Supplement of

Methanethiol and dimethyl sulfide measurements in seawater and the atmosphere around the Antarctic Peninsula and in the Weddell Sea

Charel Wohl et al.

Correspondence to: Charel Wohl (c.wohl@uea.ac.uk), Rafel Simó (rsimo@icm.csic.es) and Leah Williams (williams@aerodyne.com)

S1 Seawater Vocus PTR operation

To monitor instrument performance and drift, the seawater-sampling Vocus PTR was calibrated at least daily using a multi-compound gas standard (nominal concentration 500 nmol mol^{-1}; methanol, acetaldehyde, acetone, isoprene, DMS, benzene, toluene, m-xylene, α-pinene in nitrogen, Apel-Riemer Environmental, Inc.) diluted in zero air (Vocus PTR Clean Air System: Zero Air Generator, Tofwerk AG). Step calibrations with multiple dilutions were carried out five times during the campaign. Fig. S1 shows a step calibration at the end of the cruise with sensitivity (cps/ppb) versus the k_{PTR} (reaction rate for H+ adduct formation) in panel (a) and the calculated ion transmission, plotted as measured sensitivity divided by expected sensitivity from panel (a), as a function of m/Q in panel (b). Note the low estimated ion transmission for MeSH at m/Q 49.

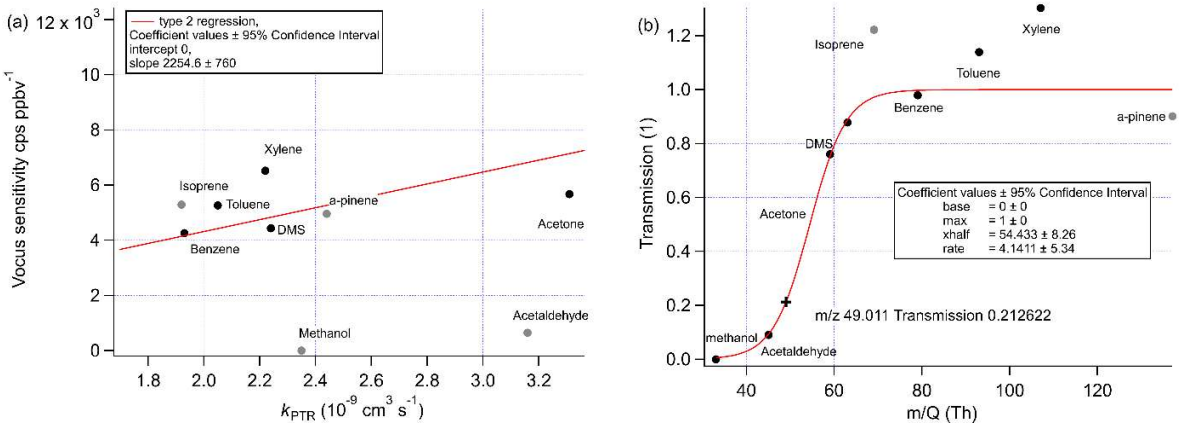

Figure S1. Vocus PTR calibration curve generated during the cruise. (a) Plot of the measured sensitivity against k_{PTR}. Methanol and acetaldehyde were excluded from this regression as their sensitivity is affected by the ion transmission. α-pinene and isoprene were excluded from the regression due to fragmentation. An orthogonal distance regression fit was used to account for potential uncertainty in k_{PTR}. (b) Ion transmission curve.

Further gas standard calibrations were performed in the field and in the lab at the same humidity as equilibrator headspace air, which confirmed that the instrument did not show a humidity dependence for the compounds in our gas standard. The instrument was operated as laid out in the appendix of a previously published manuscript (Wohl et al., 2023), with a few notable adaptations listed here. A larger PEEK inlet capillary was fitted during POLARCHANGE increasing the gas flow into the instrument from approximately 100 sccm (standard cubic centimetres) to 250 sccm. This was to reduce the frequency of quasi-daily obstruction of the inlet capillary due to salt particles coming from the SFCE equilibrator. Obstruction was monitored by the status of the Pressure Control Valve (PCV) and sample air flow into the instrument. We noticed that the sensitivity of some compounds, including DMS, changed as a function of the PCV setting, a finding backed up by observations by Jensen et al. (2023). We carried out hourly gas standard calibrations during one 24–hour period. This was used to parameterize changes in sensitivity as a function of the obstruction monitored by the step value of the PCV. DMS sensitivity changed by 5 % due to inlet obstruction. There were no obvious signs in the data that the sensitivity of methanethiol was affected by this inlet obstruction. We note that there were a high number of NO_2^+ ions suggesting a leak in the source region during the cruise.

The BSQ voltage was set to 290 V to allow higher sensitivity/transmission of lower mass compounds, such as methanethiol, while keeping total ion counts below 1 million. The reactor temperature was 100 °C while the Vocus axial voltage was 575 V. We calculate an E/N of 147 Td, consistent with an estimated E/N of around 150 Td as determined from the fragmentation of α-pinene.

