_3SbH_2
Cd	$(\text{CH}_3)_2\text{Cd}$, CH_3Cd^+	Hg	$(\text{CH}_3)_2\text{Hg}$, CH_3Hg^+ , CH_3HgH
Bi	$(\text{CH}_3)_3\text{Bi}$, $(\text{CH}_3)_2\text{BiH}$, CH_3BiH_2 , $(\text{CH}_3)_2\text{B}^+$, $\text{CH}_3\text{Bi}^{2+}$	Se	$(\text{CH}_3)_2\text{Se}_2$, $(\text{CH}_3)_2\text{Se}$, $(\text{CH}_3)_2\text{SeS}$, $(\text{CH}_3)_2\text{SeH}$
Ge	$(\text{CH}_3)_3\text{GeH}$, $(\text{CH}_3)_2\text{GeH}_2$, CH_3GeH_3 , $(\text{CH}_3)_2\text{Ge}^{2+}$, $\text{CH}_3\text{Ge}^{3+}$	Sn	$(\text{CH}_3)_4\text{Sn}$, $(\text{CH}_3)_3\text{AsH}$, $(\text{CH}_3)_2\text{SnH}_2$, CH_3SnH_3
Te	$(\text{CH}_3)_2\text{Te}$,	Tl	$(\text{CH}_3)_2\text{Te}^+$
Pb	$(\text{CH}_3)_4\text{Pb}$, $(\text{CH}_3)_3\text{PbH}$		

Table 1. Known forms of the various methylated compounds in the environment, including those that are formed by hydride generation but could exist as hydrides in the environment. Table compiled from [7-9].

Therefore, the various pathways of methylation are entirely distinct and which pathway dominates is a function of the differences in the speciation and oxidation state of the metal and metalloid in aquatic systems. For example, there is some evidence for the methylation of As and other metalloids in anoxic sediments via the cobalamin pathway [5, 10, 11]. In contrast to metal cations, the metalloids are present in environmental solutions mostly as an oxyanion of a weak acid, and therefore their form depends on pH. It has been proposed that Hg is taken up as a neutral Hg-sulfide complex via passive diffusion prior to methylation by sulfate-reducing bacteria (SRB), which are thought to be the most important methylating organisms [12]. However, there is also the potential for active transport of metals, especially through their uptake via channels designed for major ion transport, such as the channels for phosphate assimilation, or for the acquisition of required metals, such as Fe and Zn, or when combined with low molecular weight thiols [13].

Arsenic is a compound that appears to be methylated by organisms to reduce its toxicity [14]. In low phosphate environments, concentrations of arsenate can rival those of phosphate and given their similar chemistry, organisms can take up As^{V} inadvertently. Methylation appears to be a way to detoxify the As and allow for its secretion into the environment. This is more prevalent in marine waters where As concentrations are higher, as discussed further below. In contrast, methylation of Hg and other metals enhances their toxicity [15]. However, most of the methylated Se compounds are derived from the decomposition of larger organic Se biochemicals such as selenoproteins [16]. Throughout the chapter such contrasts will be illustrated.

In summary, this chapter will specifically consider the methylation of elements in Groups 12-16 of the periodic table in aquatic systems, with a focus of those present as minor or trace elements. Most of these elements, especially those lower in the periodic table (i.e. higher atomic mass) form covalent bonds with carbon because of the shielding of the nuclear

charge that occurs due to the presence of electrons in filled d and f orbitals. For the metals in Group 12, the tendency to form methylated compounds increases down the group. However, for Groups 15 and 16, the metalloids As and Se are methylated more readily than the elements below them in the periodic table, as in these cases the ionic character increases with atomic number. These and other differences within groups result in both similarities and differences in the methylation of the elements and in their stability, fate and transport in the environment, and their ability to biomagnify in aquatic food chains. Before discussing the processes whereby the metal(loid)s are methylated in the environment, it is useful to discuss briefly the distribution and fate of these elements in marine and freshwater environments.

2. The Distribution of Methylated Species in the Ocean and in Freshwaters

Representative vertical profiles in the North Pacific Ocean for the metal(loid)s discussed in this chapter are shown in Figure 2 [17]. Many of the elements that form methylated species in marine systems (e.g. As, Se, Sb, Ge) exist as oxyanions, and in a number of oxidation states [14, 18-20]. The reduced form of the element is often present because the methylation pathway involves reduction prior to methylation (the so-called Challenger mechanism), as discussed further below, or because of biological or photochemical reduction within organisms or the water column. In addition to being found as methylated compounds, many metalloids are incorporated into larger metalloid-containing species, such as arsenobetaine and selenoproteins [21, 22]. For example, As is found as As^{III} , As^{V} , mono-, di- and tri-methyl arsenic in marine waters (Figure 3a), and as arsenobetaine, arsenosugars and other As-containing carbohydrates in organisms. In the open ocean water column, methylation of As is mostly by phytoplankton as this is a detoxification/elimination mechanism. Arsenic (As^{V}) is taken up inadvertently by microorganisms in low phosphate waters (both exist as polyprotic acids with similar pK_a 's) and these relatively high concentrations of As can interfere with phosphate biochemistry within the cells.

The methylation of Hg, and other cations (e.g. Sn, Pb), does not involve oxidative methylation and therefore the reduced form of these metals, if present, is due to reductive processes that are not directly related to methylation. For Hg, however, the reduced form, elemental Hg (Hg^0) can be formed through the demethylation of CH_3Hg and its subsequent reduction [23, 24]. The presence of the reduced forms of the elements in ocean surface waters, such as Hg^0 and As^{III} is contrary to what is expected based on thermodynamic equilibrium calculations, and this further suggests their formation through microbial processes. However, reduction of Hg can be abiotic as well [25], as its redox couple is such that photochemical reduction is possible in surface waters.

As an example of the distribution of the metalloids in the ocean, profiles of the various species of As and Sb are shown in Figure 3a-c for the North Pacific Ocean. Methylated As and Sb species are present in the surface waters where phytoplankton activity occurs and the

concentrations at depth are low or below detection, depending on the stability of the methylated form. In estuarine environments and freshwaters, As^{III} and the methylated forms can be a larger fraction of the total dissolved As [20, 26]. The distribution and speciation of Sb is similar to that of As in the ocean water column [14]. The dominant oxidation state is +V, but with the presence of the +III oxidation state in the upper waters and the presence of methylated species, making up about 10% of the total dissolved Sb. The ancillary parameters shown in Figure 4 for the upper Pacific Ocean [27] give some indication of the physical factors influencing the distribution of the metalloids. The density profile shows an area of rapid changing density which coincides with rapid changes in temperature and salinity, which occurs closer to the surface in the northern latitudes. This stratification separates the more productive surface ocean, where most primary production occurs, from the deeper colder waters where microbial activity is much lower. Therefore, most of the microbial methylation of the metalloids occurs in the upper waters of the ocean, overall within the top 1000 m, and if driven mostly by phytoplankton, within the top 100 m.

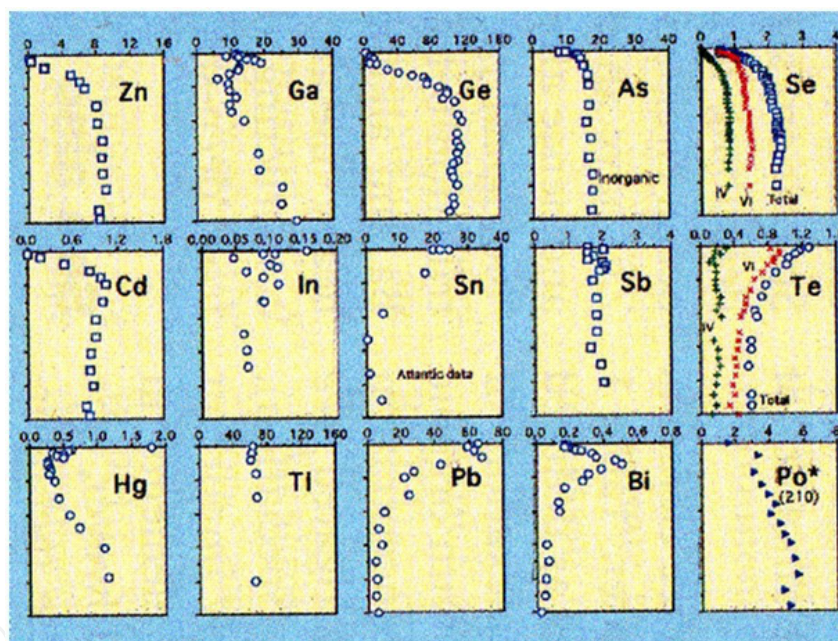


Figure 2. Vertical profiles of the total metal concentration in open North Pacific Ocean water as compiled by Nozaki 1997. The y-axis is the depth from the surface to 5 km. symbols represent the concentration range: squares for nmol/kg circles for pmol/kg and filled triangle for mBq/kg. Figure reprinted with permission from the American Geophysical Union (AGU).

