

Sensitive and high-throughput analysis of volatile organic species of S, Se, Br, and I at trace levels in water and atmospheric samples by thermal desorption coupled to gas chromatography and inductively coupled plasma mass spectrometry

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Abstract

Emissions of volatile organic sulfur (S), selenium (Se), bromine (Br) and iodine (I) species from aquatic ecosystems represent an important source into the atmosphere. Available methods to measure these species are either not sensitive enough or not automated, which hinder a full understanding of species distribution and production mechanisms. Here, we present a sensitive and high-throughput method for the simultaneous and comprehensive quantification of S, Se, Br, and I volatile organic species in atmospheric and aqueous samples using a preconcentration step onto sorbent tubes and subsequent analysis by thermal desorption coupled to gas chromatography inductively coupled plasma mass spectrometry (TD-GC-ICP-MS). Selected commercially available sorbent tubes, consisting of mixed porous polymer and graphitized black carbon, offered the highest trapping capacity and lowest loss of species when stored at -20°C for twenty-eight days after sampling. After optimization of the TD-GC-ICP-MS method, absolute detection limits were below 3.8 pg, 9.1 fg, 313 fg, and 50 fg, respectively for S, Se, Br and I species. As a proof-of-concept, the concentrations of target species were determined in aqueous and continuously collected atmospheric samples during a cruise in the Baltic and North Seas. Moreover, unknown S, Br and I volatile species were detected in both aqueous and atmospheric samples demonstrating the full potential of the method.

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Introduction

Aquatic ecosystems, especially marine ones, are an important natural source of various volatile organic species to the atmosphere, notably those containing sulfur (S), selenium (Se) and halogens such as bromine (Br) and iodine (I). Global marine emissions of S, Se, Br and I are estimated at 17.6 – 34.4 Tg S y^{-1} (as dimethyl sulfide (DMS))¹, 10.0 – 15.4 Gg Se y^{-1} ², 72-385 Gg Br y^{-1} (as bromoform (CHBr_3))³, 280 - 1100 Gg I y^{-1} ⁴. These emissions play a critical role in the global biogeochemical cycling of these elements and have important environmental and health implications.⁵⁻⁸ For example, marine emissions of Br and I volatile species affect the atmospheric oxidizing capacity through ozone depletion^{7,9} whereas the oxidation products of DMS, the main volatile species in the sulfur cycle, contribute to the formation of cloud condensation nuclei and thus influence the Earth's radiative budget.¹⁰

Volatile organic species are produced through biological activity and/or photochemical processes occurring mainly in the upper water column.^{11,12} Volatile species of S and Se result from biotic and abiotic degradation of metabolites^{13,14} whereas those of I and Br arise from reactions between organic matter and reactive forms of I and Br^{15,16} or from phytoplanktonic and macroalgae activities.^{17,18} For S, Br, and I, respectively, the main marine volatile organic species are DMS, CHBr_3 , dibromomethane (CH_2Br_2), and iodomethane (CH_3I).¹⁹ Average concentrations of these species in the surface seawater are in the low picomolar to low nanomolar range and their atmospheric mixing ratios usually in the low part per trillion (pptv) range. Several minor species were also reported for these elements in the low pM range, such as carbon disulfide (CS_2), dibromochloromethane (CHBr_2Cl), bromodichloromethane (CHBrCl_2), iodo-ethane and iodo-propane ($\text{C}_2\text{H}_5\text{I}$ and $\text{C}_3\text{H}_7\text{I}$), chloriodomethane (CH_2ICl), and diiodomethane (CH_2I_2).^{7,20,21} The concentration of volatile Se species in surface (sea)waters are several orders of magnitude lower than the other elements, from the low fM to pM range, and have thus been scarcely analyzed.^{22,23,24} From these few measurements carried out in estuarine or seawaters, DMSe was the main species detected followed by dimethyl selenenyl sulphide (DMSeS) and dimethyl diselenide (DMDSe).

The species present in highest concentrations, i.e., DMS, CHBr_3 , CH_2Br_2 , and CH_3I , are usually measured shipboard using purge and trap systems coupled to gas chromatography (GC) and specific detectors such as mass spectrometry (MS), flame ionization detection (FID), or flame photometric detector (FDP).²⁵ The advantage of using such online analytical methods is that they reduce the risk of potential losses and contaminations that might occur during sample storage and transport. However, these techniques present too high detection limits for the less concentrated volatile species. For these latter, a prior preconcentration step is required, which is usually achieved by cryogenic²⁶ or sorbent trapping.²⁷ Atmospheric samples can also be collected in canisters but the number of samples is often limited due to the space requirement for their storage. For the analysis of volatile Se species in the environment, only cryogenic trapping followed by GC-ICP-MS analyses has been implemented to

date.²⁴ Although this method is sensitive, it remains non-automated and thus time consuming and the necessity to bring liquid nitrogen in the field severely limits the number of samples that can be collected and analyzed.²² Recently, promising results have been obtained for the preconcentration of volatile Se species onto multi-bed sorbent tubes and analysis by thermal desorption (TD) coupled to GC-MS²⁸ as well as for the long-term storage of CHBr₃ and CH₂Br₂ onto sorbent tubes²⁹ or the quantification of DMS in coral incubations using a mix of porous material (Tenax® TA) and molecular sieves (Sulficarb).³⁰ However, the trapping of volatile organic species onto sorbents and their analysis has not been systematically investigated so far for simultaneous volatile organic species present at environmentally relevant concentrations.

In this work, we present a new high-throughput, very sensitive and multi-elemental method for the analysis of volatile species of S, Se, Br and I in atmospheric and aqueous samples using sorbent trapping and analyses by an automated thermal desorption unit coupled to GC-ICP-MS (TD-GC-ICP-MS). We first fine-tuned the various desorption steps of the TD unit, GC program and operating conditions of the ICP-MS instrument to ensure optimal desorption, separation and detection of volatile species while keeping the analysis time within 15 minutes per sample. Then, we investigated several commercially available sorbent tubes for their retention and storage capacity as well as optimized sampling and preconcentration for both dissolved gaseous species in aqueous samples using a purge and trap system and atmospheric samples using a commercially available automated autosampler. Our new method allows for the simultaneous quantification of targeted species over a wide range of environmentally relevant concentrations, i.e., from the fM to nM range, as well as the detection of unknown volatile species with absolute detection limits (ADLs) ranging from the femtogram to picogram level depending on the element. Finally, we measured atmospheric and aqueous samples collected from the Baltic and North Seas, covering various environmental conditions, to demonstrate the potential of this method.