S2 Calculating dissolved concentrations in seawater

To account for the larger gas flow requirements by the Vocus-PTR due to a larger diameter capillary, the SFCE was operated using a main flow (mass flow controller set point value) of 150 sccm and a dilution flow of 150 sccm. The above ambient pressure in the segmented flow tube (due to length of tube, 10 m, and seawater flow) translated to a volumetric flow of 130 ± 3 ccm. The seawater flow was set at 70 cm^3 min^{-1} and monitored at least daily. These adjustments in gas and seawater flows as well as increased pressure in the segmented flow tube were accounted for when calculating seawater concentrations. Post-cruise calibrations were carried out at these identical equilibrator flow settings including the larger inlet capillary and a leak in the source region.

Post-processing was performed using the data analysis package Tofware (version *3.3.0*, support.aerodyne.com) running in the Igor Pro (Wavemetrics) environment. Peak fits for MeSH and DMS during zero and equilibrator headspace periods are shown in Fig. S2.

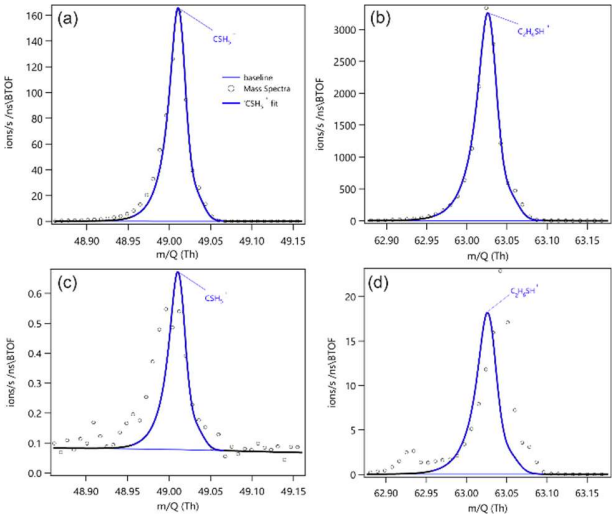

Figure S2. High resolution peak fitting. (a) MeSH equilibrator headspace and (c) zero air. (b) DMS equilibrator headspace and (d) zero air.

Hourly measurements of zero air were used for background subtraction. We note that for DMS and methanethiol, we observe good agreement between the zero air blank and a wet equilibrator blank. The wet equilibrator blank consists of stopping the water flow into the equilibrator and flushing it for 1 hour with zero air. We note that DMS and methanethiol have a high signal to background ratio; thus, reported concentrations are relatively insensitive to the choice of background.

We calibrated the SFCE coupled to Vocus-PTR for MeSH and simultaneously DMS in the laboratory after the cruise. Calibrations were done by gastight serial dilution of powdered sodium methanethiolate and liquid DMS in MilliQ water with the final dilution step done in seawater using a syringe pump. Seawater for these calibrations was collected from the shore outside the Institut de Ciències del Mar (CSIC) in Barcelona. Sodium methanethiolate dissolves to form methanethiol and sodium hydroxide in MilliQ water (Carrión et al., 2017). Calibrations were performed on 5 different days with fresh solutions each day. Calibrations of MeSH on board were not performed due to the logistical constraints of using a balance on a ship and safe/reliable shipment of weighted hygroscopic, volatile, reactive chemicals.

Calibrations with the equilibrator were carried out at approximately the same temperature (~18° C during the cruise – ~22° C post cruise) as the equilibrator was operated on the ship and using authentic seawater. DMS seawater concentrations were calculated using the technique described in Wohl et al. (2019). Gas-phase DMS measured in the SFCE headspace when sampling the calibration solutions was converted from cps (or ions/s) to nmol mol^{-1} (or ppb) using the DMS gas-phase calibration from the calibration cylinder. The DMS measured in the headspace agreed well with the expected value from the solution concentration using the recommended solubility in Sander (2023, Fig. S3). Note that the DMS background from the seawater has been subtracted in Fig. S3 so that the intercepts go through zero. For the ship data, the seawater DMS concentration was calculated from the measured headspace concentration using the Vocus-PTR cal tank gas-phase calibration during the cruise and the same recommended DMS solubility..

Correction for variations in instrument sensitivity was made using the daily DMS calibrations with the calibration cylinder.

