Chemosphere 345 (2023) 140548

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Environmental selenium volatilization is possibly conferred by promiscuous reactions of the sulfur metabolism

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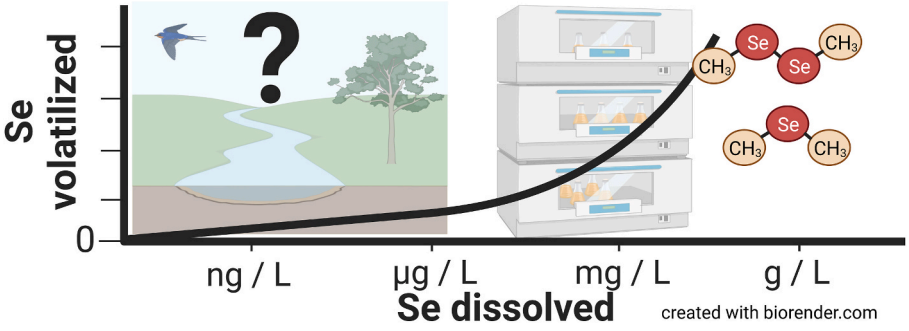
HIGHLIGHTS

- *Pseudomonas tolaasii* efficiently methylated Se at nanomolar concentrations.
- At ≤ 80 nM methylated and spiked Se showed a linear relationship.
- At ≥ 80 nM a strong increase in Se methylation efficiency was observed.
- Environmental Se concentrations are usually in the low nanomolar range.
- At environmental concentration, Se may be methylated promiscuously via S metabolism.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling editor: Petra Petra Krystek

ABSTRACT

Selenium deficiency affects many million people worldwide and volatilization of biogenically methylated selenium species to the atmosphere may limit Se entering the food chain. However, there is very little systematic data on volatilization at nanomolar concentrations prevalent in pristine natural environments. *Pseudomonas tolaasii* cultures efficiently methylated Se at these concentrations. Nearly perfect linear correlations between the spiked Se concentrations and Dimethylselenide, Dimethyldiselenide, Dimethylselenylsulfide and 2-hydroxy-3-(methylselanyl)propanoic acid were observed up to 80 nM. The efficiency of methylation increased linearly with increasing initial Se concentration, arguing that the enzymes involved are not constitutive, but methylation proceeds promiscuously via pathways of S methylation. From the ratio of all methylated Se and S species, one can conclude that between 0.30% and 3.48% of atoms were Se promiscuously methylated at such low concentrations. At concentrations higher than 640 nM (~50 µg/L) a steep increase in methylation and volatilization was observed, which suggested the induction of specific enzymes. Promiscuous methylation at low environmental concentrations calls into question that view that methylated Se in the atmosphere is a result of a purposeful Se metabolism serving detoxification. Rather, the concentrations of methylated Se in the atmosphere may be "coincidental" i.e., determined by the activity of S cycling microorganisms. Further, a steep increase in methylation efficiency when surpassing a certain threshold concentration (here ~50 µg/L) calls into question

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https://doi.org/10.1016/j.chemosphere.2023.140548
Received 22 August 2023; Received in revised form 18 October 2023; Accepted 24 October 2023
Available online 25 October 2023

that natural methylation can be estimated from high Se spikes in laboratory systems, yet highlights the possibility of using bacterial methylation as an effective remediation strategy for media higher concentrated in Se.

1. Introduction

Selenium (Se) is an element that is nutritionally essential for animals. It is involved in antioxidant defence system, human thyroid hormone metabolism and immune system through enzymes containing selenocysteine at the active site (Rayman, 2012). However, the physiological role of Se is double-edged, it is essential at low levels, but toxic at higher concentrations, with narrow safety range (Kipp et al., 2015; Monsen, 2000). Whereas Se contamination usually is a problem of local to regional scale, some estimations came to the conclusion that Se deficiency may affect as much 0.5–1 billion people worldwide (Haug et al., 2007). The problem may worsen with climate change in the future, because of less Se input from atmospheric Se deposition via precipitations in Se deficient regions (Blazina et al., 2014).