For Se, methylated Se compounds are found in natural waters, as well as both the oxidized and reduced inorganic forms (Figure 3d). The two main inorganic redox states are found but their concentrations are somewhat depleted in the surface waters (Figure 3d), likely due to their uptake and incorporation into biota [14]. Selenium is an essential element although only required at low concentrations. The distribution of organic Se (Se^{II}) suggests its persistence through the water column, either due to its continual formation and release from microbes and/or from organic matter dissolution, or due to its stability. Volatile methylated

Se compounds can be formed (analogous to methylated sulfide species, i.e. the suite of compounds: $(\text{CH}_3)_2\text{S}_y\text{Se}_z$; $y+z=0-2$; $y+z=1$ or 2) in the surface ocean through the decomposition of larger Se-containing biomolecules [28, 29]. The evasion of these compounds could also result in depletion of Se from surface waters [28, 30]. The cycling of Se in the upper ocean is not well understood and needs further study [14].

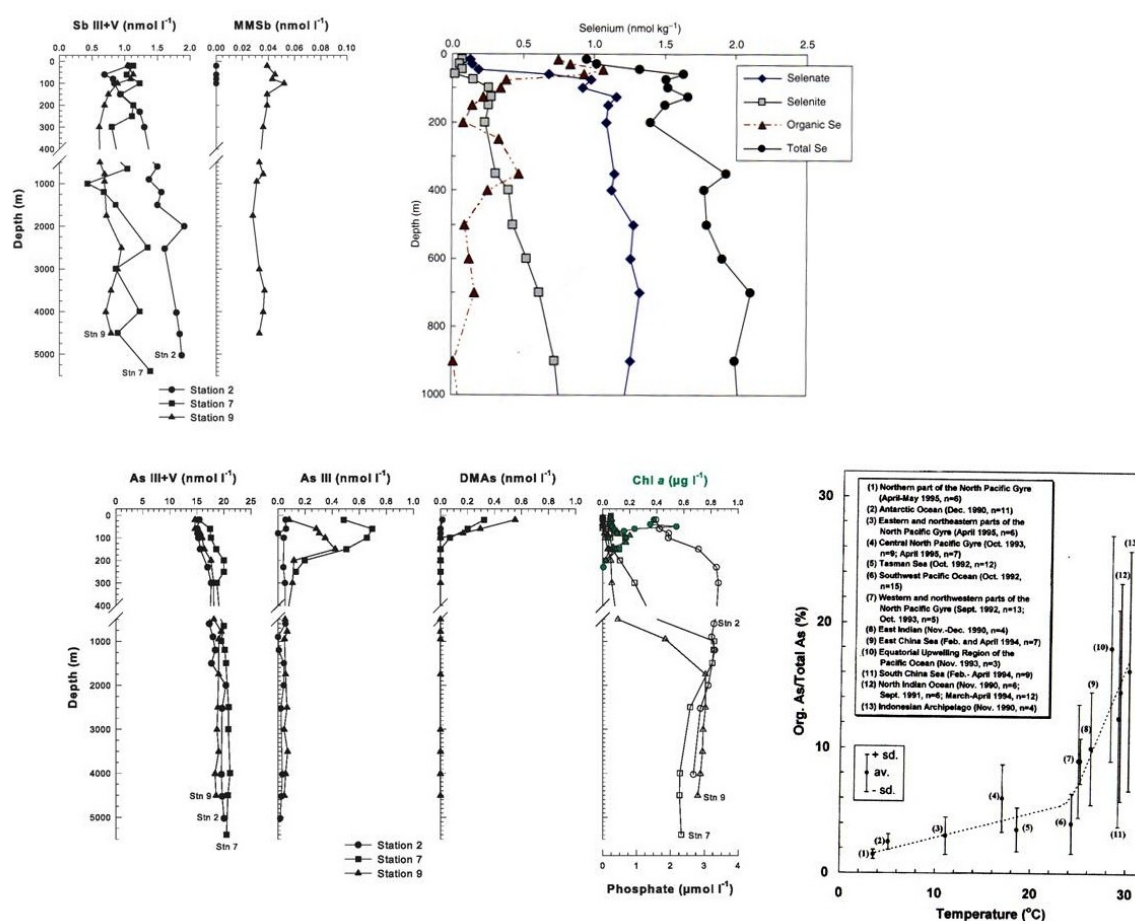


Figure 3. a) Arsenic speciation and distribution in the North Pacific Ocean. Taken from Cutter and Cutter (2006); b) relationship between the relative amount of organic As compounds in seawater and the water temperature. Taken from Santosa et al., 1997; c) Antimony speciation and distribution in the North Pacific Ocean. Taken from Cutter and Cutter (2006); d) Selenium speciation and distribution in the North Pacific Ocean. Taken from Cutter (2010). e) Speciation of germanium in the North Pacific Ocean. Taken from Cutter (2010). Figures a) and c) reprinted with permission from AGU; b) with permission from Wiley; c) and e) with permission from Elsevier

Tessier et al. [31] developed methods for the simultaneous measurement of a number of volatile metal(loid) species in various estuaries in France. They were able to detect the methylated Se species, a variety of Sn compounds, as well as Hg^0 . Many of the compounds were found at low concentrations (e.g. $(\text{CH}_3)_2\text{Se}_2$, $(\text{CH}_3)_2\text{SSe}$, $(\text{C}_4\text{H}_9)_x\text{Sn}(\text{CH}_3)_{4-x}$ ($x=1-3$), $(\text{CH}_3)_4\text{Sn}$ and $(\text{CH}_3)_2\text{Hg}$) and the dominant species for each element was Hg^0 , $(\text{CH}_3)_2\text{Se}$ and $(\text{C}_4\text{H}_9)_3\text{SnCH}_3$. The concentration of $(\text{CH}_3)_2\text{Se}$ was higher in spring, suggesting production in conjunction with phytoplankton activity. For Sn and Hg, concentrations of volatile com-

pounds were in the sub-pM range while concentrations were in the pM range for $(\text{CH}_3)_2\text{Se}$. In each case, there was some evidence of a gradient across the estuary that is likely related to water mixing and changes in ecosystem productivity.

Germanium (Ge) is a most unusual element in that its ocean distribution is dominated by its methylated forms (Figure 3e). Germanium is found as the mono- and dimethylated species with the monomethyl species being the dominant form throughout the water column [14]. It has a conservative distribution which indicates its high stability and little is known about its formation mechanisms [32]. There is also little information on the ocean distribution of tin (Sn) (Figure 2) [33]. Much of the focus of study of this element has been due to its use as antifouling agents (e.g. tetrabutyltin) and these compounds will not be discussed in detail. In the surface ocean its concentration is higher than at depth, showing that it is scavenged from the ocean by sinking particles. Bismuth is also higher in surface waters and has a deep water scavenged profile (Figure 2) [33].