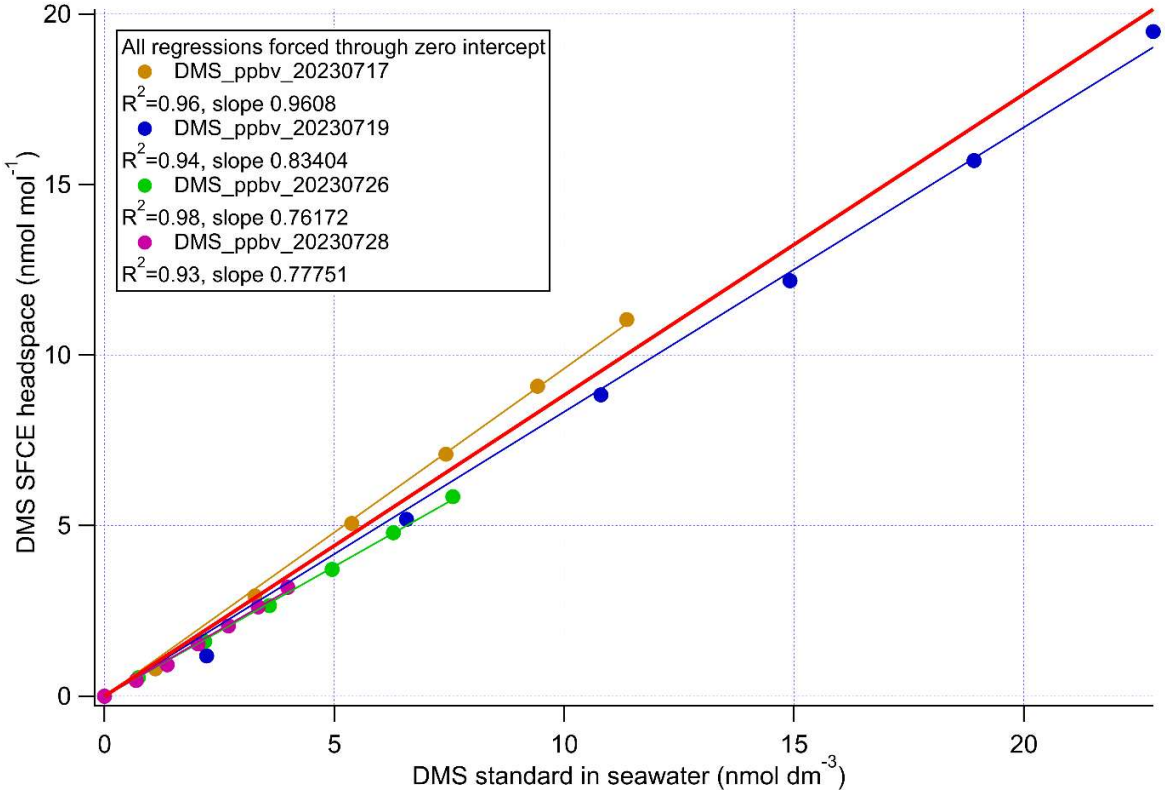

Figure S3. Equilibrator calibration on five separate days with known solutions of DMS.

For the MeSH equilibrator calibration, the headspace concentration did not agree well with the expected concentration using any of the solubilities listed in Sander (2023). Therefore, we used a different method than for DMS to calculate seawater concentrations from the cruise data. Fig. S4 shows the MeSH headspace concentration in cps versus MeSH seawater liquid concentration in nM for each of the five calibrations. Some of the variation in slopes is due to changes in instrument sensitivity. In Fig. S5 we plot the MeSH slope (cps/nM) versus concurrent gas-phase calibrations of DMS (cps/ppb). For the cruise data, we converted the headspace measurement in cps to seawater concentration in nM using the slope and intercept in Fig. S5 to reference MeSH sensitivity to the daily DMS gas-phase calibrations. We made an additional correction for the fact that the ion transmission for MeSH was 0.2 during the cruise (Fig. S1) and 0.35 during the post-cruise calibrations.

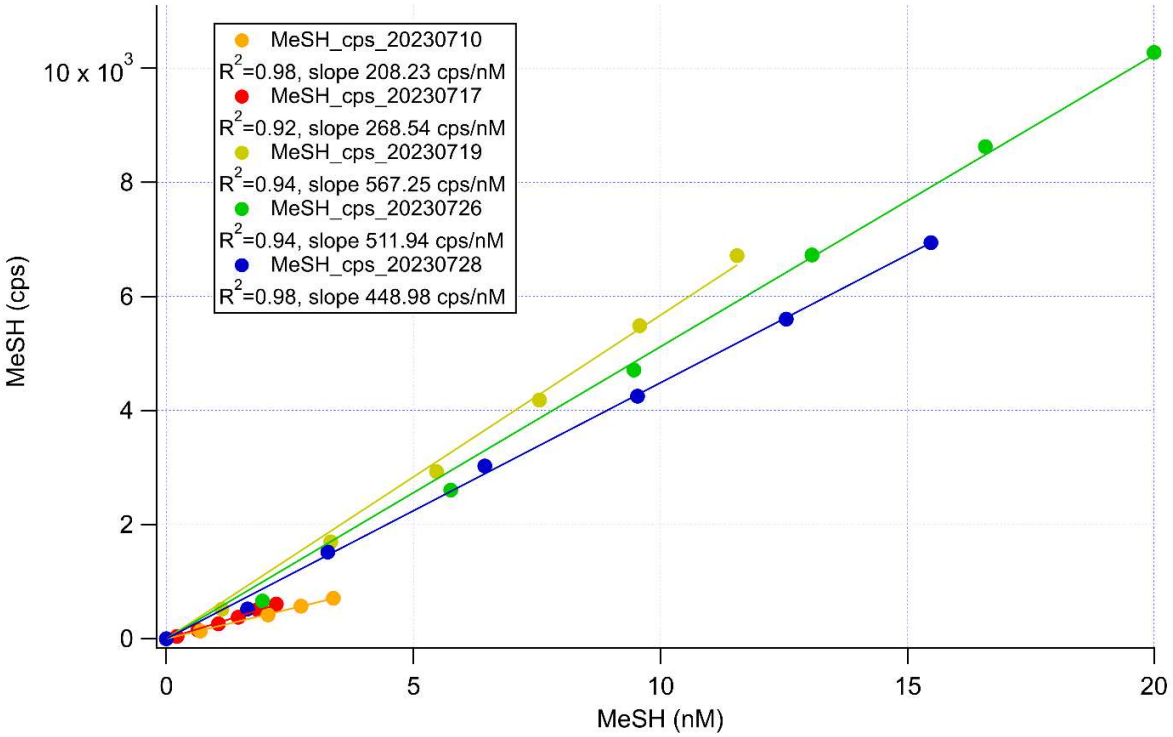

Figure S4. Equilibrator headspace (cps) versus concentration in solution (nM) for MeSH.