Material and Methods

Gas and chemicals

A mixture of He/¹²⁴Xe (100 ppm) was purchased from Linde (Switzerland) while argon, helium, hydrogen and nitrogen were purchased from PanGas AG (Switzerland). The volatile organic standards were purchased from Sigma Aldrich (Switzerland) and VWR (Switzerland). Indications on both gas and standards' purity are given in Table S1. As no DMSeS standard is commercially available, it was quantified using the average of the calibration slopes of DMDS_e and DMSe. Individual stock solutions (3000 mg.L⁻¹) were prepared in amber glass vials by diluting the pure standards in methanol (MeOH, ≥ 99.9 %, VWR) using gas-tight syringes (1700 Series, Hamilton Company). These stock solutions were sealed with PTFE-septum caps (BGB Analytik AG, Switzerland), covered with aluminum foil, and stored at -20°C. As losses of volatile species are difficult to prevent and control, these solutions were regularly

replaced, every 2 months at the latest. Fresh individual or mixed diluted solutions were prepared daily in MeOH from the stock solutions. Then, 1 μL of these fresh solutions was loaded onto sorbent tubes via an injection loop (CSLR, Markes International Limited; United Kingdom) within a N_2 flow of $50 \text{ mL}\cdot\text{min}^{-1}$ for three seconds to allow the transfer of the analytes from the MeOH solution to the gas phase and their sorption onto the sorbent materials while avoiding breakthrough.

Description, optimization and calibration of the analytical set up

The analytical setup consists of a thermal desorption unit (TD 100-xr, Markes International Limited) coupled to a gas chromatography system (model 7890B, Agilent Technologies) fitted with an HP-5 column, hyphenated with an inductively coupled plasma mass spectrometer (model 7900, Agilent Technologies). Table S2 presents the operating parameters of the analytical setup after the optimization presented in the second section of the results and discussion part. The stability of the ICP-MS during analyses was continuously monitored with ^{124}Xe and was found to be within 5 % over an analysis period of 20 hours. Further details on the TD unit operation and optimization are given in SI Section A.

Six type of commercially available multiple beds sorbent tubes (Universal (UN), Odour/Sulfur (SF), Biomonitoring (BM), Material Emissions (ME), Air Toxic (AT) and Graphitized Carbon (GR), all packed in inert stainless-steel tubes), were purchased from Markes International Limited. Their compositions in terms of sorbent material, target range, affinity to water, part number and properties are summarized in Tables S3 and S4, respectively. The (re)conditioning programs of the various sorbent tubes are given in Table S5. Calibration curves were obtained by analyzing five sorbent tubes, all loaded with 1 μL of a working solution prepared as described above. Each sorbent tube was analyzed with a different split ratio applied to the focusing trap (varying from 3.8:1 to 75:1) to control the amount of volatile species entering the GC column (Figure S1). Further details on the calibration procedure and the determination of detection limits are given in SI Section B.

Water and atmospheric sampling equipment

The sampling and analytical methods were assessed under environmental conditions using atmospheric ($n=31$) and aqueous samples (between 5-300 m depth, $n=71$), collected during a seven days cruise on the R/V Svea organized by the Swedish Meteorological and Hydrological Institute (SMHI) in the North and Baltic Sea in September 2020. A detailed description of sampling conditions and corrections applied to the data is available in SI sections C and D along with a sampling map (Figure S3). Briefly, an in-house purge and trap system (PT, Fig. SI2, A-B) with four parallel purging lines was assembled for the sampling of dissolved volatile species. An automated active sampling device (MTS - 32, Markes International Limited, Figure S2, C-D), including a sampling pump with variable flow

rate (ACTI-VOC, Markes International Limited) was used to sample atmospheric volatile species directly onto BM sorbent tubes with a 4 hours resolution (5 L of air at a flow rate of 21 mL.min⁻¹).

Results and discussion

1. Selection of the sorbent tubes

Trapping capacity

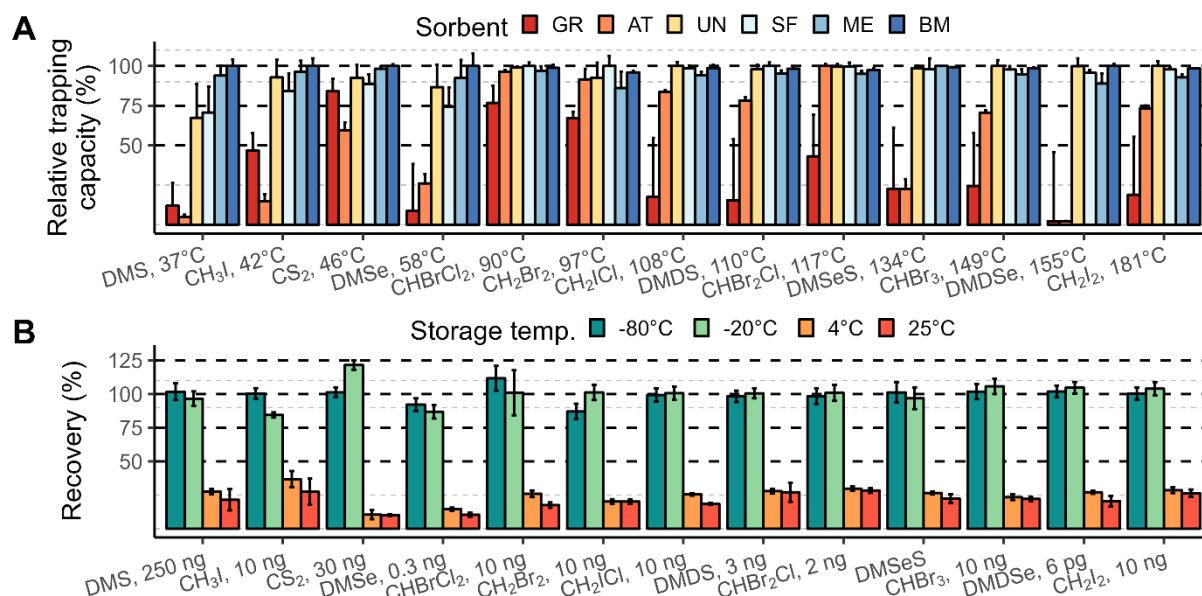


Figure 1. (A) Relative trapping capacity of sorbent tubes (graphitized carbon (GR), air toxics (AT), material emissions (ME), sulfur (SF), universal (UN) and biomonitoring (BM)) for each species. All species (each 0.05 ng) were directly loaded together onto the six different sorbent tubes and normalized to the highest intensity found for each species. (B) Recoveries of S, Se, Br and I species, trapped on BM sorbent tubes and stored for twenty-eight days at - 80°C, - 20°C, 4°C and 25°C. The amount loaded on the tubes is indicated after each species on the x-axis and is representative of seawater concentration.