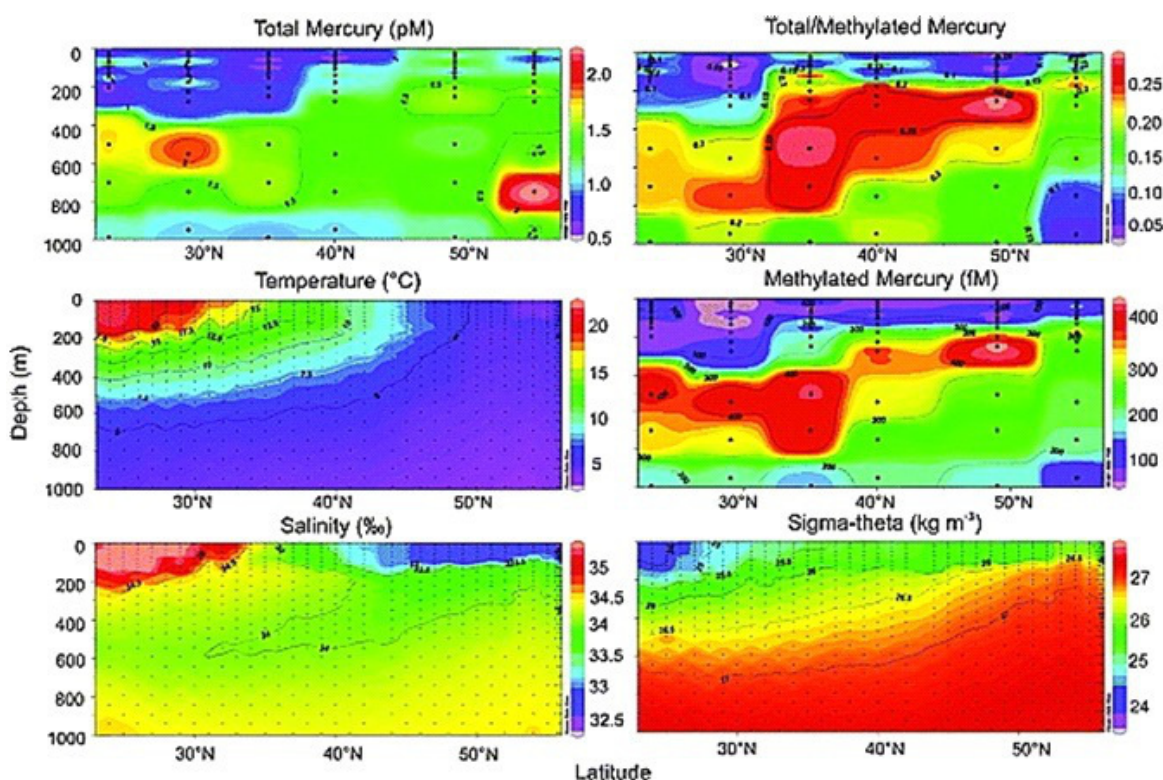


Figure 4. Distributions of total mercury, total methylated mercury (sum of mono and dimethylmercury), and their ratio, temperature, salinity and sigma-theta (a measure of water density) for a transect sampling waters at latitude 152°W in the North Pacific. Taken from Sunderland et al. (2009). Figure reprinted with permission from AGU.

In the late 1980's, methylated Hg compounds were detected in the water column of the remote ocean [25] and in lakes, and it was shown that the formation of CH_3Hg was relatively ubiquitous in aquatic systems [34]. In ocean waters, and in some freshwater systems, dimethylmercury ($(\text{CH}_3)_2\text{Hg}$) has been measured and its presence is mostly found in the water column, although there is some evidence for $(\text{CH}_3)_2\text{Hg}$ in sediment porewaters

[35]. The relative importance of different bacteria in the production of CH_3Hg and $(\text{CH}_3)_2\text{Hg}$ in these diverse natural aquatic environments is not clearly understood, although it has been a topic of recent investigation. The distribution of Hg in the North Pacific Ocean is shown in Fig 4 [27]. As can be seen, the distribution of methylated Hg is different from that of As, Sb and the other metalloids as the concentration is low in the surface waters, and maximal in the mid-depth waters. This study and a number of other investigations [25, 27, 36-38] have concluded that the profiles are best explained by formation of methylated Hg in conjunction with the decomposition of organic matter that sinks from the surface ocean, and that the formation is microbially-mediated. Studies in the Arctic Ocean have shown that in situ methylation occurs in the water column in this region [39], further confirming this pathway. This contrasts lakes where most of the methylation is thought to occur in the sediments [2].

Overall, given the limited data for some elements it is difficult to examine in detail the locations and processes of formation of many of the metal(loid)s in marine systems. In summary, the metal(loid)s show the following distributions (Figure 2): a) distributions with lower surface ocean concentrations, reflecting uptake in the surface ocean, either into plankton and the food web or by abiotic particles, and release at depth; or b) higher surface water concentrations, reflecting either the dominance of atmospheric inputs (e.g. Pb) or the strong scavenging of the element from deep waters by particles. Overall, however, their distributions are modified to a degree by the formation of methylated or reduced species and the stability and fate of these compounds relative to the more oxidized forms.

Studies of many of the metal(loid)s are also limited for freshwater environments. Mercury has been the most studied and the factors controlling Hg methylation in sediments in the Florida Everglades is summarized in Fig 5a [2]. Across the Everglades there is a strong organic matter and sulfate gradient that drives the activity of the SRB's (sulfate reduction rate (SRR) in the figure). The product of sulfate reduction, sulfide, complexes Hg and reduces its bioavailability to the methylating organisms, as discussed further below. The bioavailable fraction is represented in Figure 5a as HgS^0 , the neutral complex concentration. The maximum in methylation rate and the highest fraction as CH_3Hg in sediments (%MeHg in the figure) is found at the right combination of bioavailability and bacterial activity, at low sulfide but sufficient sulfate concentrations [2, 40]. Similar results have been found for estuarine and coastal sediments [41-44], as shown in Figure 5b. Higher sulfide levels in coastal sediments result in a strong hindrance of methylation at concentrations above 0.1 mM sulfide in sediment porewaters [2, 42]. This is shown in Figure 5. In the estuarine sediments, lower methylation rates and % CH_3Hg are found at depth as sulfide levels increase. The highest fractional conversion of Hg to CH_3Hg occurs in low organic matter, shelf sediments where microbial activity is lower but Hg is much more bioavailable [41-44]. Studies in lakes show comparable data, and also suggest that there is the potential for methylation within the water column of seasonally or permanently stratified lakes where oxygen is depleted and sulfide is present [45]. In these environments, the highest methylation is within the redox interface, which is consistent with the discussion

of methylated Hg formation in the ocean and in sediments, although truly anoxic conditions are not found in the ocean water column.

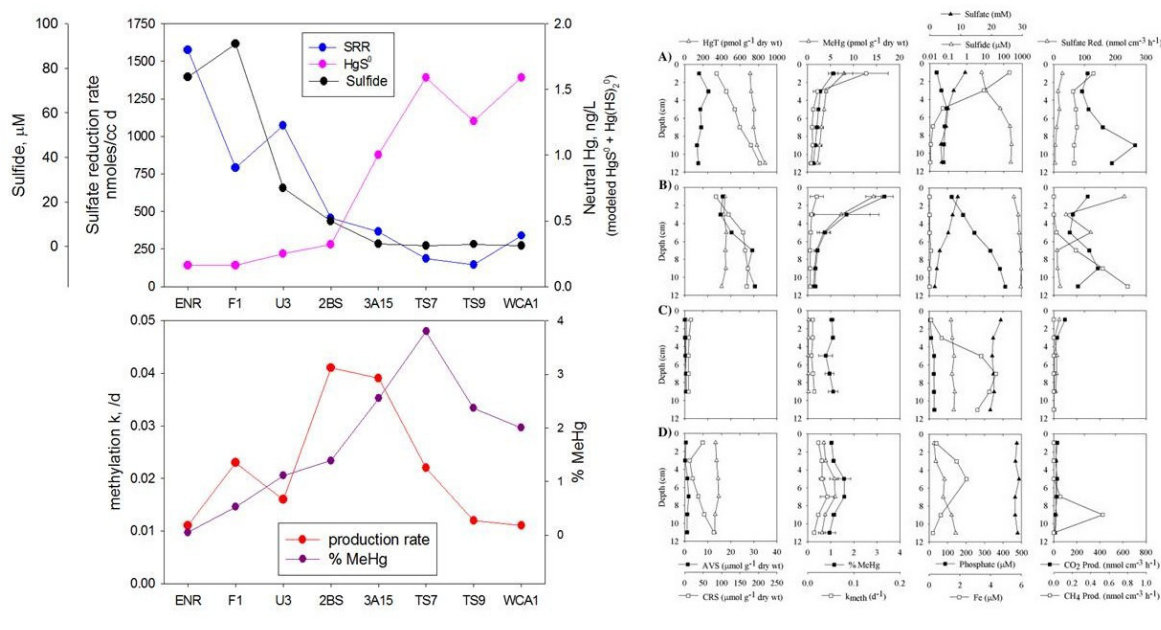


Figure 5. a) Changes in the concentration of various parameters including the concentration of bioavailable Hg (HgS^0) as well as the methylation rate for sites across the eutrophication gradient in the Florida Everglades. Taken from Benoit et al. (2003); b) The vertical distribution of parameters, including mercury speciation (total (HgT) and methyl-mercury (MeHg)), and also the rates of microbial processes (mercury methylation (k_{meth}), sulfate reduction, CO_2 and methane production). The sediment reduced sulfide content is indicated by the concentration of labile reduced sulfide (AVS) and pyrite (CRS). The four sample locations include sites in the Chesapeake Bay (A and B) and sites on the shelf (C and D). Taken from Hollweg et al. (2009). Figure a) reprinted with permission of the American Chemical Society (ACS), b) with permission from Elsevier.