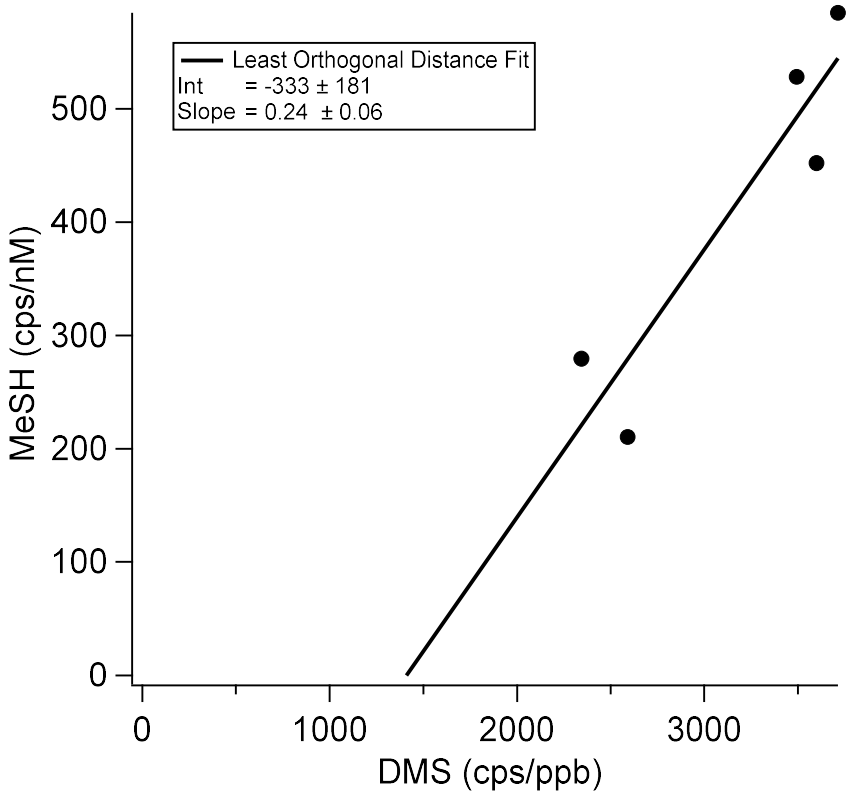

Figure S5. MeSH liquid calibration factor (cps/nM) versus DMS gas-phase calibration factor (cps/ppb).

The limit of detection was calculated as three times the standard deviation of 2 min data segments when measuring a relatively stable equilibrator headspace concentration for 30 min. This yields a limit of detection of 0.017 nmol dm^{-3} for DMS and 0.014 nmol dm^{-3} for methanethiol. This corresponds to the equivalent of 12 pptv DMS and 10 pptv MeSH in the equilibrator headspace air. We estimate that the systematic error of our seawater measurements is less than ±20 % for DMS and ±30 % for methanethiol. This is due to daily variability in sensitivity or background and higher for MeSH due to uncertainties in the ion transmission and reliance on post-cruise calibrations.

S3 Biofouling in the SFCE

We observed that biofouling in the equilibrator led to very high MeSH concentrations during part of the campaign. Figure S6 shows a timeseries of the MeSH seawater concentrations measured before and after cleaning with 3.7 % HCl (by weight). We observed a sharp drop in concentration immediately after cleaning with HCl on 26 February 2023. From then onwards, the equilibrator was cleaned daily with 3.7 % HCl. Once regular cleaning had commenced, no more sharp drops in concentrations were observed and concentrations remained persistently lower and more consistent with previous observations. This suggests that the high concentrations at the beginning of the cruise were due to biofouling. The biofouling-contaminated data is not shown in the main text.

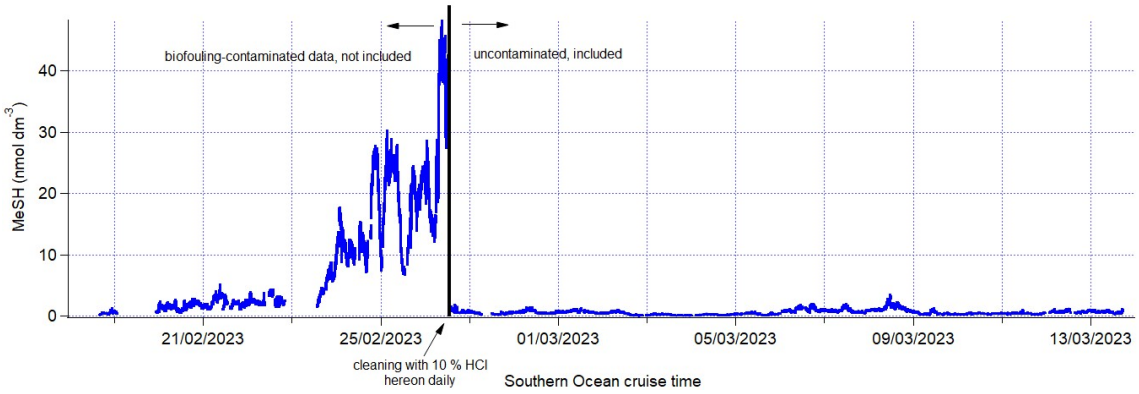

Figure S6. Impact of biofouling on measured seawater MeSH concentrations showing measurements before and after cleaning the equilibrator with 3.7 % HCl.

