

Reply to Reviewer 1 comments for: Segmented flow coil equilibrator coupled to a Proton Transfer Reaction Mass Spectrometer for measurements of a broad range of Volatile Organic Compounds in seawater

Many thanks for the thoughtful comments from this anonymous reviewer. Thank you for your time spotting some of the nomenclature errors and typos. The reviewer has been able to provide thought provoking comments and point out some of the trade-offs in our setup. Please see our responses below. Reviewer comments are in italic and author's replies can be found in normal font. The changes to the manuscript are presented as figures taken from the manuscript with the changes made indicated by red track changes.

General comments

(1) Nomenclature. Many colloquialisms are used that imprecisely describe materials and processes at in question, which obfuscates the discussion but also harms communication across fields. a. Using the IUPAC Glossary of Terms Related to Solubility (10.1351/pac200880020233) as a reference i. Instead of 'airside' use 'gas phase' ii. Instead of 'waterside' use 'dissolved gas concentration' b. While softer/harder ionization is technically correct, it's a lot more illuminating to discuss proton affinity differences and effective temperatures, which are the forces at play in the PTR-MS drift tube and ion optic system. c. The protonated target molecule is the "primary ion". A charged fragment of dissociation should be called a "product ion" or "fragment ion".

Thank you for this comment.

- a. Solubility terms
 - i. Suggestion accepted
 - ii. Suggestion accepted, except lines 300 and 630 where "dissolved gas concentration" did not fit well and was replaced by "seawater" instead. See below.

300 For evasion experiments, a solubility-dependent fraction of dissolved VOCs is transferred into the gas phase during the equilibration process. Thus, the final dissolved concentration will be somewhat lower than the initial concentrations. To account for the removal of a fraction of these gases from the waterside-seawater during equilibration, a purging factor (PF) based on mass conservation is applied. The PF is the ratio between the dissolved gas-waterside concentration before and after complete equilibration in the coil. The derivation of this compound specific purging factor is presented in the appendix. At equal air and water flow rates, it simplifies to:

$$PF = \frac{C_w(\text{before equilibration})}{C_w(\text{after equilibration})} = \frac{1}{H} + 1 \quad (4)$$

- b. Suggestion accepted, see below the applied changes to the manuscript

Humidity has several potential effects on the measurement: (i) The additional water molecule stabilises the primary ion by sharing the positive charge thus increasing its proton affinity (Blake et al., 2009). For example benzene and toluene possess intermediate proton affinities and are ionised by the primary ion, but not the water cluster (Warneke et al., 2001). On the other hand, this process decreases the proton affinity difference between the primary ion and the VOCs and ~~thus so~~ the excess energy released on proton transfer reaction (de Gouw ~~and~~ Warneke, 2007). This leads to less fragmentation for example of isoprene in the drift tube (Schwarz et al. 2009); (ii) humidity in

...

For isoprene, the opposite effect is observed (Fig. B4) where the stabilising water cluster from humidity makes ionisation softer decreases the excess energy released upon ionisation thus increasing the yield of the parent ion at m/z 69. Note that humidity dependant fragmentation of isoprene in PTR-MS has been observed before (Schwarz et al. 2009). Other masses that isoprene fragments can be found are m/z 39 and m/z 41.

c. Suggestion accepted, see below the applied changes to the manuscript

Humidity has several effects on the measurement: (i) The additional water molecule stabilises the primary ion by sharing the positive charge thus increasing its proton affinity (Blake et al. 2009). For example benzene and toluene possess intermediate proton affinities and are ionised by the primary ion, but not the water cluster (Warneke et al. 2001). On the other hand, this process decreases the proton affinity difference between the primary ion and the VOC and thus the excess energy released on proton transfer reaction ionisation by the water cluster is softer and hence. This leads to less fragmentation for example of isoprene in the drift tube (Schwarz et al. 2009); (ii) humidity in the drift tube leads to non-collision rate limited reactions; (iii) large water

...

For isoprene, the opposite effect is observed (Fig. B4) where the stabilising water cluster from humidity makes ionisation softer decreases the excess energy released upon ionisation thus increasing the yield of the primary parent ion at m/z 69. Note that humidity dependant fragmentation of isoprene in PTR-MS has been observed before (Schwarz et al. 2009). Other masses that isoprene fragment ions fragments can be found are m/z 39 and m/z 41.

(2) Uncertainty. Consistently state and propagate uncertainty and significant figures.
a. Section 3.2 needs attention. The reader cannot determine the input concentrations for the evasion experiments with the information provided. Are the purge factors really known to the stated (per-mil) precision?