The trapping capacity of the six sorbent tubes was first determined at low amount (0.05 ng; Figure 1, Table S6). GR and AT were the least performing sorbent tubes with average trapping capacities of 34 ± 26 % and 56 ± 35 %, respectively. UN (94 ± 9 %) and SF (93 ± 10 %) overall performed better but were not adequate for low boiling point species, particularly DMS and DMSe. ME and BM overall presented the best trapping capacities with average recoveries of 94 ± 4 % and 99 ± 1 %, respectively. However, BM showed better trapping capacities for the volatile species with a low boiling point, notably for DMS (100 ± 4 %), DMSe (100 ± 8 %), CS₂ (100 ± 1 %), and CH₃I (100 ± 5 %).

In a second step, the trapping capacity was evaluated for 100 times higher amounts, i.e., 5 ng of volatile species. A comparison with 0.05 ng is presented in Table S6. No clear pattern in the trapping capacity of the sorbent tubes was observed between these two amounts. The trapping capacities of UN, SF, ME, and BM sorbent tubes were not significantly affected by these higher amounts, demonstrating the absence of a saturation effect. However, compared to the lower concentration level (0.05 ng), the

average trapping recovery increased from $34 \pm 26 \%$ to $44 \pm 26 \%$ for GR and from $56 \pm 35 \%$ to $64 \pm 36 \%$ for AT, indicating that some irreversible adsorption or degradation occurred with lower amounts of volatile species. Considering this problem and their overall low trapping capacity, GR and AT sorbent tubes were not further considered. Unlike the other sorbent tubes tested here, AT and GR do not contain the porous polymer Tenax® TA (Table S) suggesting its importance for trapping the targeted species. ME and BM sorbent tubes, combining graphitized carbon material with Tenax® TA, presented the best trapping capacity for the tested volatile species.

Stability of species during storage

Species recoveries after storage at -80°C , -20°C , 4°C and 25°C for 28 days are presented in Figure 1 for BM and Figure S4 for ME and SF sorbent tubes. In addition, Figure S5 and SI-6 show species recoveries at 14, 21 and 28 days for ME and BM sorbent tubes stored at 4°C and 25°C . Based on preliminary results showing a large broadening of the CS_2 peak that impacted the quantification of DMS (not shown), UN sorbent tubes were discarded. The recoveries after storage at -20°C for 28 days were generally good with average values of $96 \pm 20 \%$, $102 \pm 7 \%$, and $100 \pm 9 \%$, respectively for SF, ME, and BM tubes. The lowest recoveries at -20°C for all the sorbent tubes were found for the species with low boiling points, e.g., CH_3I ($82 \pm 21 \%$), DMS ($80 \pm 22 \%$), and DMSe ($87 \pm 2 \%$). Similar results were obtained for storage at -80°C for species with high boiling points, however, DMS ($91 \pm 11 \%$), DMSe ($94 \pm 2 \%$), and CH_3I ($98 \pm 5 \%$) showed better recoveries at -80°C indicating eventually losses occurring at higher storage temperatures.

Species recoveries after 14 days for storage at 4°C and 25°C were on average $87 \pm 26 \%$ and $84 \pm 24 \%$, and $81 \pm 26 \%$ and $80 \pm 23 \%$, respectively for BM and ME sorbent tubes but they were much lower after 28 days, between 10 and 37 % depending on the species for both storage temperatures. These low recoveries demonstrate the inability of ME and BM sorbent tubes to retain the selected volatile species for a longer period at storage temperatures of 4°C and 25°C . However, SF sorbent tubes showed high recoveries after 28 days for CHBr_2Cl ($91 \pm 5 \%$), CHBr_3 ($91 \pm 4 \%$), CH_2I_2 ($89 \pm 4 \%$) at 25°C . Overall, it can be concluded that ME, BM and SF sorbent tubes have better trapping capacities at low storage temperatures with -20°C being sufficient for storage over one-month. Based on the trapping and storage results as well as their hydrophobic character, BM sorbent tubes were selected for our application. SF could be an interesting alternative for the volatile compounds mentioned above when low storage temperature at -20°C is not available.

2. Optimization of instrumental parameters

Species desorption from sorbent tubes

The efficiency of species desorption from the BM sorbent tubes was evaluated for different times (1 to 4 min), temperatures (150 to 225 °C) and gas flow rates (25 to 100 mL.min⁻¹); the results are presented in Figure S7. Regarding the tube desorption time (Figure S7, A), one minute was not long enough as many species, i.e., DMDS, DMDSe, CHBrCl₂, CHBr₂Cl, CHBr₃, CH₃I, CH₂ICl and CH₂I₂ accounted for 3.3 ± 0.3 % to 29 ± 1 % of the total amount detected after the second tube desorption. No significant difference was observed for tube desorption times of 2 and 4 minutes. For desorption temperature, less than 5 % of the initial amount loaded was detected after the second desorption regardless of the temperature applied (Figure S7, B). Therefore 200 °C was chosen to prevent excessive TD maintenance resulting from too high desorption temperature.

Different N₂ flow rates applied during tube desorption (Figure S5, C) did not result in significantly different recoveries of the volatile species. Only CH₃I showed lower recoveries with increasing N₂ flow rates. The loss of CH₃I can be explained by a breakthrough effect on the focusing trap as CH₃I is not well retained by the SF sorbent tube as demonstrated above. To prevent potential breakthrough that might occur once the volatile species are transferred to the focusing trap, we suggest using a low N₂ flow rate. Based on these results, we finally selected a tube desorption time of two minutes at 200°C and a N₂ flow rate of 25 mL.min⁻¹ (Table 1) as these conditions gave optimal desorption results for most species, while preventing damage to the TD unit.

Species desorption from the focusing trap

Preliminary tests showed that (i) the highest heating rate of the focusing trap ($\geq 24^{\circ}\text{C}.\text{min}^{-1}$) was required to avoid peak tailing and (ii) the residual peak areas of each species found after a second desorption of the focusing trap were maximum 0.6% of the first peak areas regardless the desorption time (2, 3 and 4 min tested, data not shown). To remove water vapor that would potentially come from the sorption tubes and thus preserve the GC column, we also tested the effect of the initial temperature of the focusing trap within the range -30°C to -5°C. The recoveries of the volatile species were found better when the initial temperature of the focusing trap was higher (Figure S7, D), suggesting that lower temperatures hinder the adsorption of species to the sorbents present in the cold trap. The most important variations were observed when the initial temperature of the focusing trap was set at -30°C vs. -20°C for DMS (85 ± 1 vs. 92 ± 8 %), CS₂ (71 ± 15 vs. 77 ± 7 %), CHBrCl₂ (93 ± 4 vs. 90 ± 1 %), CH₃I (96 ± 1 vs. 76 ± 16 %). At -30 °C, the average recovery for the tested volatile species was 86 ± 15 % whereas better recoveries were observed at -10°C and -5°C with 97 ± 10 % and 98 ± 10 %, respectively. Therefore, -5 °C was selected as initial temperature for the focusing trap followed

by a 3 min desorption at a heating rate of $\geq 24^{\circ}\text{C}\cdot\text{min}^{-1}$ (Table 1) as the best combination to maximize recoveries while minimizing the overall running time of the method.