S4 CTD to underway comparison

During CTD casts, we compared seawater concentrations measured from the 5 m Niskin bottle and the underway seawater tap (Fig. S7) to check for contamination from the underway seawater inlet, for example. due to biofouling. The MeSH and DMS concentrations measured from the underway seawater inlet and 5 m CTD are fairly evenly scattered around the 1:1 line and scattered within ± 25%, which is consistent with the estimated uncertainty.

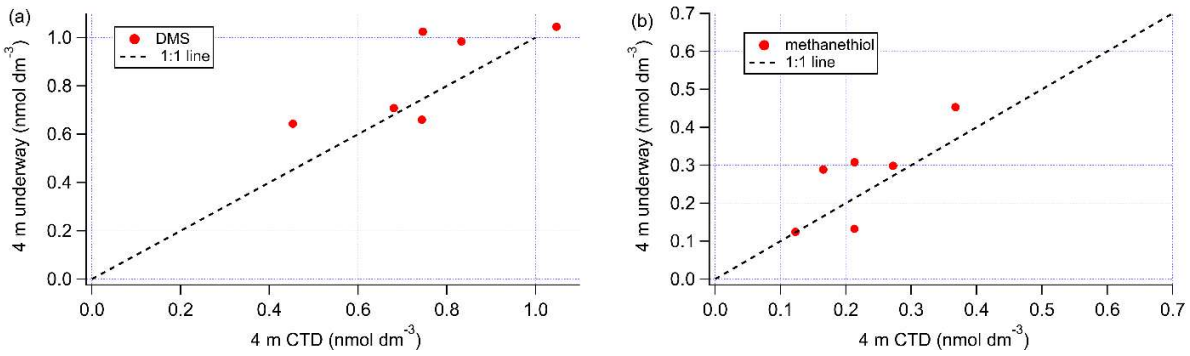

Figure S7. Comparison of seawater concentrations measured from 5 m CTD and the underway seawater tap.

S5 Ambient air Vocus PTR data analysis

High-resolution peak fitting was performed on the ambient air Vocus PTR data using Tofware 4.0.2. For the DMS analysis at nominal m/Q 63, there were identifiable contributions from DMS (C2H7S+), CClO+, CH3O3+ and C2H7O2+ plus an unknown ion at exact mass 63.024 (Fig. S8). During ambient sampling, including the unknown ion reduced DMS by a small amount (~1-4%) but slight variations in the m/Q calibration caused the DMS to be much noisier than when not fitting the unknown. Therefore, the unknown was not included during analysis of the ambient data. The fraction of signal at m/Q 63 that was due to DMS during ambient data was 0.9 ± 0.09. In contrast, during the zeros, the unknown was more than 50% of the signal (Figure S8c and d) and it was necessary to fit it to bring the DMS during the zero below the DMS during ambient during the parts of the campaign when air DMS concentrations were very low. Therefore, the unknown was included in the fits during the zeros. The fraction of signal at m/Q 63 that was due to DMS during the zeros was 0.3 ± 0.05.