Suggestion accepted, see below the applied changes to the manuscript

Two methods are used to assess the equilibration efficiency of the SFCE: evasion and invasion. In evasion experiments, liquid standards of methanol, acetone and acetaldehyde were prepared by serial dilution of the pure solvent in the same batch of MilliQ water. Aliquots of pure, undiluted methanol (For spectroscopy Uvasol) and acetone (HPLC standard) were dispensed using volumetric pipettes. A 1 cm³ volumetric flask was used to aliquot pure acetaldehyde (>=99.5%, A.C.S. Reagent). Subsequent dilutions utilised a volumetric pipette and volumetric flask to prepare liquid standards ranging from 3 to 30 nM for acetone and acetaldehyde and 30 to 300 nM for methanol. Liquid standards of Isoprene and DMS were prepared gravimetrically airtight each day. A syringe pump (New Era Pump Systems) was used to dynamically dilute DMS and isoprene standards in a flow of MilliQ water. This yielded DMS standards of up to 7 nM and isoprene standards of up to 2 nM. For this calibration, the flow rate of MilliQ water is measured at the drain. ForIn evasion experimentscalibrations, a solubility-dependent fraction of dissolved VOCs is transferred into the gas phase during the equilibration process. Thus, the final dissolved concentration will be somewhat lower than the initial concentrations. To

The precision of the purging factor depends on the precision of the solubility measurement. Since we report solubilities with two significant figures, we decide to report the purging factor with two significant figures as well.

For freshwater, computed purging factors assuming full equilibration and equal zero air: water flows are: 1.00015 for methanol, 1.00111 for acetone, 1.00225 for acetaldehyde, 1.063 for DMS, 1.184 for benzene, 1.2109 for toluene and 2.5768 for isoprene. The same computation in seawater gives the following purging factors: 1.00015 for methanol, 1.00122 for acetone, 1.0025 for acetaldehyde, 1.0875 for DMS, 1.221 for benzene, 1.2655 for toluene and 2.961 for isoprene. We see that PF varies from being insignificant (~=1) for highly soluble VOCs to quite large (>>1) for the sparingly soluble gases. To compute the expected headspace

(3) Harmonize section 3 and 4. These sections seem a bit repetitive and scattered, conceptually jumping back and forth between PTR-MS and SFCE tests. I suggest moving the theoretical/math into Section 3, and calling it "Derivation of Dissolved VOC concentrations from SFCE/PTR-MS

measurements". The experimental/operational work (3.1 Determination of System Background and 3.2 Estimation of Equilibration Efficiency) could be moved into section 4. Section 3.2 and 4.2 seem like they could be combined. Another thought is that the SFCE testing is largely disconnected from the PTR-MS humidity and calibration testing, so those phases could each get their own sections (Section 3: "PTR-MS operation", Section 4 "SFCE testing and operation").

Suggestion accepted. Section 2.2 Field deployment and section 5 Field testing have been merged to one section 5 at the end of the manuscript. Following the comments, section 4.1. Effect of humidity on the PTR-MS measurements has been moved to a new section 2.2 entitled PTR-MS operation, thus removing the operation/testing of the PTR-MS detector from the description of the SFCE equilibration system. Section 3 and 4 have been renamed according to the reviewer's comments. Further following the reviewer's comments, section 3.2 estimation of equilibration efficiency has been moved to a new section 4.1. This has been combined with section 4.2 Measurement sensitivity toward air:water flow ratio and presumably also 4.3 Equilibration efficiency. In this merged section, new subsections have been made to avoid an overwhelmingly large and unstructured section.

(4) Since the manuscript deals with both gas phase mixing ratios and dissolved concentrations, I suggest using "ppbv" instead of "ppb", as gas mixing ratios are typically by molar volume while aqueous mixing ratios are often by mass.

Suggestion accepted, including in the figure notations

(5) Instead of a long series of appendixes, could that information just be put in the supplemental material? Using the PTR-MS at 160 Td yields some unusual data, but in this case PTR-MS is fundamentally just the detector and the main focus of the manuscript is the SFCE application.

Suggestion accepted. The appendix will be included as supplemental information instead. Thank you for your feedback. We have deployed PTR-MS at 150 Td during a more recent campaign. The high Td value is mainly due to the higher than ambient drift tube temperature (80 deg C) in our setup, which was recommended by the manufacture for measurements of these VOCs.

Specific comments and suggestions:

Line 16: 1 min instead of 1min.

Suggestion accepted

Line 43-60: Are the authors aware of any investigators using hollow fiber membrane contactors for online dissolved gas analysis in seawater? (I am not aware of any example, but they are popular in inland surface water, groundwater, and industrial settings. So perhaps there is an example that escapes my limited search and knowledge?)

Thank you for pointing this out. We added a few examples in the section where membrane equilibrators are discussed in the relevant section of the introduction.

75 from the showerhead lengthens the equilibrators's response time for highly soluble gases, making it less suitable for high frequency measurements of highly soluble VOCs such as methanol (Kameyama et al., 2010). Membrane equilibrators avoid spray formation and allow for selective diffusion. Hollow fibre membranes have previously been used for measurement of dissolved CO₂ (Hales et al., Takahashi, & Bandstra, 2005; Sims et al., 2017) and DMS (Tortell, 2005; Yang, Blomquist, Fairall, Archer, & Huebert et al., 2011) They have previously been used to extract volatile compounds from the water phase continuously (Tortell, 2005). By using a hydrophobic

Line 90: Consider rephrasing to "In this paper we extend the application of the segmented flow coil equilibrators ..." The core design is substantially similar, but the target analytes are hitherto undocumented. 120-135 and 195-220: I note that the inlet water is warmed to 20 °C. I wondered how much N₂ would exsolve from the water and add to the total gas flow, as this would effectively dilute the measured VOCs. Air is about 25% less soluble at 20 °C than at 0 °C, and using the solubilities of O₂ and N₂ as proxies, it seems like the amount of air exsolved from a 100 cm³/min flow of water warming from 0 to 20 °C would be about 0.5 sccm: so the temperature change is not causing enough off gassing to measurably modify the mixing ratios measured in the equilibrators.