Arsenic speciation and methylation in freshwater ecosystems has also received attention and this has been driven mostly by studies in As contaminated environments. Methylation processes are similar to that found in the ocean with most of the methylated species being confined to the surface waters and levels in deeper waters depending on a variety of conditions [46-50]. Both seasonally and permanently stratified lakes have been examined and while high levels of the inorganic forms of As are found in anoxic waters, this is not the case for the methylated species. A study in the hydrothermal environment at Yellowstone National Park, USA found that there were volatile As compounds emitted in locations with high aqueous As (up to 50 μM levels) [51]. Concentrations of volatile As in surface waters were from <1 to 2.5 μM . Species identified were $(\text{CH}_3)_2\text{AsCl}$, $(\text{CH}_3)_3\text{As}$, $(\text{CH}_3)_2\text{AsCCH}_3$ and $(\text{CH}_3)_2\text{AsCl}_2$. There are also some reports of volatile As compounds in some marine environments [52]. Studies of the other methylated metal(loid)s in freshwater environments are very limited, with some examination of the formation pathways and speciation of Sb and Se [53-55]. Aspects of the factors influencing formation will be discussed further below. Overall, there is a need for further research on the methylation of metal(loid)s besides As and Hg in aquatic systems.

3. Biotic Transformations

Of the species that exist in solution as cations, Hg is the element that is methylated to the highest extent, and has been the most studied, primarily as a result of concerns of the human and environmental impact of the accumulation of CH_3Hg in fish, and their consumption [56]. The results of these extensive studies can be extrapolated to other cations that are methylated, but more study is also required to investigate their fate and how they are methylated and bioaccumulated. In terms of the oxyanions, As has received the most attention and again this is driven by concerns over toxicity and the fact that methylation reduces the toxicity of As relative to reduced inorganic As. Methylated compounds of both As and Se can also be formed by the decomposition of larger biochemicals produced in microbes and larger organisms. These pathways will also be discussed in addition to the discussion of the direct methylation pathways.

3.1. The biotic methylation of mercury

Acute exposure incidents in Japan and elsewhere in the 1960's provided the first evidence that inorganic Hg could be converted into the more toxic and bioaccumulative CH_3Hg [15, 56]. Methylation of Hg in sediments by the resident microorganisms was subsequently demonstrated and many of the early studies examining the role of microbes in methylation were in coastal and estuarine sediments [34]. Selective microbial inhibition studies indicated that methylation was primarily mediated by SRB's [57, 58] but recent studies suggest that phylogenetically similar microbes (e.g. Fe-reducers in the genera *Geobacter*) can also methylate Hg [3, 59]. Additionally, there has been recent demonstration of methylation being related to the activity of methanogens in lake periphyton [60] and it is possible that further examination of different environments may lead to further understanding of the Hg methylation process. The site, or more likely sites, of methylation within cells has not been clearly identified and not all SRB's methylate Hg, and even organisms from the same genus has different abilities to methylate Hg [2]. While initial studies suggested that methylation was associated with the Acetyl-CoA pathway and cobalamin in one estuarine organism (*Desulfovibrio desulfuricans* LS) [61-63], this link does not hold across a variety of organisms, as organisms without this pathway methylate Hg, and *vice versa* [64, 65]. For SRB's, both complete and incomplete organic carbon oxidizers are methylators of Hg. Recent studies have also shown differences in the rate of methylation in biofilms compared to free living SRB in culture [66]. It was shown that the gene expression, and in particular the activity of the Acetyl-CoA pathway, was different for the same organism when growing under these different conditions and that the expression of the pathway coincided with the increased methylation in the biofilms. These results appear to confirm the notion that methylation is accidental and not a detoxifying mechanism in these organisms.

In a number of ecosystems, CH_3Hg production has been shown to be strongly related to Hg interactions with sulfide, e.g. [2, 43, 44, 67]. Neutrally charged dissolved Hg-S species (HOHgSH and $\text{Hg}(\text{SH})_2$) are believed to be much more bioavailable to sulfate-reducing bacteria [12, 68] than charged complexes. They have a relatively high K_{ow} and dominate at low

environmental sulfide concentrations. At higher sulfide, negatively charged Hg-S species and Hg polysulfide species dominate [69]. Therefore, methylation is most prevalent in environments where sulfate reduction is high, but sulfide accumulation is low (Figure 5) [2]. These locations are often the upper layers of sediments, as inputs of fresh organic matter and oxygen diffusion into sediments result in high rates of Fe and sulfate reduction in regions of relatively low sulfide content. Other complexes of Hg are potentially bioavailable and complexes with small organic ligands can have a relatively high K_{ow} [70]. This is demonstrated by the fact that a bacterial culture of *Geobacter sulfurreducens* can methylate Hg^{II} when present in the medium as a cysteine complex at a much faster rate than as either sulfide or chloride complexes [71, 72]. Most studies therefore highlight the importance of speciation in determining the rate of methylation in sediments and freshwater systems but the role and activity of the methylating bacteria cannot be ignored. It has been well demonstrated that speciation affects the uptake and methylation of inorganic Hg and the same impact is probable on the rate of demethylation of CH_3Hg , and on the uptake and methylation of other cations.

The discussion above about methylation in sediments and freshwater systems does not explain the sources and sinks for CH_3Hg in the open ocean. A recent examination of the sources and sinks for CH_3Hg and $(CH_3)_2Hg$ (hereafter represented as ΣCH_3Hg) to the ocean [25] suggest that external sources (riverine inputs and coastal sources and atmospheric deposition) are insufficient to account for the ΣCH_3Hg sinks in the ocean, which include accumulation into biota and removal by fisheries, photochemical and biological degradation into inorganic Hg, and net removal to the deep ocean and deep sea sediments. This indicates that production within the ocean water column is important. While both CH_3Hg and $(CH_3)_2Hg$ are broadly distributed throughout the ocean water column, they have observed concentrations are difficult to explain without *in situ* production [25]. Initial studies in the equatorial Pacific Ocean suggested sub-thermocline maxima in both CH_3Hg and $(CH_3)_2Hg$ [38, 73-75] have been confirmed by more recent studies in the North and South Atlantic and Pacific Oceans, the Mediterranean Sea, the Southern Ocean and other locations [27, 36, 37, 76-80]. Figure 4 is representative of a typical profile for the upper ocean. These vertical distributions are most consistent with *in situ* formation of ΣCH_3Hg in association with the decomposition of organic matter. The link to organic carbon degradations is demonstrated, for example, by the relationship between the amount of ΣCH_3Hg and the extent of organic carbon remineralization [27], and correlations between ΣCH_3Hg and apparent oxygen utilization, another measure of carbon degradation [36-38, 75, 78]. The ΣCH_3Hg distribution across studies suggests that the transition regions (the base of the euphotic zone), and subsurface waters where particulate organic matter is being degraded, are locations of enhanced net methylation of Hg. However, there is still little concrete information about the microbes responsible for Hg methylation and for the primary factors driving the relative magnitude of this process across ocean basins.

3.2. The biotic methylation of arsenic and antimony

The methylation of As (Figure 6) is thought to be a detoxifying mechanism for bacteria and phytoplankton [5], especially those in the marine environment where the concentration of As is relatively high compared to the required nutrient phosphate, as both exist in solution as oxyanions. However, the first indication of As methylation was the demonstration of the release of volatile As-containing compounds from wallpaper in the 1800's in Europe, from the use of As-containing pigments in their coloration [4, 5]. It was further realized that mold and damp enhanced their formation and therefore a biological role for the production of these volatile compounds was concluded, mostly based on work done by an Italian physician, Gosio. This early work was followed by Challenger and his colleagues in the early 20th century, who developed the original mechanism for As methylation that still bears his name [4].