Selenium is known to form alkylated species as a result of microbial, plant, fungal and animal metabolism e.g. [(Eswayah et al., 2019; Fukumoto et al., 2020; Kagami et al., 2013; Kubachka et al., 2007; Lenz et al., 2008; Schilling et al., 2011; Vriens et al., 2016; Wells and Stolz, 2020)]. Some methylated species have boiling points sufficiently low to be transferred to the gas phase in the environment. Volatilization has thus been found to be a source for short and long range atmospheric Se transport (Winkel et al., 2012). Volatile Se species from biogenic sources have been estimated to account up to 50% of total atmospheric Se budget on global scale (Wen and Carignan, 2007). Se volatilization will decrease available Se in soils and prevent its entry into the food chain, thus worsening Se deficiency in some regions. Estimating atmospheric Se fluxes is challenging and only few field studies have been done to measure Se volatilization from natural environments [e.g. (Amouroux and Donard, 1996; Be'eri-Shlevin et al., 2021; Lanceleur et al., 2019; Pécheyran et al., 1998; Vriens et al., 2014; Ye et al., 2021)]. Historically, Se volatilization was often studied in the frame of bioremediation of contaminated locations [e.g. (Huang et al., 2013; Lin et al., 2000)]. This may be one reason why many studies have used high Se spikes, often in the μM to mM range (see Table S1, supplementary information). Despite, Se concentrations in both terrestrial and marine environments are generally low: soils contain typically <0.4 mg/kg (Jones et al., 2017) (and correspondingly low concentrations in the soil solution); the world average Se concentration in seawater is below 1 nM (Mitchell et al., 2012). Some German river- and lake waters contained 2.5–3.8 and 2.5–10.1 nM (Tanzer and Heumann, 1991), respectively, whereas the median concentration in Finnish groundwaters, lakes and rivers is as little as 0.76–0.89 nM [refs in (Wang et al., 1994)].

Alkylation is often interpreted as a detoxification mechanism since dissolved Se concentration is reduced through volatilization [e.g. (Choudhury et al., 2011; Peitzsch et al., 2010)]. Despite the fact that enzymes involved in microbial Se alkylation are hardly known [e.g. (Favre-Bonté et al., 2006; Ranjard et al., 2002; Swearingen et al., 2006b)], it can be expected that a specific detoxification pathway (in particular, if it requires energy) is induced only at high Se concentrations. For instance, dimethylsulfoniopropionate lyase, which can cleave the Se analogue dimethylselenoniopropionate to dimethylselenide (DMSe) has been induced at concentrations as high as 50 μM (Ansede and Yoch, 1997), which is several orders of magnitude higher than average environmental concentrations.

It may be doubted such low Se concentrations (i.e., in the nanomolar range) would induce detoxification enzymes. Rather, at low concentrations Se may be alkylated by promiscuous reactions of the sulfur metabolism, whose environmental concentrations are orders of magnitudes higher. For instance, the S average crust concentration is ten thousand times higher than that of Se (Stillings, 2017), whereas oceans contain as much as 28 mM sulfate in average (Riley and Chester, 1971). Sulfur as the "sister element" of Se shares many chemical and structural similarities (Reich and Hondal, 2016). Enzymes involved in sulfur metabolism are less discriminating in terms of preventing selenium incorporation into proteins than vice versa (Johnstone et al., 2021). In some marine systems, Se alkylation was indeed found to be positively correlated with S methylation (next to coccolithophorids concentration) (Amouroux et al., 2001), whereas others found correlations with chlorophyll content (Amouroux and Donard, 1996), temperature (Amouroux and Donard, 1997) or presence of bacterial biomass (Luxem et al., 2017). For terrestrial systems being naturally low in Se, drivers for volatilization are less studied and the connection with S metabolism is not established.

Therefore, we conducted a study on Se methylation by pure cultures of *Pseudomonas tolaasii* – an ubiquitous soil bacterium with a known ability to methylate both selenium and sulfur (S). We used Se spikes down to the nM range and quantified volatile Se and S species by headspace solid phase microextraction gas chromatography mass spectrometry (SPME-GC-MS) and the concentration and speciation of soluble Se was measured by triple quadrupole inductively coupled plasma mass spectrometry (QqQ- ICP-MS) and ion chromatography (IC). To achieve necessary limits of detection, we synthetized selenite (Se^{IV}) isotopically enriched in ^{74}Se.