3. Optimization of sampling parameters

Breakthrough volumes for atmospheric samples

For most of the species, the breakthrough remained negligible for all N_2 volumes tested and volumes sampled in urban area ($< 2.9\%$ for 5, 10 and 15 L, data not shown). However, significant breakthrough was observed for CH_3I , DMS and CS_2 (Figure S8). The breakthrough for CH_3I varied from $57 \pm 18\%$, to $2 \pm 1\%$ and from $33 \pm 16\%$ to $21 \pm 21\%$ for 5, 10 and 15 L, in the laboratory and in the urban area, respectively. The decrease in breakthrough with increase sampling volume demonstrates the low retention capacity of BM sorbent for CH_3I as soon as a higher sampling volume is applied compared to the sorbent selection test (Section 1) where the volatile species were directly injected to the sorbent tube with a little volume of N_2 ($< 10\text{ mL}$). A third BM sorbent tubes connected in series at 15 L confirmed the presence of CH_3I in the third tube (data not shown). The breakthrough increased from $2 \pm 3\%$ to $91 \pm 2\%$ and from $4 \pm 2\%$ to $31 \pm 17\%$ when the N_2 volume increased from 5 to 15 L, respectively, for DMS and CS_2 . In urban area, the breakthrough varied from $9 \pm 9\%$ to $36 \pm 24\%$ and from $9 \pm 11\%$ to $37 \pm 14\%$, with sampling volumes from 5 to 15 L, for DMS and CS_2 respectively. Similar results were obtained when sorbent tubes were flushed with urban air of varying humidity suggesting that matrix effects are limited. However, these conditions certainly do not represent all possible sampling conditions and future users would have to determine breakthroughs for their specific applications. To both maximize the pre-concentration of species while minimizing DMS, CH_3I and CS_2 losses from BM sorbent tubes, 5 L was selected as the best compromise for a safe sampling of most of the target volatile species.

Estimation of the PT parameters for aqueous samples

Recoveries and breakthrough of the PT system for the various volatile species trapped onto BM sorbent tubes are presented in Figure S9 as a function of the volume of N_2 (flow rate of $400\text{ mL}\cdot\text{min}^{-1}$). It is important to note that the same results were obtained regardless the N_2 flow rate applied (250 , 400 or $500\text{ mL}\cdot\text{min}^{-1}$, Figure S10) for the same N_2 volume demonstrating that the flow rate does not influence the PT recovery and breakthrough. Moreover, the recovery was also similar when artificial seawater (Milli-Q containing NaCl) or only Milli-Q were used (Figure S11). For species with boiling point (BP) $> 100^{\circ}\text{C}$, *i.e.*, CH_2I_2 , DMDS, CHBr_2Cl , DMSeS , CHBr_3 , DMDS , and CH_2I_2 , recoveries increased with increasing N_2 volume and reached between $57 \pm 3\%$ (CH_2I_2) and $100 \pm 6\%$ (CHBr_3) at 25 L of N_2 while the breakthrough remained negligible ($< 3.1\%$). For DMS and CS_2 the recovery of the PT system was however maximal at 10 L N_2 with $61 \pm 2\%$ and $35 \pm 2\%$, respectively while the breakthrough was limited to $11 \pm 0.4\%$ and $14 \pm 1\%$, respectively. DMSe recovery also reached its maximum ($28 \pm 2\%$)

at 10 L while the breakthrough was still very low (0.8 ± 0.1 %) pointing to a degradation of DMSe, likely by oxidation. Despite a rather low DMSe recovery in general, the low SD values indicated high reproducibility of DMSe trapping. A maximum recovery of 14 ± 2 % was observed for CH_3I at 2 L of N_2 . High breakthroughs were observed for CH_3I whatever the N_2 volume (up to 68 ± 7 % was found in the second tube). It was even detected in a third tube (data not shown) demonstrating again the inability of the BM sorbent tubes to trap this species. When considering all these results, 10 L of N_2 was selected as the best compromise between the recovery for most species and the breakthrough observed for DMS and CS_2 .

4. Analytical performances and proof-of-concept with environmental samples

Detection limits

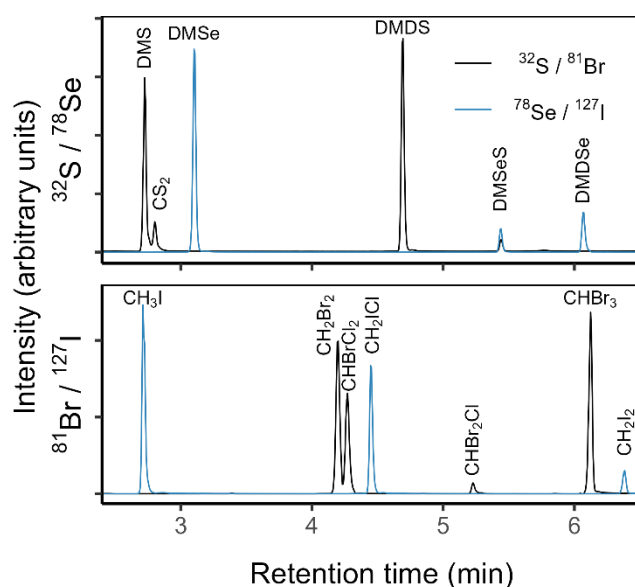


Figure 2. Typical chromatograms obtained with the optimized TD-GC-ICP-MS method and S, Se, Br and I standards loaded onto BM sorbent tubes. The amounts loaded are DMS: 150 ng; CS_2 : 50 ng; DMDS, CHBrCl_2 and CHBr_2Cl : 0.5 ng; DMSe: 10 pg; DMDSe: 1 pg; CH_3I , CH_2I_2 and CH_2ICl : 1 ng; CHBr_3 : 20 ng.