It is now known that methylation of As and other metalloids is carried out by a wide variety of fungi, yeasts and bacteria, and eukaryotes [4, 21, 81]. Methylation of As is the most prevalent of the elements in Group 15 occurring in microbes, algae, plants and animals while methylation of Sb is more restricted to eukaryotic and prokaryotic microorganisms. It is thought that As is mainly taken up by phytoplankton through phosphate uptake channels. It is however also possible that the methylated As species are formed during the degradation of As biochemicals during degradation of cellular material [4]. Inorganic As is present in environmental waters as an oxyacid in both oxidation states: arsenic acid (arsenate) $\text{AsO}(\text{OH})_3$ or H_3AsO_4 ($\text{pK}_{\text{a}1} = 2.2$; $\text{pK}_{\text{a}2} = 7.0$; $\text{pK}_{\text{a}3} = 11.5$) and arsenous acid (arsenite) $\text{As}(\text{OH})_3$ ($\text{pK}_{\text{a}1} = 9.3$). The pK_{a} 's of arsenic acid are very similar to those of phosphate (respectively, 2.1, 7.2 and 12.4) and therefore the speciation of As^{V} and phosphate in most environmental waters is analogous. At the typical pH of environmental waters, the major species will be H_2AsO_4^- and HAsO_4^{2-} . It generally appears that phosphate uptake is active and in conjunction with Na^+ co-transport and therefore a similar mechanism is likely for As. In open ocean surface waters, phosphate concentrations are often very low ($<0.5 \mu\text{M}$) and As concentrations are typically around 10-20 nM [14, 20]. Therefore, given this relatively small difference in concentration, inadvertent uptake of As is possible [21]. The methylated forms of As can be released from the cells into the environment or they can be incorporated into larger molecules and their toxicity reduced as a result.

The Challenger mechanism of As, and other metalloid, methylation involves a series of reductive methylation steps where the addition of the methyl group is via a carbocation addition reaction (Figure 6). The details of the mechanism are relatively well known although some aspects of the biochemistry within the cell are not entirely elucidated. It is thought that cellular thiols, such as glutathione, are involved in the reduction steps and that S-adenosylmethionine (SAM) is the main methylating agent. The reduction is linked to glutathione oxidation and is enzymatically controlled. Arsenite and related methyltransferase enzymes are associated with the methylation step [4, 8]. The products are the simple reduced methylated species ($(\text{CH}_3)_x\text{AsO}(\text{OH})_{3-x}$, $x=1-3$) as well as oxidized forms, such as trimethylarsine oxide ($(\text{CH}_3)_3\text{AsO}^+$). Volatile forms are also produced by some organisms (Table 1), and these are the methylated As hydrides, such as $(\text{CH}_3)_x\text{AsH}_{3-x}$; $x = 1-3$) [9]. In marine algae, As is found in a variety of organic compounds, such as arsenosugars and As-containing carbohydrates,

with the most common compound being arsenobetaine (trimethylarsinio acetate) $((\text{CH}_3)_3\text{AsCH}_2\text{COO}^-)$ [21]. It is thought that these products are formed from further reactions of the methylated derivatives and that they are ultimately generated by processes similar to that invoked in the Challenger mechanism. The methylated species are also found in measurable concentrations in many environmental waters, both freshwater and marine, as discussed above, and their presence has mostly been correlated with phytoplankton activity although their production via bacteria present in conjunction with the algae is also possible. It is suggested that these compounds are actively exported by the phytoplankton.

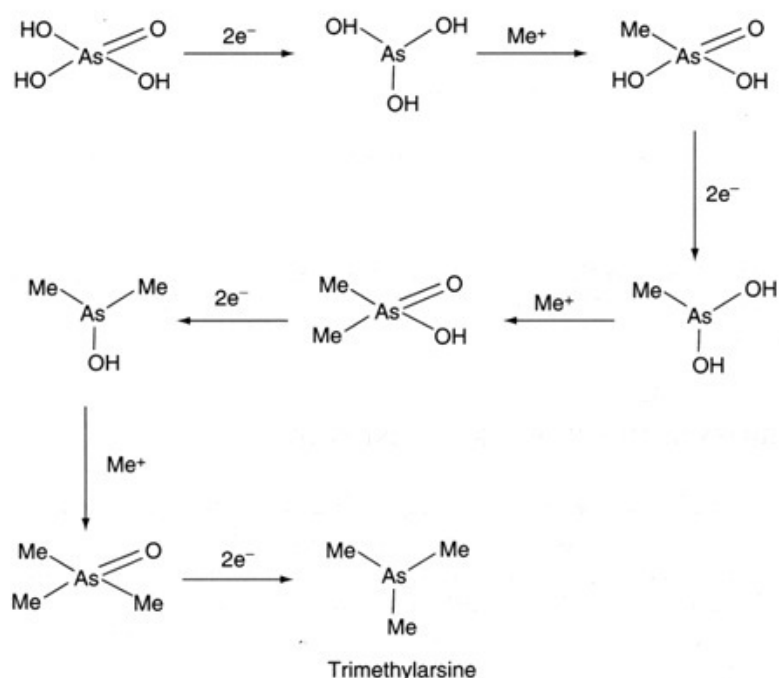


Figure 6. Representation of the steps involved in the methylation of arsenic via the Challenger process. Figure taken from Feldman (2003) and used with permission from Wiley.

Based on the pK_a values, it is evident that the reduced form of As is present as an undissociated acid at physiological pH's and in most environmental solutions, and therefore that there is the possibility of its loss via passive diffusion from the cells into the surrounding media. There are a number of instances where measurements in the environment have shown that the concentration of reduced inorganic As is greater than that of As^{V} , and release of As^{III} after microbial reduction is the most likely explanation [16]. There have been a number of As reductases identified in microbes and these processes appear to be separate from the methylation pathways, and therefore involve different reductants, such as thioredoxin and glutaredoxin [4]. Similar to other metal reductases, the operons are attached to plasmids in bacteria.

Antimony (Sb) has a similar chemistry to As and therefore it is expected to behave in a similar manner to As in terms of uptake and methylation [7]. Its compounds have been widely

used in industry, medicine, as a poison, and as cosmetics. The methylated forms, $(\text{CH}_3)_x\text{Sb}_{3-x}$ ($x = 1-3$), are well-known (Table 1), as are many other organo-Sb compounds, and many have been synthesized for industrial purposes. Volatile Sb compounds were suggested as a possible cause for Sudden Infant Death Syndrome, as Sb compounds were used as flame retardants in mattresses, and this led to the examination of the mechanisms of their formation [4, 7]. A number of fungi and bacteria have been identified that can methylate Sb, and methylation is much higher in the presence of Sb^{III} and it is apparent that many organisms are not able to reduce and methylate Sb^{V} [54]. Therefore, the methylation of Sb may be less ubiquitous than that of As, and there appears to be complex interactions if both As and Sb are present in the same culture in terms of relative methylation [4, 7]. Overall, little is known of the speciation and form of Sb in natural waters, and the formula is given either as $\text{Sb}(\text{OH})_5$ or $\text{HSb}(\text{OH})_6$, which dissociates in water to form the anion, $\text{Sb}(\text{OH})_6^-$ ($\text{pK}_{\text{a}1} = 2.2$). There is evidence from measurements in seawater and in the presence of marine algae that reduction to Sb^{III} occurs and that the monomethylated form exists in environmental waters [54]. It is also present in freshwaters, and evidence for its formation in environments such as landfills [56]. Overall, however, it appears that Sb^{V} is the major form in environmental solutions. The presence of volatile Sb compounds in landfill gases and other methanogenic environments confirms that methylation of Sb is microbially mediated [4, 82].

Most studies have invoked the Challenger mechanism to explain the methylation of As and other metalloids by SAM in the environment, especially in oxic waters but there is some speculation that the pathway of methylation may be different for anaerobic organisms. In this case, it has been suggested that methylation may involve cobalamin and therefore involve a different mechanism whereby a carbanion or a radical from methylcobalamin is added to As^{III} in the presence of mediating enzymes [4, 7]. Methanogenic *Achaea*, for example, were shown to methylate a variety of metalloids of Groups 15 and 16 (As, Se, Sb, Te, and Bi) [10]. The mechanism was attributed to side reactions with methylcobalamin. Additionally, it was demonstrated that methylation of As(V) did not occur and that methylation of As(III) did not involve oxidation, and was therefore similar in process to the methylation of Hg whereby the methyl group is added as a carbanion rather than a carbocation. While Weufel et al. [10] were able to demonstrate the formation of higher methylated compounds, another study [11] suggested that the reaction pathway produces only monomethylated forms, which contrasts the environment where higher methylated forms are often more abundant. In addition to methylation of As, cobalamin has also been shown to methylate Sb [11].

Studies have also focused on the methylation of As and other metalloids in sediments [83]. Laboratory incubation of marine sediments have produced volatile arsines ($(\text{CH}_3)_x\text{AsH}_{3-x}$; $x=0-3$) and other methylated compounds ($(\text{CH}_3)_x\text{AsO}(\text{OH})_{3-x}$; $x=1-3$). In other experiments, incubation of sediments showed the production of both methylated As and Sb species [84]. It appeared that the dimethylated species dominated for both metalloids. Also, the initial rate of formation of the methylated species was faster for As than for Sb. After the completion of the experiment (76 days) all methylated forms of As and Sb were found distributed through the sediment column (0-12 cm) and in the overlying water. While the experiment lasted 76 days, in many instances the peak in concentration occurred relatively early in the experiment suggesting demethylation was occurring in the latter parts of the experiment.