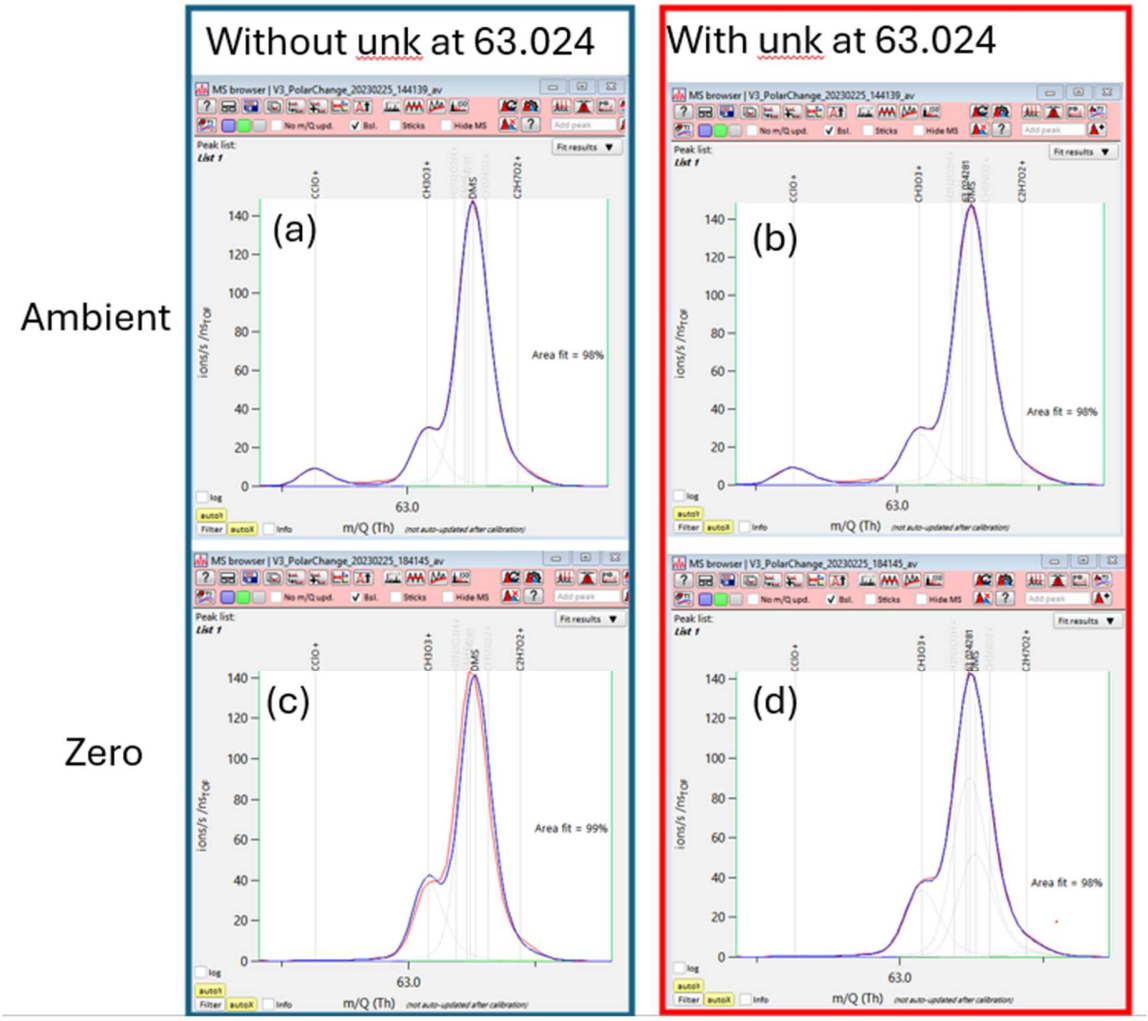

Figure S8. High resolution fitting at m/z 63 during ambient sampling (a) without and (b) with the unknown at exact mass 63.024. Panel (c) shows the fit during a zero without the unknown and panel (d) shows the fit during a zero with the unknown.

For the MeSH analysis at nominal m/Q 49, there were several unidentified ions in addition to methanethiol (CH5S+) and CH5O2+. Because the ambient levels of methanethiol were very low, it was necessary to include unknowns on both the right and left shoulders of the methanethiol peak during both ambient and zeros (Fig. S9). The fraction of signal at m/z 49 attributed to methanethiol was 0.7 ± 0.2 during ambient and 0.2 ± 0.1 during zeros.