Typical chromatograms for our target species after the full optimization of the TD-GC-ICP-MS are shown in Figure 2. Absolute and methodological detection limits (ADLs and MDLs, respectively) are given in Table 2 and compared to other techniques offering the lowest MDLs described in the literature, regardless of the published year (Figure 3). All species were fully resolved particularly due to the controlled temperature applied during the two successive desorptions of the volatile species from the sorbent tubes in the TD unit. Very good linearity was observed for all species over environmentally relevant concentration ranges with correlation coefficients better than 0.98. The volatile S species showed the highest MDLs ranging from 23 to 122 fM in aqueous samples and 0.06 – 0.3 pptv in atmospheric samples due to a higher S background in the analytical system coupled with poor ionization by the ICP. Nevertheless, these high highest MDLs do not prevent their detection at

environmental concentrations ranging in the low nanomolar range. The lowest ADLs were found for Se species (8.3-9.1 fg) equivalent to MDLs of 88 - 167 amol.L⁻¹ and 0.2 - 0.4 ppqv in aqueous and atmospheric samples, respectively, due to a very low Se instrument background as a result of the efficient removal of interferences by H₂ gas and a good ionization by the ICP. It should be noted that potential interferences between CHBr₃ on DMD⁸⁰Se, and generally from Br compounds on Se ones, can be easily overcome by using ⁷⁸Se. MDLs for Br and I volatile species in aqueous samples were in the low fmol.L⁻¹ range (0.3 - 3.6 fmol.L⁻¹) while they ranged from 0.7 to 8.8 ppqv in atmospheric samples. Both for atmospheric or aqueous samples, our newly developed analytical method achieves detection limits at least one order of magnitude lower compared to the best methods available that are tailored for only a few species. Moreover, it should be noted that the sampling, transport, and analyses based on sorbent tubes offer certain advantages over canister sampling due to their easy deployment and implementation, low space requirement, straightforward reconditioning and reuse of sorption tubes (> 100 reconditioning steps).

Table 1. Absolute (ADLs) and methodological detection limits (MDLs) for each species in either aqueous or atmospheric samples using the optimized method and BM sorbent tubes.

Species	ADLs (fg)	MDLs aqueous ^a (fmol.L ⁻¹)	MDLs atmospheric ^b (ppqv)	R ² ^c
DMS	4 10 ³	122	299	1.00
CS ₂	2 10 ³	51	124	0.999
DMDS	1 10 ³	23	57	0.999
CH ₂ Br ₂	313	4	9	0.998
CHBrCl ₂	269	3	8	0.999
CHBr ₃	183	1	4	0.998
CHBr ₂ Cl	162	2	4	0.983
CH ₂ ICl	50	566 10 ⁻³	1	0.997
CH ₂ I ₂	39	293 10 ⁻³	715 10 ⁻³	0.998
CH ₃ I	22	316 10 ⁻³	772 10 ⁻³	0.994
DMSe	9	167 10 ⁻³	407 10 ⁻³	0.998
DMS ₂ Se	9	123 10 ⁻³	301 10 ⁻³	
DMDSe	8	88 10 ⁻³	216 10 ⁻³	0.996

^a MDL aqueous calculated for a purging volume of 0.5 L of water

^b MDL atmospheric calculated for 5 L of air pumped through the sorbent tube

^c linear correlation coefficient of calibration curves

Analyses of water and atmospheric samples from the Baltic and North Seas

We applied the developed method to quantify volatile species of S, Se, Br and I in both atmospheric and aqueous samples collected in the North and Baltic Seas. Typical chromatograms for both aqueous and atmospheric samples are presented in Figure S12 (overlaid with standards) and the distribution of the measured concentrations is shown in Figure 3. The targeted S, Se, Br and I species were always detected and quantified in aqueous samples from all depths. Although the amount of CH₃I trapped on the sorbent tubes was always quantifiable, large uncertainties on CH₃I concentrations remained

because of low PT recovery (2.1 ± 1.5 %). For future work aiming at CH_3I quantification, fine-tuning would be required to address this problem. Only in few atmospheric samples, DMDSe concentrations were below DLs. The average concentrations of dissolved species found in the Baltic and North Seas were 1.8 ± 2.9 nM DMS, 7.4 ± 21 pM CHBr_3 , 3.4 ± 6.4 pM CH_2Br_2 , and 0.94 ± 0.81 pM DMSe. These concentrations are in good agreement, though on the lower side (likely due to the low productivity of the waters at the time of the cruise), with values previously reported in the literature for the main volatile species in aqueous samples: from 1 to 7 nM DMS, 6 to 42 pM CHBr_3 , 1 to 9 pM CH_2Br_2 , and 0.14 to 4.71 pM DMSe.^{1,23,37} The average of the mixing ratio in atmospheric samples were 14.5 ± 13.9 DMS pptv, 5.3 ± 4.6 CHBr_3 pptv, 0.35 ± 0.13 CH_2Br_2 pptv, 0.20 ± 0.09 DMSe pptv which are within the range described in the literature: 3.0 - 261 pptv levels for DMS, 1 - 10 CHBr_3 pptv, 0.5 – 13.2 CH_2Br_2 pptv.^{31,37,38} It is worth noting that some of the concentrations measured with our method were below or close to the DLs of other techniques, *i.e.*, for DMSe, DMDSe and CH_2I in atmospheric samples as well as DMDSe, CHBrCl_2 , CHBr_2Cl , CHBr_3 and CH_2I in aqueous samples (Figure 3).

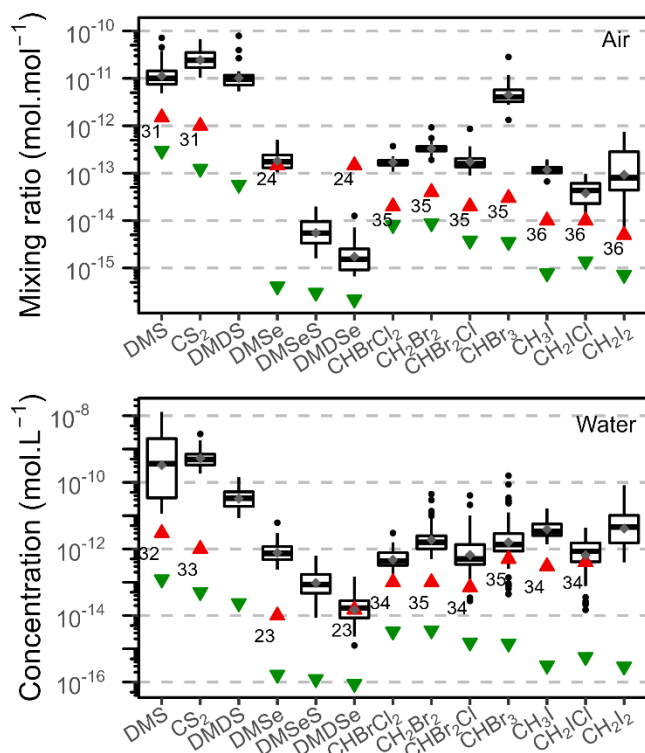


Figure 3. Distribution of mixing ratios and concentrations of volatile species in atmospheric (upper panel, $n = 32$) and water samples (lower panel, $n = 71$) collected during a cruise in the North and Baltic Seas in September 2020. Green triangles indicate our methodological detection limits whereas red triangles the ones of the best previously available methods: offline preconcentration GC-MS³¹; PT-GC-FDP³²; on-board PT-GC-MS³³; PT offline GC-ICP-MS²³; PT offline GC-AFS²⁴; on-board PT-GC-ECD³⁴; offline preconcentration GC-MS³⁵; on-board PT-GC-ECD³⁵; online preconcentration GC-MS³⁶.