Also, in most cases the porewater concentrations were similar or lower than those of the overlying water.

The relative concentration of the various compounds changed over the course of the incubations in both these experiments [83, 84] and these changes are likely related to the changing microbial community with time and the sequential nature of the methylation processes, as well as demethylation. Field sampling of sediment porewater confirmed the presence of these compounds in the environment, but also showed that these compounds were a small fraction (<1%) of the total As. Another study of estuarine porewaters also found the presence of methylated As, but again these were a relative small fraction of the total (<4%) [85]. This contrasts the oxic water column where higher relative amounts occur (Figure 3). Results with lake sediments [86] were similar as these studies also suggested that anaerobic bacteria (Fe, Mn or sulfate-reducing bacteria) were mostly responsible for the transformations found. Overall, these studies suggest that methylation of As and other metalloids can occur in sediments and that anaerobic bacteria are responsible for the methylation, contrasting the formation mechanisms in the oxic environment. Overall, the links and interactions between the various pathways are complex, and it is difficult to distinguish the relative importance of the various processes in As methylation in sediments and other environments.

3.3. The biotic formation of methylated selenium compounds

Selenium, an element in Group 16, has important and complex organometallic chemistry, and is readily methylated. In organisms, Se has a large number of biochemical roles as it is incorporated into a number of enzymes [52]. The methylation of Se was first investigated by Challenger and since these early studies it has been shown that Se has an extensive biochemistry and that compounds, such as selenoproteins are important constituents of organisms as they act as anti-oxidants and have other roles in the cellular machinery [16, 81, 87]. Compounds such as selenomethionine and Se-adenosylselenomethionine (SeSAM), are found in cells, where Se has replaced S, as could be expected as these elements are from the same group of the periodic table. The methylating ability of SeSAM has been shown to be greater than that of SAM [7].

It has been suggested that CH_3SeH and the cation CH_3Se^+ are some of the compounds responsible for the toxicity of Se. Additionally, analogs to the methylated S-containing compounds $(\text{CH}_3)_2\text{S}$ (DMS) and $(\text{CH}_3)_2\text{S}_2$ have been identified ($(\text{CH}_3)_2\text{Se}$, $(\text{CH}_3)_2\text{SSe}$ and $(\text{CH}_3)_2\text{Se}_2$) [7]. It appears likely that these compounds are the degradation products produced by certain microorganisms that exist in ocean waters, being formed from the decomposition of 3-dimethyl-selenopropionate ($(\text{CH}_3)_2\text{Se}^+\text{CH}_2\text{CH}_2\text{COO}^-$) (Figure 7) [7]. Similar processes likely account for their formation in terrestrial waters and other environments. The importance of this pathway was confirmed by growing a freshwater green algae on selenate in the absence of sulfate and showing the formation of the volatile methylated species [53]. This production was reduced when sulfate was added to the medium. Another study also demonstrated the release of volatile methylated Se compounds from green algae. This study also showed the potential for As to inhibit the formation of the Se compounds

[55]. Overall, the formation of methylated Se compounds is relatively ubiquitous as they are apparently produced by both bacteria and algae.

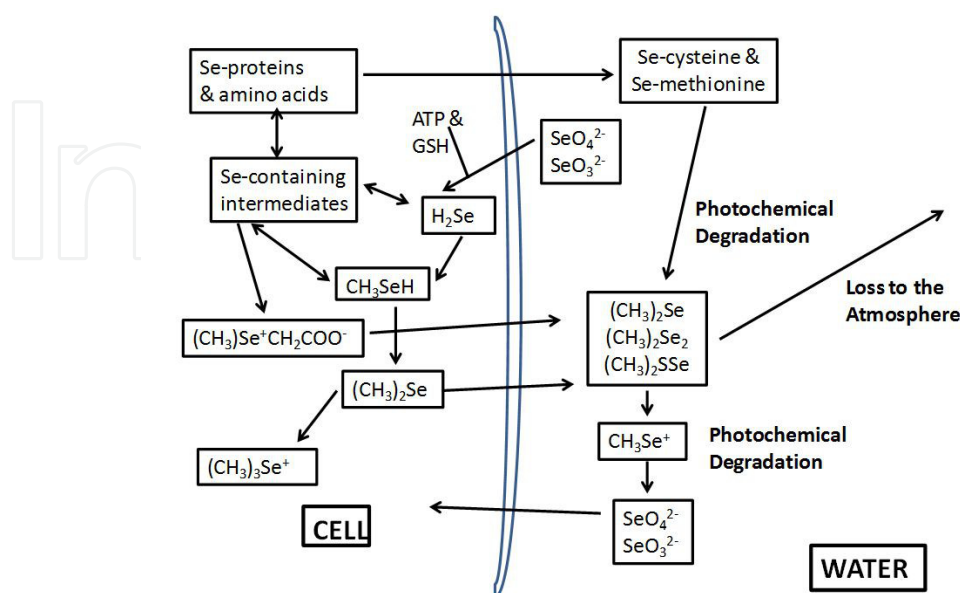


Figure 7. Pathways for the formation and decomposition of methylated selenium compounds in the environment

However, direct methylation is also possible. In freshwater environments, γ -Proteobacteria, such as *Pseudomonas* spp. have been identified as Se methylators. Additionally, a gene encoding for the bacterial thiopurine methyltransferase has been shown to methylate selenite and (methyl)selenocysteine into dimethylselenide and dimethyldiselenide [88]. One potential pathway of formation that interlinks the Se and Hg cycles relates to the potential for CH_3Hg , present in the cell as a thiol complex (represented here as CH_3HgR), to bind to Se-containing amino acids or thiols (represented here as SeR). It is proposed that two CH_3HgSeR react to form $(\text{CH}_3\text{Hg})_2\text{Se}$ and R_2Se , and then $(\text{CH}_3\text{Hg})_2\text{Se}$ decomposes to $(\text{CH}_3)_2\text{Hg}$ and HgSe [89]. A similar pathway was proposed many years ago involving $(\text{CH}_3\text{Hg})_2\text{S}$ for the formation of $(\text{CH}_3)_2\text{Hg}$, which was purportedly formed in sediments [90]. Demethylation of $(\text{CH}_3)_2\text{Se}$ is found in anoxic sediments and it is speculated that methanogens are using this compound for growth in an analogous fashion to their utilization of DMS. In summary, it is likely that in sediments and other low oxygen/anoxic environments, direct methylation is occurring while in the water column the production of the methylated Se compounds results from decomposition of Se-containing biomolecules.

3.4. The biotic formation of other methylated compounds

A number of metal(loid)s not yet discussed are known to form organometallic compounds although there is little information on the formation, stability and toxicity of many of them, or on how they are formed in aquatic systems. In Group 12, Zn does not form any stable small methylated compounds in aquatic systems. In contrast, Cd, above Hg in the periodic table, has been isolated from the environment as methylated compounds [9], although

$(\text{CH}_3)_2\text{Cd}$ is relatively unstable in water. There have been few studies of organic Cd compounds in the environment in contrast to the inorganic chemistry of Cd that has been well-studied. Initial evidence for the formation of CH_3Cd^+ was by bacterial cultures isolated from polar waters [91], and these same cultures also produced methylated Pb and Hg compounds. In the environment, evidence suggests that the peak concentration of these methylated species coincided with that of chlorophyll a, suggesting a microbial role in the formation of these compounds in polar waters. These studies of the formation of methylated Cd compounds in ocean waters require more confirmation. It is known that Cd can be abiotically methylated by methylcobalamin so this represents the potential biotic methylation pathway in aquatic systems [7].

For the other Group 13 elements, there is little evidence for the formation of methylated compounds except for Tl. This is a potentially toxic and bioaccumulative metal and the chemistry of inorganic Tl has received some attention [7]. It appears that Tl^{I} is oxidized and methylated at the same time (i.e. likely via the Challenger mechanism) producing a mono-, di- or trimethylated product of, respectively, +2, +1 and 0 charge. This process occurs under anaerobic conditions with little evidence of aerobic methylation [82]. None of these compounds are highly stable but there is some initial evidence for the presence of these compounds at low pM concentrations in the Atlantic Ocean, mostly as $(\text{CH}_3)_2\text{Tl}^+$ [92], and ranging up to nearly 50% of the total Tl, and present throughout the water column. The profile of the methylated species correlated with chlorophyll a in the upper waters, suggesting its microbial production. These authors also found methylation to occur in an anaerobic lake sediment [92]. There is no evidence for methylated In and Ga complexes in the environment.