2. Materials and methods

a Chemicals

Dimethylsulfide (DMS), dimethyldisulfide (DMDS), dimethylselenide (DMSe), dimethyldiselenide (DMDSe) (96%), dimethyl trisulfide (DMTS), sodium selenite, sodium selenate and elemental selenium (99.99% trace metals basis) were purchased from Sigma-Aldrich (Buchs, Switzerland) with high purity (≥99%). Dimethylselenylsulfide (DMSeS) cannot be isolated due to dynamic Se/S exchange reactions and was produced and quantified as described before (Liu et al., 2021). Concentrated HNO_3 (69%) in semiconductor grade was purchased from Roth (Karlsruhe, Germany). For volatile compounds, the individual stock solutions were prepared in methanol at concentration of 100 mg. L^{-1} and stored at −20 °C. Working solutions (individual compounds or mixed) were diluted freshly with ultrapure H_2O (18.2 Ω cm, Thermo Scientific, NANOpure, Reinach, Switzerland) from those stock solutions. The selenite (Se^{IV}) stock solutions were prepared by dissolving sodium selenite in ultrapure H_2O followed by filtration (0.22 μm syringe filter). The concentrations of the Se stock solutions were verified by triple quadrupole inductively coupled plasma mass spectrometry (QqQ-ICP-MS). A minor impurity of selenate (~6%) was found in the sodium selenite salts, despite of different stocks tested. Isotopically labelled Se^{IV} was prepared from ^{74}Se enriched elemental Se (98.2% ^{74}Se, 99.95% chemical purity) purchased from Cambridge Isotope Laboratories, Inc. (Andover, USA) (Supplementary Information).

b Bacterial incubations

Pseudomonas tolaasii obtained from DSMZ (Leibniz Institute German Collection of Microorganisms and Cell Cultures) (strain number 19342) was recovered in King's B medium and transferred to King's B medium agar plates at 28 °C. Precultures of *P. tolaasii* were inoculated from single colonies and grown to stationary phase in glutamine glucose minimum (GGM) medium (28 °C, 180 rpm, 18 h) as described previously (Liu et al., 2021). Sulfate was the only S source in GGM medium (Worm et al., 2000). To avoid possible loss of volatile compounds during sample preparation, bacteria were cultured directly in headspace vials.

Incubations were carried out in 20 mL amber glass headspace vials (Agilent, Basel, Switzerland) containing 5 mL of GGM medium inoculated with 2% (v/v) *P. tolaasii* precultures. GGM medium were amended with 0, 10, 20, 40, 60, 80, 100, 125, 160, 200, 240, 280, 320, 480, 640 and 960 nM ^{74}Se-selenite. The vials were sealed with gas-tight PTFE/-silicone septa and stainless-steel screw caps. The headspace was sufficient to ensure aerobic conditions (see Supplementary Information). Cultures were incubated at 28 °C, 180 rpm for 17 h in a rotary shaker.

c Analysis of Se speciation

Volatile methylated Se species were determined by SPME-GC-MS as previously described (Liu et al., 2021) (details in supplementary information). Measurements were conducted in triplicate by sacrificing 3 SPME vials per sampling point. Incubations were stopped by freezing samples at −20 °C. All samples were thawed and analysed for volatile sulfur and selenium compounds with SPME-GC-MS. Mass acquisitions were performed in selected ion mode and quantifying ions were monitored: *m/z* 62 (DMS), 110 (DMSe), 94 (DMDS), 142 (DMSeS), 190 (DMDSe), 126 (DMTS). 104 (DM^{74}Se), 136 (DM^{74}SeS), 178 (DMD^{74}Se). Volatile Se was found in traces in non-spiked control cultures with maximum 3.9 nM (data not shown), possibly through residual medium from pre-cultures and/or degrading biomass containing Se traces. No ^{74}Se was recorded in non-amended cultures. After SPME-GC-MS measurements, *P. tolaasii* cells were harvested by centrifugation (20, 000×*g*, 5 min). Supernatants were filtrated with 0.45 μm PVDF syringe filters (Thermo scientific, United states) and diluted with ultrapure H_2O for aqueous Se species measurement with IC-QqQ- ICP-MS as previously described (Liu et al., 2021). One non-volatile, methylated Se metabolite, 2-hydroxy-3-(methylselanyl)propanoic acid (2H3MSePA), was shown to form on expense of previously volatilized DMSeS and DMDSe (Liu et al., 2021). Therefore, "volatile Se" (DMSe, DMDSe and DMSeS) was distinguished from "methylated Se" (volatile Se plus 2H3MSePA). DMS, DMDS and DMSeS are referred to as "methylated S" from here on.