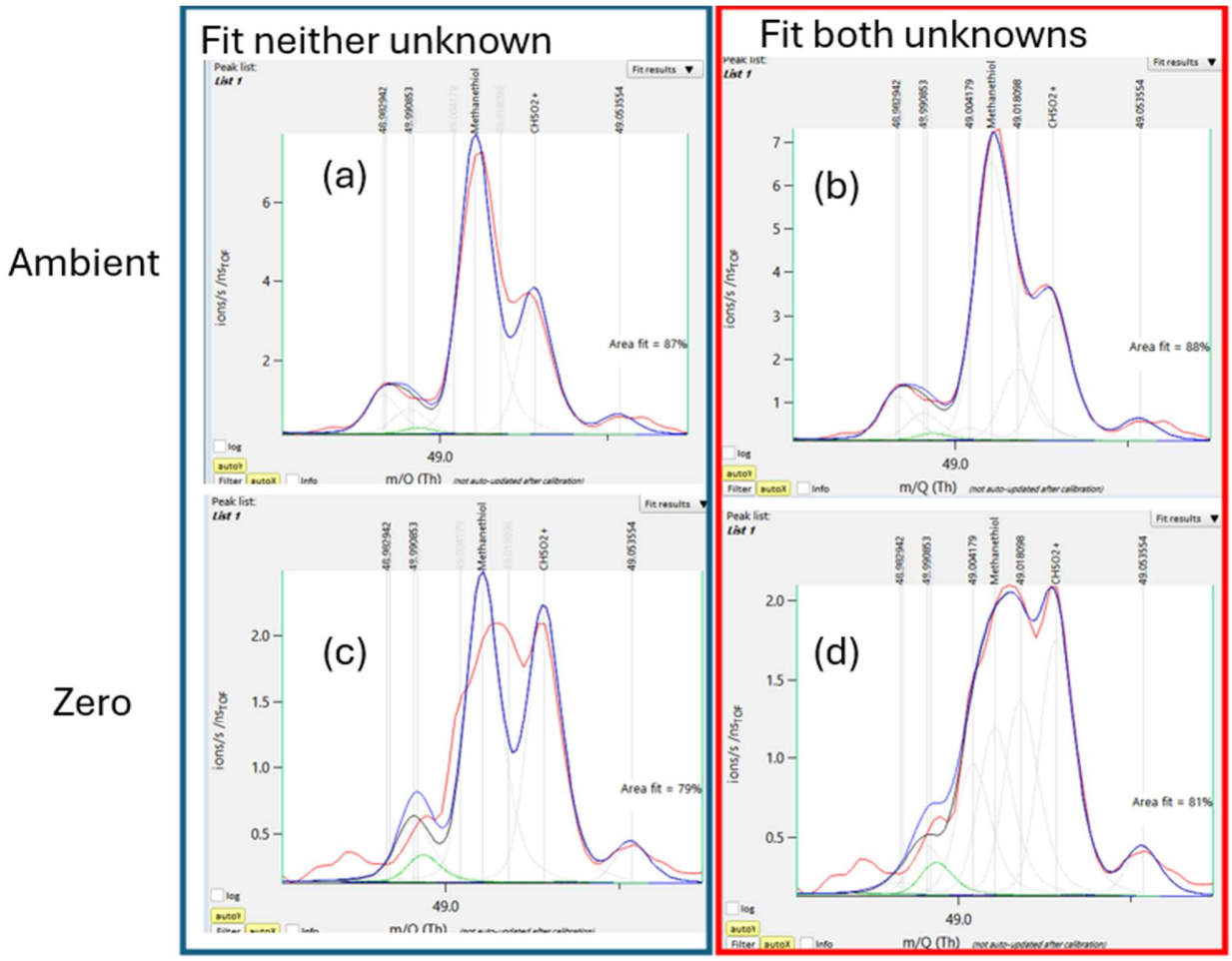

Figure S9. High resolution fitting at m/z 49 during ambient sampling (a) without and (b) with the unknowns on the right and left shoulders of methanethiol. Panel (c) shows the fit during a zero without the unknowns and panel (d) shows the fit during a zero with the unknowns.

We performed a zero/calibration/zero sequence every 4 hours during the campaign using the same calibration gas as the Vocus PTR measuring seawater concentrations. The second zero always had higher concentrations of the calibration gases than the first zero and there was a 10 – 15 minute decay in concentration after returning to ambient sampling. We therefore used only the first zero and removed twenty minutes of data after each zero/calibration/zero sequence. Data from a step calibration was converted to sensitivity vs kPTR and ion transmission graphs as shown in Fig. S10. The ion transmission correction at m/Q 49 was 0.64 for this Vocus PTR. We calibrated for MeSH after the cruise using a perm tube and had good agreement with the expected sensitivity for MeSH from the slope of sensitivity vs kPTR. The cruise MeSH data in cps was converted to ppb by first applying the transmission correction, then applying the relative sensitivity for MeSH compared to DMS from the post-cruise calibration, and then applying the relative variations in DMS sensitivity from the every 4 hour calibrations.

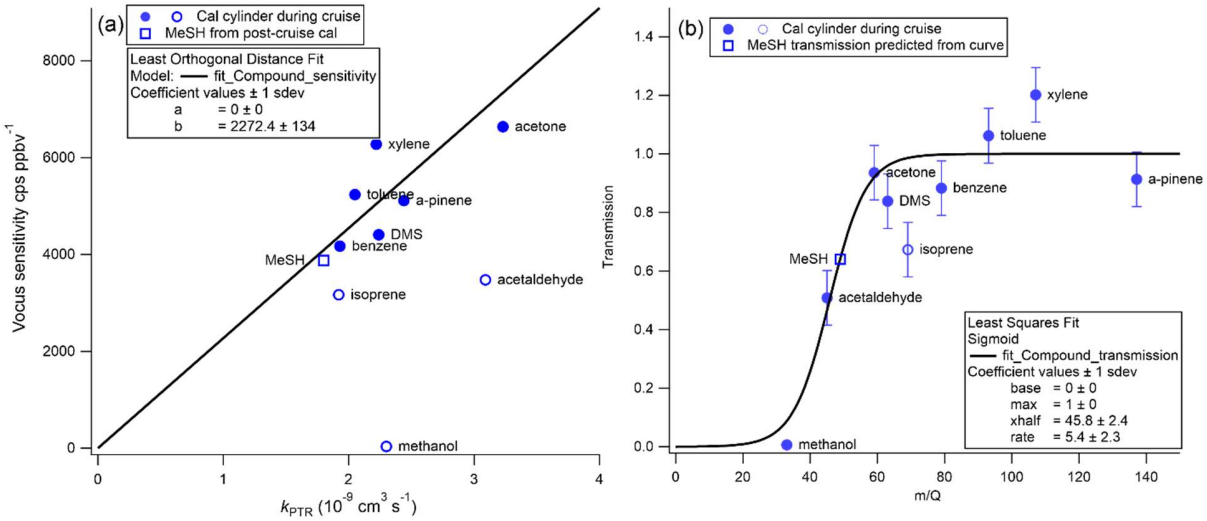

Figure S10. (a) Plot of sensitivity vs k_{PTR} for the air Vocus PTR during the cruise. Methanol, acetaldehyde and isoprene are omitted from the fit. The relative sensitivity of MeSH from post-cruise calibrations is shown with a square. (b) Ion transmission vs m/Q during the cruise. The predicted ion transmission for MeSH is shown with a square.