Another advantage of using ICP-MS compared to other commonly used detectors lies in the opportunity to detect unknown species. We defined unknown species when no standard matched the peaks detected on the chromatograms. The major and minor unknown species detected in both

atmospheric and water samples are summarized in Table S7. These unknown species can be identified through matching retention times with standards, if available or through their BPs. These latter can be estimated from the relationship between BPs and retention times from known standards given in Figure S13. For Se, no other species than the target ones were detected in water or atmospheric samples. For S, the peak seen at 2.3 minutes was likely methanethiol (MeSH) as confirmed with a standard. Although MeSH has been difficult to measure due to its reactivity, it has been detected in marine bacteria³⁹ and in seawater.⁴⁰ A peak containing both Br and I was detected at 5.4 minutes corresponding to a theoretical BP (th. BP) of 131 ± 1 °C that would match to CH₂BrI (BP 139°C), which was previously reported as a minor species⁷. Regarding I, various peaks that did not match the standards were detected in atmospheric and especially in aqueous samples. The peaks at 3.4 min and 4.4 min were later confirmed with standards to be C₂H₅I and C₃H₇I, respectively, two species that have been previously detected in seawater.^{19,41} The large peak observed at 6.5 min (th. BP 172 ± 1 °C) could not be attributed to any species and further work is thus needed to identify remaining unknowns as well as their importance in other marine waters. However, these proof-of-concept analyses clearly showed the potential of the method for the simultaneous quantification of targeted volatile species and screening of unknown ones.

Conclusion

A novel and highly sensitive method for the determination of 13 targeted S, Se, Br and I volatile organic species in atmospheric and aqueous samples was successfully developed. Volatile species from aqueous samples were first collected on commercially available sorbent tubes using a custom-made purge and trap system. Volatile species in air were collected using a commercially available autosampler that can be easily deployed in the field. The pre-concentrated/trapped species were separated and quantified within 15 minutes using a high-throughput, automated thermal desorption unit coupled to GC-ICP-MS. Our method presents the lowest MDLs to date in the literature for all target species in both compartments. Volatile species are stable on sorbent tubes stored at -20°C for at least 28 days allowing extended field campaigns. The potential for environmental sample analysis, including the detection of unknown species, was demonstrated by analyzing samples collected from the North and Baltic Seas. This new multi-elemental method represents a great opportunity for a better characterization of the environmental distribution of trace S, Se, Br and I volatile organic species and their cycling in aquatic ecosystems and in the atmosphere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional information on standards, sorbent tube properties and their trapping capacities, optimization of the TD unit, preparation of calibration curves and determination of detection limits. Description of the sampling procedure and optimization for the water and atmospheric samples. Breakthrough for PT system and atmospheric samples. Map of the sampling stations. Recovery of the volatile species upon storage at various temperatures and for various sorbent tubes. Typical chromatograms for water and atmospheric samples and list of unidentified volatile species in the latter. Measured retention time as a function of boiling point of standards.

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Notes

The authors declare no competing financial interest.

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References

(1) Lana, A.; Bell, T. G.; Simó, R.; Vallina, S. M.; Ballabrera-Poy, J.; Kettle, A. J.; Dachs, J.; Bopp, L.; Saltzman, E. S.; Stefels, J.; Johnson, J. E.; Liss, P. S. An Updated Climatology of Surface Dimethylsulfide Concentrations and Emission Fluxes in the Global Ocean. *Global Biogeochem Cy* **2011**, 25 (1). <https://doi.org/10.1029/2010GB003850>.