3. Results

P. tolaasii cultivated in minimum medium produced several volatile and methylated species from ^{74}Se-selenite spiked at trace concentrations in the nM range. Se species formed were found in the concentration order DMSeS > DMDSe > 2H3MSePA > DMSe (Fig. 1). Maximal concentrations of 413 ± 35 nM DMSeS, 287 ± 35 nM DMDSe, 134 ± 15 nM 2H3MSePA and 9 ± 4 nM DMSe corresponded to 43 ± 4%, 60 ± 7% (2 Se atoms), 14 ± 2% and 1 ± 0% of the 960 nM Se spike. Selenite was completely depleted from the medium (data not shown).

All Se species showed a linear increase in measured concentration at low concentrations of spiked Se (up to 80 nM) (inserts in Fig. 1A–D). At spiked concentrations higher than 640 nM, a strong increase in

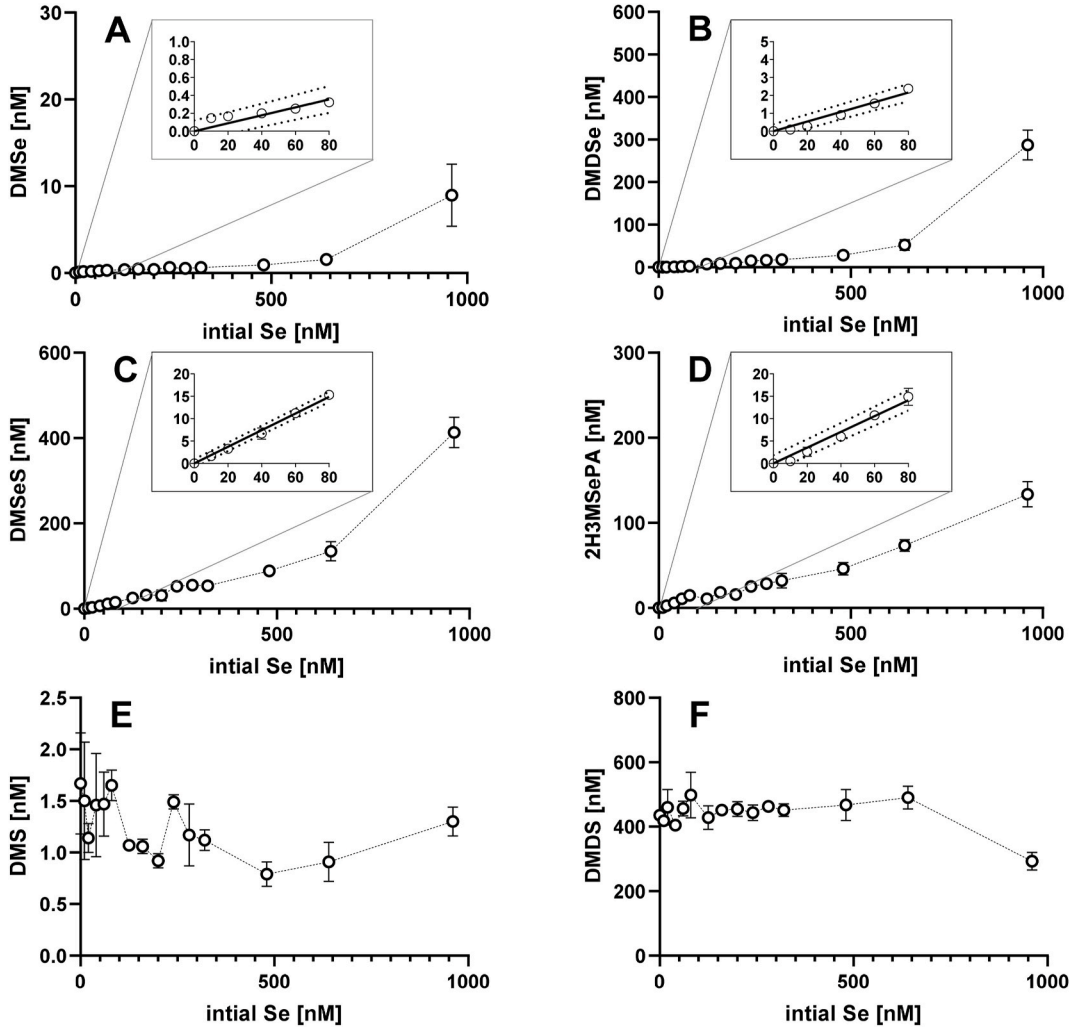

Fig. 1. Transformation of ^{74}SeIV by *Pseudomonas* to individual Se species, ie. DMSe (A), DMDSe (B), DMSeS (C) and 2H3MSePA (D) and formation of DMS (E) and DMDS (F) with linear regressions (with 90% prediction bands; compare Table 1) in inserts. Note that the fit in (B) is based on the concentration of compounds, not the concentration of Se (Table 1).

concentration was observed for all species except for 2H3MSePA, which remained a linear response (Fig. 1A–D). Two species containing only S were quantified, namely DMS and DMDS (Fig. 1E–F), with maximum concentrations of 1.7 nM and 498 nM, respectively. Summing all methylated S species (DMS, DMDS and DMSeS), the extent of transformation was nearly constant over the whole range of tested Se concentrations, accounting to 945 ± 77 nM of S (Fig. 2).

The sum of methylated Se (DMSe, DMDSe, DMSeS and 2H3MSePA), in contrast, increased constantly with increasing Se concentrations from low nanomolar concentrations to max. 315 nmol at 640 nM initial Se. At the highest initial Se concentration, the amount of all methylated Se exceeded that of S (Fig. 2A). The efficiency of methylation and volatilization increased from ~25 ± 4% and ~20 ± 1% at the lowest Se spike to 49 ± 4% and 38 ± 4%, resp., at 640 nM initial Se (Fig. 2B). At an even higher spike of Se, somewhat more Se was found as methylated and volatilized species in comparison to spiked Se (118 ± 5% and 104 ± 