Alkylation of Group 14 elements occurs for Sn and Pb and Ge. Alkyl Pb and Sn compounds have been widely produced for use in industrial and other applications, but these will not be discussed here. Studies have shown that a variety of microbes can methylate Sn [8]. For Ge, the mono-, di-, tri- and tetramethylated compounds have been found in the environment. In the ocean, Ge^{IV} has its highest concentrations in deep ocean waters with depleted concentrations in surface waters (Figure 3e) ([82] and references therein). For much of the ocean, the dominant form is monomethylated ($\text{CH}_3\text{Ge}^{3+}$), and its distribution suggests it is relatively stable. The other methylated Ge species ($(\text{CH}_3)_2\text{Ge}^{2+}$ and $(\text{CH}_3)_3\text{Ge}^+$) occur in seawater at somewhat lower concentrations (Figure 3e). It is apparent that methylated Ge compounds can be produced under anaerobic conditions and that these species are not produced in oxic waters in the presence of algae. These compounds can also be made in the laboratory through reactions with CH_3I and methylcobalamin, suggesting that this is the pathway for methylation in the environment, although it has also been suggested that these compounds are formed via the Challenger mechanism [7].

Besides As and Sb, bismuth (Bi) is found under some conditions as methylated compounds, although the methylation is restricted to prokaryotes [5, 82]. As the compounds of Bi are used in industrial and pharmaceutical applications, such as Pepto-Bismol, its presence in sewage treatment plants, and in municipal waste deposits, and the loss of volatile forms of Bi from these environments is not surprising [9]. Bismuth, in contrast to As and Sb, exists in environmental media as a +3 ion rather than as an oxyanion. It also can be found in the

mono-, di- and tri- methylated form, and $(\text{CH}_3)_3\text{Bi}$ is non-polar while the other forms are ions, which exist as complexes in solution (Table 1). The trimethylated form is less stable than its As and Sb analogs. For example, methylated Bi compounds are produced by methanogens in culture [7]. The hydride (BiH_3) has also been isolated from bacterial cultures (Table 1). In the biotic formation of methylated Bi compounds, it is possible that the methyl group is donated by methylcobalamin, which is consistent with its form in solution as ionic complexes [5, 82]. This contrasts the methylation of As and Sb. However, there is little detailed information available about the exact nature of the methylation process for Bi.

There is evidence for the formation of organo-Te compounds and the mechanisms for their formation appear to be similar to the mechanisms for the formation of organic Se-containing compounds [82], which is also in Group 16 of the periodic table. Certain bacteria have been shown to methylate Te and form dimethylated compounds, and there is a complex interaction between the ability of these organisms to methylate and the Se concentration [8]. This suggests that Se and Te, which are electronically similar, behave similarly in this regard. Both exist in solution as oxyacids although the pK_a 's of the selenic and selenous acid are much lower than the corresponding values for telluric and tellurous acid [93]. There has been some suggestion that Po can be methylated but the conditions under which this occurred suggests that these compounds are unlikely in natural environments [7]. The mechanism of methylation is not known and as Po exists in various oxidation states, there are a number of potential methylation pathways. More research is needed to examine in more detail the methylation and cycling of Po and the other less-studied heavy metals and metalloids.

4. Microbially-Mediated Decomposition of Methylated Compounds

The pathways for the decomposition of organometal(loid)s often occur in a stepwise fashion with the removal of successive methyl (or other alkyl) groups from the central metal(loid) atom. Examples include the decomposition of $(\text{CH}_3)_2\text{Hg}$ to CH_3Hg^+ to $\text{Hg}^{\text{II}}/\text{Hg}^0$ and $(\text{CH}_3)_4\text{Sn}$ or $(\text{CH}_3)_4\text{Pb}$ to the tri, di and monomethyl forms. Microbial demethylation is likely to be a detoxifying mechanism in many cases, but there is also evidence that some microbes can use the low molecular weight methyl compounds as a carbon source. Both of these pathways will be highlighted with specific examples. For most of the metal(loid)s, the degradation pathways are less studied than the methylation reactions. The one exception is the demethylation of CH_3Hg using the *mer* operon [23] (Figure 8). This pathway can decompose other alkyl as well as phenyl Hg compounds.

A number of microbes appear to be important in the demethylation of CH_3Hg although the mechanisms are not as well understood in many environments [23, 24]. In uncontaminated environments, the major products appear to be Hg and CO_2 and therefore this pathway has been termed *oxidative demethylation*, in contrast to *reductive demethylation*, where CH_4 is the major carbon product [24]. The mechanism of oxidative demethylation may be analogous to monomethylamine degradation by methanogens or acetate oxidation by SRB's. Reductive demethylation appears to be prevalent in more contaminated environments and

at high CH_3Hg and Hg concentrations it has been shown that a series of inducible genes can be activated (the *mer* operon) that can aid in detoxification of CH_3Hg via demethylation (the *mer B* gene which encodes for organomercury lyase), and reduction of Hg^{II} to Hg^0 (the *mer A* gene which produces mercury reductase) (Figure 8). The *mer B* gene can decompose a variety of organomercury compounds. There is also a regulatory gene (*mer R*), as well as transport genes and their transport proteins in the cell membrane [23]. The overall operon is contained on a plasmid and is readily transferred between bacteria in the environment. However, while membrane Hg^{II} transport proteins are present in bacteria with the *mer* operon, they are absent in SRB and therefore are not involved in the transport of Hg associated with methylation.

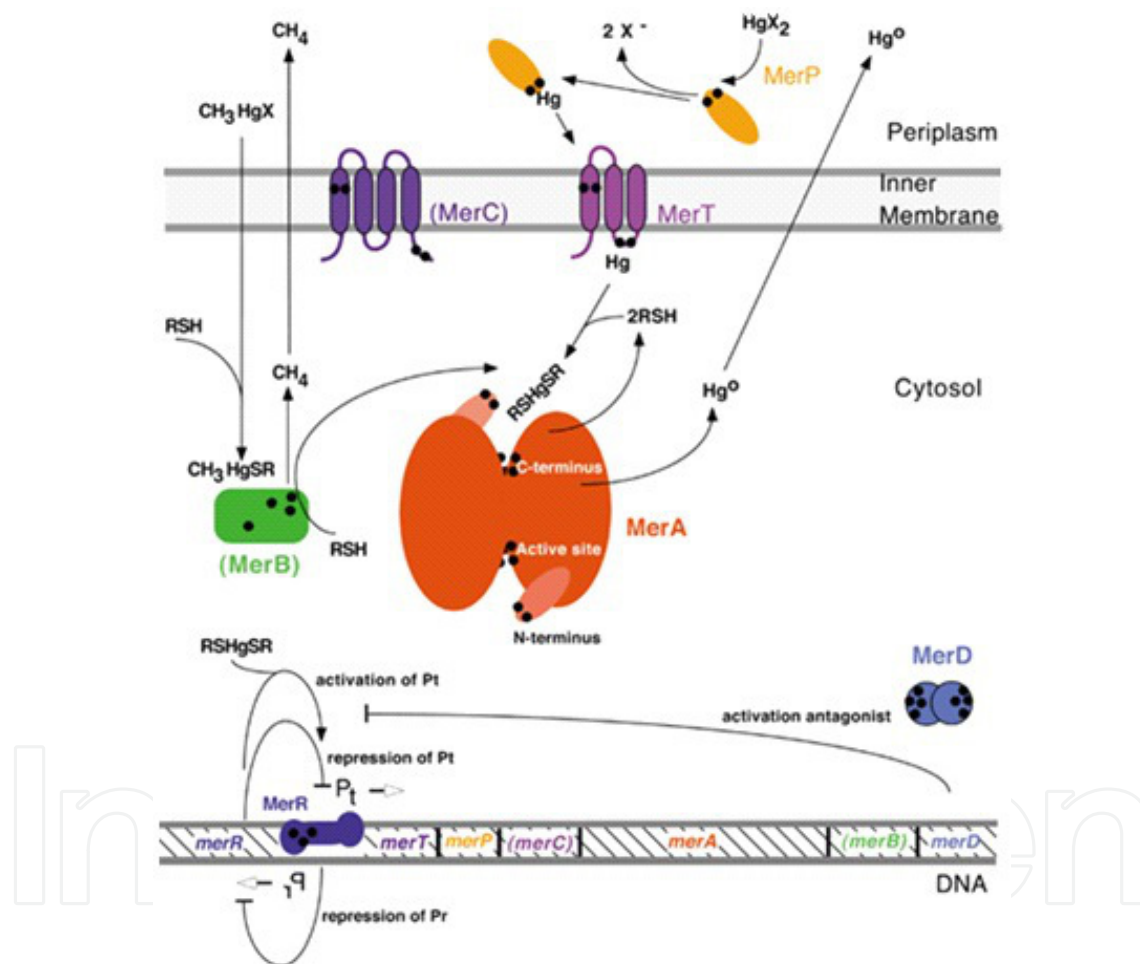


Figure 8. Representation of the *mer* operon and the processes whereby mercury species are transformed. Taken from Barkay et al. (2003) and used with permission from Elsevier.