- (2) Feinberg, A.; Stenke, A.; Peter, T.; Winkel, L. H. E. Constraining Atmospheric Selenium Emissions Using Observations, Global Modeling, and Bayesian Inference. *Environ. Sci. Technol.* **2020**, *54* (12), 7146–7155. <https://doi.org/10.1021/acs.est.0c01408>.
- (3) Wang, S.; Kinnison, D.; Montzka, S. A.; Apel, E. C.; Hornbrook, R. S.; Hills, A. J.; Blake, D. R.; Barletta, B.; Meinardi, S.; Sweeney, C.; Moore, F.; Long, M.; Saiz-Lopez, A.; Fernandez, R. P.; Tilmes, S.; Emmons, L. K.; Lamarque, J.-F. Ocean Biogeochemistry Control on the Marine Emissions of Brominated Very Short-Lived Ozone-Depleting Substances: A Machine-Learning Approach. *J. Geophys. Res.-Atmos.* **2019**, *124* (22), 12319–12339. <https://doi.org/10.1029/2019JD031288>.
- (4) Jones, C. E.; Hornsby, K. E.; Sommariva, R.; Dunk, R. M.; von Glasow, R.; McFiggans, G.; Carpenter, L. J. Quantifying the Contribution of Marine Organic Gases to Atmospheric Iodine. *Geophys. Res. Lett.* **2010**, *37* (18). <https://doi.org/10.1029/2010GL043990>.
- (5) Bates, T. S.; Charlson, R. J.; Gammon, R. H. Evidence for the Climatic Role of Marine Biogenic Sulphur. *Nature* **1987**, *329* (6137), 319–321. <https://doi.org/10.1038/329319a0>.
- (6) Winkel, L. H. E.; Johnson, C. A.; Lenz, M.; Grundl, T.; Leupin, O. X.; Amini, M.; Charlet, L. Environmental Selenium Research: From Microscopic Processes to Global Understanding. *Environ. Sci. Technol.* **2012**, *46* (2), 571–579. <https://doi.org/10.1021/es203434d>.
- (7) Saiz-Lopez, A.; Lamarque, J.-F.; Kinnison, D. E.; Tilmes, S.; Ordóñez, C.; Orlando, J. J.; Conley, A. J.; Plane, J. M. C.; Mahajan, A. S.; Sousa Santos, G.; Atlas, E. L.; Blake, D. R.; Sander, S. P.; Schauffler, S.; Thompson, A. M.; Brasseur, G. Estimating the Climate Significance of Halogen-Driven Ozone Loss in the Tropical Marine Troposphere. *Atmos. Chem. Phys.* **2012**, *12* (9), 3939–3949. <https://doi.org/10.5194/acp-12-3939-2012>.
- (8) Fuge, R.; Johnson, C. C. Iodine and Human Health, the Role of Environmental Geochemistry and Diet, a Review. *Appl. Geochem.* **2015**, *63*, 282–302. <https://doi.org/10.1016/j.apgeochem.2015.09.013>.
- (9) Hossaini, R.; Chipperfield, M. P.; Montzka, S. A.; Rap, A.; Dhomse, S.; Feng, W. Efficiency of Short-Lived Halogens at Influencing Climate through Depletion of Stratospheric Ozone. *Nat. Geosci.* **2015**, *8* (3), 186–190. <https://doi.org/10.1038/ngeo2363>.
- (10) Ayers, G. P.; Gillett, R. W. DMS and Its Oxidation Products in the Remote Marine Atmosphere: Implications for Climate and Atmospheric Chemistry. *J. Sea Res.* **2000**, *43* (3), 275–286. [https://doi.org/10.1016/S1385-1101\(00\)00022-8](https://doi.org/10.1016/S1385-1101(00)00022-8).
- (11) Yamamoto, H.; Yokouchi, Y.; Otsuki, A.; Itoh, H. Depth Profiles of Volatile Halogenated Hydrocarbons in Seawater in the Bay of Bengal. *Chemosphere* **2001**, *45* (3), 371–377. [https://doi.org/10.1016/S0045-6535\(00\)00541-5](https://doi.org/10.1016/S0045-6535(00)00541-5).
- (12) Brimblecombe, P.; Shooter, D. Photo-Oxidation of Dimethylsulphide in Aqueous Solution. *Mar. Chem.* **1986**, *19* (4), 343–353. [https://doi.org/10.1016/0304-4203\(86\)90055-1](https://doi.org/10.1016/0304-4203(86)90055-1).
- (13) Simó, R. From Cells to Globe: Approaching the Dynamics of DMS(P) in the Ocean at Multiple Scales. *Can. J. Fish. Aquat. Sci.* **2004**, *61* (5), 673–684. <https://doi.org/10.1139/f04-030>.
- (14) Stefels, J.; Steinke, M.; Turner, S.; Malin, G.; Belviso, S. Environmental Constraints on the Production and Removal of the Climatically Active Gas Dimethylsulphide (DMS) and Implications for Ecosystem Modelling. *Biogeochemistry* **2007**, *83* (1–3), 245–275. <https://doi.org/10.1007/s10533-007-9091-5>.
- (15) Moore, R. M.; Zafiriou, O. C. Photochemical Production of Methyl Iodide in Seawater. *J. Geophys. Res.* **1994**, *99* (D8), 16415. <https://doi.org/10.1029/94JD00786>.
- (16) Wever, R.; van der Horst, M. A. The Role of Vanadium Haloperoxidases in the Formation of Volatile Brominated Compounds and Their Impact on the Environment. *Dalton Trans.* **2013**, *42* (33), 11778–11786. <https://doi.org/10.1039/C3DT50525A>.
- (17) Moore, R. M.; Webb, M.; Tokarczyk, R.; Wever, R. Bromoperoxidase and Iodoperoxidase Enzymes and Production of Halogenated Methanes in Marine Diatom Cultures. *J. Geophys. Res.-Oceans* **1996**, *101* (C9), 20899–20908. <https://doi.org/10.1029/96JC01248>.

- (18) Lin, C. Y.; Manley, S. L. Bromoform Production from Seawater Treated with Bromoperoxidase. *Limnol. Oceanogr.* **2012**, *57* (6), 1857–1866. <https://doi.org/10.4319/lo.2012.57.6.1857>.
- (19) Ooki, A.; Nomura, D.; Nishino, S.; Kikuchi, T.; Yokouchi, Y. A Global-Scale Map of Isoprene and Volatile Organic Iodine in Surface Seawater of the Arctic, Northwest Pacific, Indian, and Southern Oceans. *J. Geophys. Res.-Oceans* **2015**, *120* (6), 4108–4128. <https://doi.org/10.1002/2014JC010519>.
- (20) Inomata, Y.; Hayashi, M.; Osada, K.; Iwasaka, Y. Spatial Distributions of Volatile Sulfur Compounds in Surface Seawater and Overlying Atmosphere in the Northwestern Pacific Ocean, Eastern Indian Ocean, and Southern Ocean: Importance of DMS emission in marginal ice zones. *Glob. Biogeochem. Cy.* **2006**, *20* (2).. <https://doi.org/10.1029/2005GB002518>.
- (21) Carpenter, L. J.; Liss, P. S. On Temperate Sources of Bromoform and Other Reactive Organic Bromine Gases. *J. Geophys. Res.-Atmos.* **2000**, *105* (D16), 20539–20547. <https://doi.org/10.1029/2000JD900242>.
- (22) Amouroux, D.; Donard, O. F. X. Evasion of Selenium to the Atmosphere via Biomethylation Processes in the Gironde Estuary, France. *Mar. Chem.* **1997**, *58* (1–2), 173–188. [https://doi.org/10.1016/S0304-4203\(97\)00033-9](https://doi.org/10.1016/S0304-4203(97)00033-9).
- (23) Amouroux, D.; Liss, P. S.; Tessier, E.; Hamren-Larsson, M.; Donard, O. F. X. Role of Oceans as Biogenic Sources of Selenium. *Earth Planet. Sc. Lett.* **2001**, *189* (3–4), 277–283. [https://doi.org/10.1016/S0012-821X\(01\)00370-3](https://doi.org/10.1016/S0012-821X(01)00370-3).
- (24) Amouroux, D.; Donard, O. F. X. Maritime Emission of Selenium to the Atmosphere in Eastern Mediterranean Seas. *Geophys. Res. Lett.* **1996**, *23* (14), 1777–1780. <https://doi.org/10.1029/96GL01271>.
- (25) Yu, Z.; Li, Y. Marine Volatile Organic Compounds and Their Impacts on Marine Aerosol—A Review. *Sci. Total Environ.* **2021**, *768*, 145054. <https://doi.org/10.1016/j.scitotenv.2021.145054>.
- (26) Quack, B.; Atlas, E.; Petrick, G.; Stroud, V.; Schauffler, S.; Wallace, D. W. R. Oceanic Bromoform Sources for the Tropical Atmosphere: Oceanic bromoform for the atmosphere. *Geophys. Res. Lett.* **2004**, *31* (23). <https://doi.org/10.1029/2004GL020597>.
- (27) P. Bianchi, A.; S. Varney, M.; Phillips, J. Analysis of Industrial Solvent Mixtures in Water Using a Miniature Purge-and-Trap Device with Thermal Desorption and Capillary Gas Chromatography—Mass Spectrometry. *J. Chromatogr. A* **1991**, *557*, 429–439. [https://doi.org/10.1016/S0021-9673\(01\)87150-8](https://doi.org/10.1016/S0021-9673(01)87150-8).
- (28) Eswayah, A. S.; Smith, T. J.; Scheinost, A. C.; Hondow, N.; Gardiner, P. H. E. Microbial Transformations of Selenite by Methane-Oxidizing Bacteria. *Appl. Microbiol. Biot.* **2017**, *101* (17), 6713–6724. <https://doi.org/10.1007/s00253-017-8380-8>.
- (29) Hughes, C.; Chuck, A. L.; Rossetti, H.; Mann, P. J.; Turner, S. M.; Clarke, A.; Chance, R.; Liss, P. S. Seasonal Cycle of Seawater Bromoform and Dibromomethane Concentrations in a Coastal Bay on the Western Antarctic Peninsula. *Glob. Biogeochem. Cy.* **2009**, *23* (2). <https://doi.org/10.1029/2008GB003268>.
- (30) Swan, H. B.; Crough, R. W.; Vaattovaara, P.; Jones, G. B.; Deschaseaux, E. S. M.; Eyre, B. D.; Miljevic, B.; Ristovski, Z. D. Dimethyl Sulfide and Other Biogenic Volatile Organic Compound Emissions from Branching Coral and Reef Seawater: Potential Sources of Secondary Aerosol over the Great Barrier Reef. *J. Atmos. Chem.* **2016**, *73* (3), 303–328. <https://doi.org/10.1007/s10874-016-9327-7>.
- (31) Zhu, R.; Yang, G.; Zhang, H. Temporal and Spatial Distributions of Carbonyl Sulfide, Dimethyl Sulfide, and Carbon Disulfide in Seawater and Marine Atmosphere of the Changjiang Estuary and Its Adjacent East China Sea. *Limnol. Oceanogr.* **2019**, *64* (2), 632–649. <https://doi.org/10.1002/lno.11065>.
- (32) Galí, M.; Simó, R.; Vila-Costa, M.; Ruiz-González, C.; Gasol, J. M.; Matrai, P. Diel Patterns of Oceanic Dimethylsulfide (DMS) Cycling: Microbial and Physical Drivers: diel patterns of DMS cycling. *Glob. Biogeochem. Cy.* **2013**, *27* (3), 620–636. <https://doi.org/10.1002/gbc.20047>.
- (33) Lennartz, S. T.; Marandino, C. A.; von Hobe, M.; Andreae, M. O.; Aranami, K.; Atlas, E.; Berkelhammer, M.; Bingemer, H.; Booge, D.; Cutter, G.; Cortes, P.; Kremser, S.; Law, C.; Marriner, A.;