5%, resp.) which may be due to degradation of Se-containing biochemicals and proteins (Mason et al., 2018) or simply due to the experimental uncertainty. Inhibition of growth was not indicated even at the highest Se concentration tested (see supplementary information, Figure S2). At low Se concentrations (up to 80 nM), the sum of all methylated and volatilized Se was as well described by a linear regression (Fig. 3, Table 1).

4. Discussion

a. Volatilization of selenite by *Pseudomonas* at trace concentrations

Pseudomonas. tolaasii, an ubiquitous soil bacterium, has been known to produce volatile S and Se compounds (Liu et al., 2021; Lo Cantore et al., 2015). Here, for the first time, this capacity was studied using extremely low, environmentally relevant concentrations in the nanomolar range. For all individual methylated Se species studied, methylation efficiency was linearly depending on the applied Se concentrations up to ~80 nM (Fig. 1, inserts). At the highest concentration tested a considerable increase in volatilization and methylation was observed, so that all Se given at 960 nM was ultimately converted (Fig. 2). At concentrations ≤960 nM, not all Se was found as methylated species (see supplementary information, Table S3), which can be explained either by elemental Se formation and/or formation of intracellular Se compounds (such as selenoaminoacids). If intracellular Se compounds were formed, these may be ultimately converted to volatile species as well upon decay of biomass, which warrants further studies.

The main species formed here was DMSeS, which contrasts with some previous works, where DMSe and DMDSe were the major volatile Se species (supporting information, Table S2). The difference may be explained by the fact that in open systems such as classical aerobic incubation systems using cotton plugs or in environmental water/soil samples, the low boiling point and high vapour pressure of DMSe (bp = 52 °C) in contrast to those of DMSeS (bp = 132 °C) and DMDSe (bp = 156 °C) can explain differences in the prevalent species found. DMSe will preferably be detected in the gas phase (for instance in trapping experiments) enriching the DMDSe/DMSeS ratio left in the aqueous