We examined the data for interference from ship exhaust using the Vocus PTR signals for benzene (for engine exhaust), acetone and nonanal (for kitchen exhaust). Time periods with high benzene but no nonanal did not interfere with the measurement of DMS and MeSH as determined by looking at the correlation between benzene and the sulfur compounds. Time periods with high nonanal and acetone did interfere with the measurement of DMS and MeSH and were removed from the time series presented in Figure 6.

We estimated the limit of detection as three times the standard deviation of the ambient signal when it is close to zero and flat. The limit of detection for DMS was 3 pptv (0.00013 nmol dm^{-3}) and for MeSH was 1 pptv (0.00004 nmol dm^{-3}). The uncertainty estimated from the standard deviation of low, flat ambient signal was ± 8% for DMS and ± 18% for MeSH. The estimated systematic error due to the calibration procedure is ± 15% for DMS and ±20% for MeSH given the additional uncertainty in the ion transmission.

S6. Comparison or air concentrations with Quad PTR

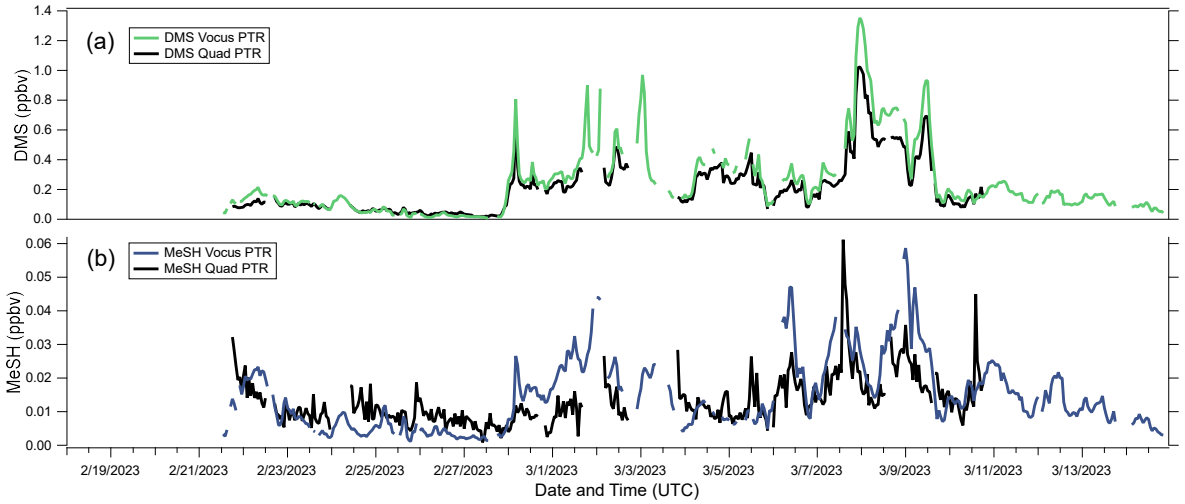

Figure S11. Comparison of (a) air DMS and (b) air MeSH measured with the Vocus PTR and the Quad PTR during POLAR-CHANGE.

Figure S11 presents the comparison of DMS and MeSH measured with the Vocus PTR and the Quad PTR during the POLAR-CHANGE cruise. The correlation between Vocus PTR DMS and Quad PTR DMS was excellent (R2=0.99) although the Quad PTR reported a roughly 25% lower concentration than the Vocus PTR (slope = 0.74). We did a cross comparison of the two calibration cylinders used for the two PTRs and the calibration DMS agreed within 1%. Thus, the disagreement was not due to a difference in the calibration standard. The agreement between the two instruments was less good for MeSH with a correlation coefficient (R2) of 0.43 and a slope of 0.48. The Quad PTR MeSH measurements may be less accurate than the Vocus PTR due to lack of a calibration with MeSH and potential interferences at m/Q 49 that are not identified in the unit mass resolution analysis (see Chamba et al., 2026).

Table S1. Statistics for measurements in the main text.

	Mean	Std Dev	Min	Max	Q25	Median	Q75
Seawater DMS (nmol dm^{-3})	1.6	1.1	0.45	11.3	0.9	1.3	1.9
Seawater MeSH (nmol dm^{-3})	0.50	0.27	0.11	1.7	0.30	0.44	0.63
Seawater ratio MeSH/DMS	0.41	0.16	0.14	1.0	0.31	0.39	0.48
Seawater MeSH/(DMS+MeSH)	0.28	0.08	0.12	0.51	0.23	0.28	0.33
Air DMS PTR (ppb)	0.25	0.24	0.008	1.35	0.1	0.17	0.31
Air MeSH (ppt)	15	10	1	60	7	12	21
DMS Flux (µmol m^2 d^{-1})	1.7	1.4	-0.6	8.6	0.77	1.5	2.3
DMS Flux (µmol m^2 d^{-1}), same	1.5	1.3	-0.6	8.6			

time as MeSH Flux							
MeSH Flux (μmol m^2 d^{-1})	0.90	0.64	0.03	4.3	0.45	0.76	1.3

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