- Simó, R.; Quack, B.; Uher, G.; Xie, H.; Xu, X. Marine Carbonyl Sulfide (OCS) and Carbon Disulfide (CS₂): A compilation of Measurements in Seawater and the Marine boundary Layer; *Earth Syst. Sci. Data*, **12**, 591–609, <https://doi.org/10.5194/essd-12-591-2020>, **2020**.
- (34) Chuck, A. L. Oceanic Distributions and Air-Sea Fluxes of Biogenic Halocarbons in the Open Ocean. *J. Geophys. Res.* **2005**, *110* (C10), C10022. <https://doi.org/10.1029/2004JC002741>.
- (35) Li, Y.; He, Z.; Yang, G.-P.; Wang, H.; Zhuang, G.-C. Volatile Halocarbons in the Marine Atmosphere and Surface Seawater: Diurnal and Spatial Variations and Influences of Environmental Factors. *Atmos. Environ.* **2019**, *214*, 116820. <https://doi.org/10.1016/j.atmosenv.2019.116820>.
- (36) Yokouchi, Y.; Saito, T.; Ooki, A.; Mukai, H. Diurnal and Seasonal Variations of Iodocarbons (CH₂ClI, CH₂I₂, CH₃I, and C₂H₅I) in the Marine Atmosphere. *J. Geophys. Res.-Atmos.* **2011**, *116* (D6). <https://doi.org/10.1029/2010JD015252>.
- (37) Ziska, F.; Quack, B.; Abrahamsson, K.; Archer, S. D.; Atlas, E.; Bell, T.; Butler, J. H.; Carpenter, L. J.; Jones, C. E.; Harris, N. R. P.; Hepach, H.; Heumann, K. G.; Hughes, C.; Kuss, J.; Krüger, K.; Liss, P.; Moore, R. M.; Orlikowska, A.; Raimund, S.; Reeves, C. E.; Reifenhäuser, W.; Robinson, A. D.; Schall, C.; Tanhua, T.; Tegtmeier, S.; Turner, S.; Wang, L.; Wallace, D.; Williams, J.; Yamamoto, H.; Yvon-Lewis, S.; Yokouchi, Y. Global Sea-to-Air Flux Climatology for Bromoform, Dibromomethane and Methyl Iodide. *Atmos. Chem. Phys.* **2013**, *13* (17), 8915–8934. <https://doi.org/10.5194/acp-13-8915-2013>.
- (38) Lee, G.; Park, J.; Jang, Y.; Lee, M.; Kim, K.-R.; Oh, J.-R.; Kim, D.; Yi, H.-I.; Kim, T.-Y. Vertical Variability of Seawater DMS in the South Pacific Ocean and Its Implication for Atmospheric and Surface Seawater DMS. *Chemosphere* **2010**, *78* (8), 1063–1070. <https://doi.org/10.1016/j.chemosphere.2009.10.054>.
- (39) Kiene, R. P.; Linn, L. J.; González, J.; Moran, M. A.; Bruton, J. A. Dimethylsulfoniopropionate and Methanethiol Are Important Precursors of Methionine and Protein-Sulfur in Marine Bacterioplankton. *Appl. Environ. Microb.* **1999**, *65* (10), 4549–4558. <https://doi.org/10.1128/AEM.65.10.4549-4558.1999>.
- (40) Kiene, R. P.; Williams, T. E.; Esson, K.; Tortell, P. D.; Dacey, J. W. H. Methanethiol Concentrations and Sea-Air Fluxes in the Subarctic NE Pacific Ocean. **2017**, *2017*, OS21A-1356.
- (41) Hughes, C.; Malin, G.; Turley, C. M.; Keely, B. J.; Nightingale, P. D. The Production of Volatile Iodocarbons by Biogenic Marine Aggregates. *Limnol. Oceanogr.* **2008**, *53* (2), 867–872. <https://doi.org/10.4319/lo.2008.53.2.0867>.

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