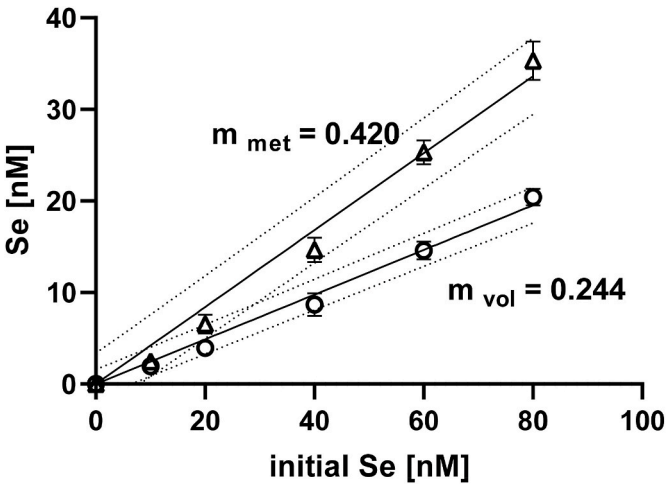

Fig. 3. Linear regressions with 90% prediction bands of methylated Se species (triangles), volatile Se species (circles) in ^{74}SeIV spiked *Pseudomonas* cultures.

Table 1
Linear regressions between 0 and 80 nM ^{74}SeIV. Note all slopes refers to nM Se in species/nM ^{74}SeIV initial.

	Slope	Std. error slope	95% Confidence intervals	Goodness of fit[d]
DMSeS	0.1858	0.003980	0.1774 to 0.1942	0.7583
DMSe	0.0044405	0.0003023	0.003803 to 0.005078	0.05759
DMDSe	0.04697	0.004076	0.03847 to 0.05547	1.049
Methylated Se species[a]	0.4203	0.01519	0.3812 to 0.4593	1.670
Volatile Se species[b]	0.2441	0.007112	0.2258 to 0.2623	0.7824
Se/S[c]	0.0004393	1.016e-005	0.0004132 to 0.0004654	0.001118

[a] DMSe, DMDSe, DMSeS, 2H3MSePA.
[b] DMSe, DMDSe, DMSeS.
[c] Se/S = methylated Se (DMSe, DMDSe, DMSeS, 2H3MSePA)/methylated S (DMS, DMDS, DMSeS).
[d] $Sy.x = \sqrt{\frac{\sum(residual^2)}{n-K}}$; K, number of parameters fit by regression.

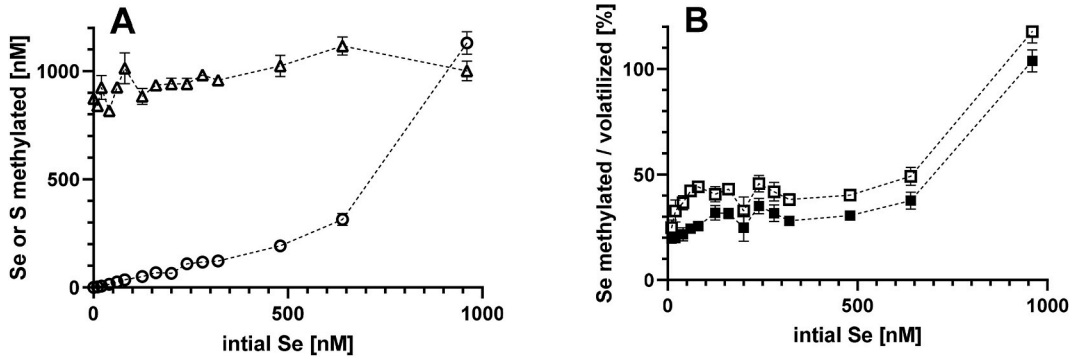

Fig. 2. Formation of methylated Se (circles) and S (triangles) species (A) as well as methylation (empty squares) and volatilization (filled squares) efficiency in regards to initial Se (B).

phase (such as in grab samples). In our experiments, a closed system was used with cultures incubated aerobically in an airtight SPME vial. The main species, DMSeS, is commonly found in cultures of algae, bacteria and plant amended with selenite or selenate (Kubachka et al., 2007; Swearingen et al., 2006a; Vriens et al., 2016). Rather than being specifically produced, DMSeS forms spontaneously in a chalcogen disproportionation reaction from DMDS and DMDSe (Chasteen, 1993). In this study, concentrations of DMDS were tens to hundreds of times higher than DMDSe. Therefore, the equilibrium of the exchange reaction DMDS + DMDSe ↔ DMSeS will be shifted to the right side and DMDSe will be consumed to form DMSeS. The closed system with little headspace (vol: vol 1:3) may have increased the chance of chalcogen disproportionation reactions. Further, 2H3MSePA was observed as the second highest concentrated species (Fig. 1, D), which is formed on the expense of previously formed DMDSe and DMSeS (Liu et al., 2021).