However, while methane and Hg^0 are the primary products of *mer*-mediated Hg demethylation, CO_2 has also been observed as a major demethylation product in many studies [24, 94, 95] and this oxidative demethylation is not considered an active detoxification pathway. A variety of aerobes and anaerobes have been implicated in carrying out oxidative demethylation which has been observed in freshwater, estuarine and alkaline-hypersaline sediments

[24, 94, 96]. However, the identity of the organisms responsible for oxidative demethylation in the environment remains poorly understood and no specific organism has been isolated. One study confirmed the ability of two sulfate reducing bacterial strains and one methanogen strain to demethylate mercury in pure culture [97]. The authors however argued that the CO_2 seen in these studies resulted from oxidation of methane released from CH_3Hg after cleavage via organomercurial lyase and was actually a secondary product and not the primary product of demethylation. However, this view is not universally accepted based on other their studies under both aerobic and anaerobic conditions [24]. Overall, the relative importance of *mer*-mediated versus oxidative demethylation is poorly understood. In systems that are not highly contaminated, oxidative demethylation appears to dominate, under both aerobic and anaerobic conditions. The Hg concentrations that would cause a switch from one pathway to the other are only loosely defined. The end-product of oxidative demethylation has been presumed to be Hg(II) , but that has not been confirmed in most studies.

Studies in freshwater and marine sediments [24, 42, 67, 94, 98] however confirm that the rate of demethylation is rapid, and that the rate constant for this process is higher than that of methylation, and that demethylation occurs across the redox gradient. Many of these studies have used stable isotope approaches, where isotopically-labelled inorganic Hg, and CH_3Hg made using a different isotope of Hg, are spiked into sediments or water and the transformations of each followed under the same conditions. Another approach is to use radiolabelled Hg and ^{14}C -labelled CH_3Hg but these approaches cannot be done at the trace levels of the stable isotope method. There is an obvious advantage of simultaneously examining both of the reactions in the same experiment. These studies [42, 67, 98] have shown overall that the fraction of Hg as CH_3Hg in sediments is often closely related to the ratio of the rate constants, which suggests that both reactions are pseudo first order and that the system reaches steady state relatively rapidly. Given that demethylation rate constants on the order of 10 d^{-1} have been measured in some sediment, the time to steady state is a few days.

Biodegradation studies of other methylated compounds are limited but these are likely to occur in sediments and reduced environments [82, 99]. One study examining the degradation of methylated As compounds in a lake showed that the decomposition occurred in the presence of suspended particulate but not in filtered water, implicating microbial processes in the decomposition. Degradation occurred in the dark under anaerobic conditions. Studies of alkylated Sn compounds have similarly shown their degradation in the sediment and it is likely that anaerobic microbes can demethylate most of the commonly found methylated metal(loid)s in the environment.

5. Abiotic Formation and Degradation Pathways in Aquatic Systems

A variety of methyl donors exist in environmental solutions and these have the potential to methylate the metal(loid)s discussed here. Pathways include the following primary mechanisms: 1) cross-methylation i.e. transfer of a methyl group from one metal(loid) compound to another e.g. $(\text{CH}_3)_4\text{Pb} + \text{Hg}^{\text{II}} \rightarrow (\text{CH}_3)_3\text{Pb}^+ + \text{CH}_3\text{Hg}^+$; and 2) methylation by other methyl-

containing compounds such as methyl iodide (CH_3I). For example, experiments examining the potential for the abiotic methylation of As^{III} by CH_3I found that the reaction proceeded, but only at very high pH's (>10), above those typically found in the environment [100]. Monomethylarsenic was the only product formed. This study therefore suggests that abiotic formation of methylated As is not likely in the environment. Other studies have shown that CH_3I can methylate Pb, Sn and Ge [8], and there are also studies showing the methylation of Hg^0 by CH_3I , but not with Hg^{II} [101]. Again, these studies do not suggest that these reactions are important in the environment. For example, the rate of formation of CH_3Hg from Hg^0 in the presence of CH_3I , given typical environmental concentrations of these species, is insufficient to account for any substantial portion of the CH_3Hg found in natural waters. For Hg, the same conclusion is reached in terms of methyl transfer reactions between methylated tin compounds and Hg^{II} , even though it appeared that the presence of Cl and high pH, which would be found in seawater, enhanced the reaction rate [101]. Overall, the results of a number of studies over time [52, 101-104] lead to the conclusion that abiotic formation of CH_3Hg in the environment by these pathways is not important.

There have been a number of studies that have shown the potential for the transfer of a methyl group from an organic compound to Hg^{II} , and the formation of CH_3Hg in environmental waters [102, 104, 105], including precipitation [106]. However, most of these experiments have been conducted at unrealistic concentrations of both Hg and the organic compound, as well as having a ratio of Hg/organic matter much greater than found in the environment. Additionally, the reactions are often done at low pH or high temperature. Clearly, these experiments show that CH_3Hg can be manufactured abiotically, which is no surprise, but the results of these studies have little environmental relevance. For example, in the laboratory, CH_3Hg is routinely manufactured through the reaction with cobalamin. This does not however suggest that this is occurring abiotically in the environment.

In terms of abiotic decomposition, the stability of organometal(loid)s in water is related to the polarity of the metal carbon bond with more polarity enhancing hydrolysis and decomposition [107]. However, while many organometal(loid)s may be thermodynamically unstable, they are often kinetically stable and are not degraded abiotically as readily as may be expected. For example, CH_3Hg which is less stable in water at low pH but the reaction is kinetically hindered [108]. Photochemical processes however can enhance the degradation rate. This is an important loss process for methylated Hg. Dimethylmercury is much less stable to photochemical degradation than CH_3Hg [109]. In the ocean, the rate of CH_3Hg photodecomposition varies, with some studies showing relative rapid rates of degradation, while others have shown little degradation [110-112]. It is likely that complexation to Cl or NOM in seawater impacts this rate, but these effects have been little studied compared to in freshwater systems [111, 113, 114]. The degradation of CH_3Hg in freshwater has received more study and photochemical oxidants and UV radiation are important in driving the degradation [114-117] with various reactive oxygen species implicated in the reactions [113, 118]. For the methylated Se compounds, it is likely that oxidation occurs in the presence of light, especially UV radiation, as has been found for methylated S compounds (e.g. $(\text{CH}_3)_2\text{S}$) [29, 119].

A photochemical degradation study with tetraethyllead showed that first order decrease of the reactant with the subsequent buildup and decay of the intermediates [120]. The final product was Pb^{II} . It is likely that tetramethyllead would be degraded in a similar fashion. For Se, photodecomposition of selenoamino acids can produce significant amounts of volatile selenium species in both light and dark conditions in the laboratory, with $(\text{CH}_3)_2\text{SSe}$ and $(\text{CH}_3)_2\text{Se}_2$ being the major products, with small amounts of $(\text{CH}_3)_2\text{Se}$ being formed [29]. Inorganic selenium oxyanions did not produce any volatile products. It was hypothesized that formation of H_2O_2 under the experimental conditions initiated the decomposition reactions. Overall, it is likely that multi-methylated species can be photochemically decomposed by the stepwise removal of methyl groups. This is discussed above and is true for the decomposition of $(\text{CH}_3)_2\text{Hg}$.

6. Conclusion

The methylation of metal(loid)s in the environment is important to the fate and transport of many of the elements in Groups 12-16 of the periodic table. This is true for elements besides those that have received the most attention (Hg, As and Se). Much of the research done on these three elements can be extrapolated to the other elements based on knowledge about the chemistry of the elements in environmental waters and the uptake and fate of the elements within cells. While there is still more research needed to fully understand the methylation, demethylation and fate and transport of Hg, As and Se, this is even more necessary for the other metal(loid)s discussed in this chapter.

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