b. Volatilization of Se by promiscuous reaction of the S metabolism

Microbial methylation and volatilization of Se have been widely studied as a detoxification strategy since the volatile Se compounds are easier to diffuse from the cell. Several genes responsible for Se resistance have been identified which encode methyltransferase activities towards Se oxyanions: The tpmT gene isolated from *Pseudomonas syringae pathovar pisi* encodes thiopurine methyltransferase which mediates methylation of inorganic Se and selenocysteine to DMSe and DMDSe (Cournoyer et al., 1998; Ranjard et al., 2002). Expression of the ubiE gene from *Geobacillus stearothermophilus* V in *E. coli* resulted in the production of DMSe and DMDSe from selenite and selenate (Swearingen et al., 2006b). The tehB gene from *E.coli* K-12 was expressed and purified showing methylation of both selenite and tellurite by SAM (S-adenosyl-L-methionine)-dependent mechanisms (Choudhury et al., 2011; Liu et al., 2000). It can be questioned that the experimental time was sufficient to allow for organic Se species to be formed. Still, selenomethionine (SeMet), Se-(methyl)-selenocysteine (MeSeCys) and hydrogen selenide are precursors of methylselenol (MeSeH) which spontaneously oxidizes to DMDSe, through degradation of MeSeCys and SeMet by L-methionine-γ-lyase and direct methylation of hydrogen selenide by thiol methyltransferase (Drotar et al., 1987; Gabel-Jensen et al., 2010; Ranjard et al., 2002). For DMSe, a further methyl transfer for MeSeH is needed. A pathway as in algal (e.g. *Chlorella* sp) or plant species (e.g. *Brassica juncea*) via specific precursors in the form of a dimethylselenonium compound [$(CH_3)_2$Se–R] (such as dimethylselenoniopropionate, DMSeP and Se-(methyl)-selenomethionine, MeSeMet) have not yet been found in bacteria so far (Bottino et al., 1984; de Souza et al., 2000; Kubachka et al., 2007; Larsen et al., 2001). However, in particular at the lowest concentrations tested here (10 nM = 790 ng/L), it is unlikely that specific Se detoxification genes are upregulated, in particular considering Se is an essential element in bacteria and that they may require an investment of energy.

Unfortunately, except for the above-mentioned bacterial enzymes, there is currently little information on enzymes involved in Se detoxification via methylation. Consequently, a threshold concentration at which these are induced is also not known. Comparison with other toxic metalloids like As suggests that the concentration determined here (~640 nM) is comparable with the minimal As(III) concentrations to induce genes: arrA was shown to be induced at 100 nM whereas arsC required a higher concentrations [500x (Tsuchiya et al., 2019) to 1,000x (Saltikov et al., 2005) that of arrA]. Previously, some studies have found that Se is more efficiently volatilized than S (Vriens et al., 2014) according to the ratio of Se/S volatilized compounds versus inorganic (non-volatile) compounds left in the aqueous phase. Following a similar calculation, here S methylation efficiency (i.e., methylated S versus initial S) was around ~945 nM/~0.83 mM = ~0.11%, whereas Se methylation efficiency was above 25% in all treatment groups. Thus, Se was at least 200 times more efficiently methylated than S regardless initial spiked Se here. Nevertheless, as since this study concerned only a single organism and no direct data on induction on specific detoxification enzymes is available, a general statement of Se being more prone to volatilization is perhaps premature.

The question remains of what drives Se methylation (and volatilization) at very low concentrations that are too low to induce specific detoxification pathways (here down to 10 nM). Certainly, one may argue that there may be constitutive enzymes regardless of the presence or absence of the specific substrate. If serving the true role as a biocatalyst, the enzyme can catalyse the specific reaction without being used up. As a consequence, one may expect that at least low nanomolar concentrations of selenite are fully methylated. This was not the case here: whereas at the lowest Se concentration, ~25% of Se was methylated, the share increased somewhat with increasing concentration, but only around 43% were volatilized at 80 nM (Fig. 2B). The same was true when considering only volatile species (Fig. 2B).

Alternatively, it can be hypothesized that Se was transformed promiscuously via S methylating pathways at low initial Se concentrations. Enzymes involved in sulfur metabolism have been claimed to be less discriminate in terms of preventing selenium incorporation than vice versa (Johnstone et al., 2021). Regrettably, there is no information available which enzymes may have a promiscuous activity in *P. tolaasii* (in *Escherichia coli*, some promiscuous enzymes that can misincorporate Se include O-acetylserine sulfhydrylase and cysteinyl-tRNA synthetase) (Johnstone et al., 2021). One can still assume that sporadically Se becomes methylated instead of S. *P. tolaasii* cells appeared to have a certain inherent capacity for S methylation which remained fairly constant (945 ± 77 nM; Fig. 2). If the concentration of Se is increased (without inducing enzymes specific for metabolizing Se), the probability of such promiscuous methylation is increased as well. Under these assumptions, the specificity (or better the promiscuity) of the overall reaction may be derived. At the lowest Se concentration tested, the ratio of Se methylated to S methylated was 0.0030, increasing to 0.0348 at 80 nM. Thus, between every ~29th (or 3.48%) and every ~333rd atom (or 0.30%) would be Se promiscuously methylated via the sulfur pathway. Interestingly, the slopes in linear regression of Se methylation versus initial Se where different for individual compounds, which may point into the direction that different compounds were possibly cycled by different promiscuous S pathways (Table 1). Unfortunately, there is still no information available on the enzymes involved either in promiscuous cycling of Se via S pathways or on the enzymes specific for methylation of Se (as detoxification strategy) in *P. tolaasii*. In the future, studying the differences in gene expression between this strain at very low nanomolar concentrations and higher concentrations (equal to or greater than 640 nM) using RNA-sequencing of the entire transcriptome could help to understand the pathways that are involved.

c. Implications for environmental Se cycling and outlook.

There is a consensus that atmospheric transport represents a major path for Se distribution on earth [e.g. (Winkel et al., 2012)] and that a major proportion of atmospheric Se stems from biological volatilization (Wen and Carignan, 2007). It would be desirable to have precise and accurate models for predicting Se transfer from the geosphere/hydrosphere to the atmosphere. As shown here, there is no linear relationship between dissolved Se concentration and Se volatilized when a certain threshold concentration is exceeded (Fig. 1). Therefore, data from laboratory and field studies that used high spikes of Se (commonly some μM to mM; compare supporting information, Table S1) cannot be used to predict environmental volatilization quantitatively (mostly environmental concentrations are <10 nM, see introduction). Certainly, future studies should proof the hypothesis of promiscuous Se cycling in soils by using cultures with different capacity for S methylation at constant Se spikes (which should then result in different methylation efficiency).

In marine systems, different factors such as S methylated, DOC, phaeopigments, water temperature, chlorophyll and phosphate concentrations [e.g. (Amouroux et al., 2001; Amouroux and Donard, 1997;

Luxem et al., 2017)] have been associated to increased Se volatilization in marine environments. Whereas there is certainly a good logic in using proxies for higher/lower biological activity, here we demonstrate that the Se concentration itself can be a major driver determining volatilization efficiency. Regrettably, to the best of our knowledge, there is no study available that reports selenite, methylated Se and methylated S concentrations at once [only those reporting either selenite or methylated species (Amouroux et al., 2001; Cutter and Cutter, 2001; Olivas et al., 1995)]. It remains to be determined, if promiscuity is driving Se cycling in marine systems and if in consequence the amount of S methylated can be used to predict Se methylated. This is important in the light that the marine environment is a major driver in the atmospheric Se cycle [e.g. (Amouroux et al., 2001)].

CRediT authorship contribution statement

Ying Liu: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Andreas Schäffer:** Writing – review & editing, Supervision. **Mathieu Martinez:** Writing – review & editing, Supervision. **Markus Lenz:** Conceptualization, Formal analysis, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the Swiss National Science Foundation (200021_178784) and the Chinese Scholarship Council (201408320144).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.140548.

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