Suggestion accepted. As the reviewer stated, dilution due to N₂ exsolving with warming does not significantly affect the VOC concentrations measured.

In this paper we extend the application of the segmented flow coil equilibrators (SFCE). In this paper, we present a segmented flow coil equilibrators (SFCE) that is adopted from the designs used by Xie et al. (2001) and Blomquist et al. (2017) for measurements of carbon monoxide and DMS, respectively. We couple this

95 equilibrators to a PTR-MS with the settings optimised for measurement of VOCs in the water phase. The main

Line 197: It would be more clear to write "R=8.314 J C⁻¹ mol⁻¹ dm³ Pa mole⁻¹ K⁻¹" or similar.

Suggestion accepted

200 Where n (mol) represents the quantity of matter, V (dm³) represents the volume of gas, P (Pa) represents the pressure, $R = 8.314$ (m³ Pa K⁻¹ mol⁻¹) represents the gas constant of 8.314 and $T = 293.15$ (K) represents the temperature in the segmented flow tube of 293.15 K. A conversion factor of 0.001 is applied to convert from m³ to dm³.

Line 260-270: PTFE has a measurable permeability to many gases, and at thin cross sections, is used as a membrane material, leveraging that property. Looking at some manufacturer datasheets, acetone and methanol are among the most permeable gases in PTFE. It seems like switching to the PTFE tee fitting improves the situation by reducing residence times of gas/fluid and minimizing unswept volumes. Would you recommend stainless steel or glass for future designs?

Thank you for this advice. We note our system is slightly overpressured, such that contamination from lab air should not occur even if PTFE is slightly permeable towards OVOCs. The effect of different materials for OVOC measurements has been investigated for example on methanol (Beale et al., 2011, supplementary material figure S1). They found that methanol strongly adsorbs on the walls of stainless-steel tubing. Albeit possibly costly, glass may be a good idea indeed. However, this would make ship board deployment more complicated due to the fragility of glass.

Line 260: Can you give us an idea of what volume of water was in the PTFE jar and tee at steady state here? That would help give us an idea of water residence time in the entire system. (Figure 1 gives a hint about the tee seems like about 10 cm³, but

the jar is unknown.)

Suggestion accepted.

260 The final blank we determined was the “wet equilibrator” blank. This consisted of stopping the water flow into the equilibrator and purging the wet equilibrator (that had been coated with bottom seawater) with zero air for 20 min. During this blank measurement, humidity in the headspace remained constant as small water droplets remained inside of the coil and were not substantially dried by the zero air. During the Arctic cruise, the wet equilibrator blank consistently resulted in the lowest blank reading on the PTR-MS for all VOCs except for methanol and acetone as a result of a contamination (discussed below). Thus, in practice the wet equilibrator blank seems to be the best surrogate for a “true” water blank for almost all VOCs measured here.

265 During the wet equilibrator blank, the bottom of the PTFE jar or PTFE tee is filled with approximately 5 mL of seawater. In the case of the tee, the water leaves the tee approximately immediately. During measurement of seawater, the residence time of zero air and seawater in the equilibrator is approximately 1 min. The residence time of zero air in the wet equilibrator blank doubles during the blank.

Line 285-295: Can you include some more detail, or perhaps expand the appendix/SI to include more specific information about how the evasion standards were made and used. How much MilliQ water was used? What was the pipette volume/precision? What was the dilution volume/mass and precision? How many dilutions were done to get to the final stock? How long was the SFCE purged before measurement?

Thank you for this suggestion. A paragraph addressing these questions has been added to supplementary material E.

Here we provide more detail on how the evasion standards of methanol, acetone and acetaldehyde were prepared in MilliQ water. For this, 303 mm³ of pure methanol (For spectroscopy Uvasol) and 55 mm³ acetone (HPLC standard) were diluted in a 0.5 dm³ volumetric flask labelled as “A”. In a 1 dm³ volumetric flask labelled “B”, 1 cm³ acetaldehyde was dissolved as measured out using a 1 cm³ volumetric flask ($\geq 99.5\%$, A.C.S. Reagent). A third flask labelled “C” of 0.5 dm³ was used to further dilute 330 mm³ of flask “A” and 330 mm³ of flask “B”. Different amounts of the flask labelled “C” were dissolved in 800 cm³ sampling bottles filled with MilliQ water. Standards were typically analysed within 4 h of dissolving the pure OVOC in water. The same 10 dm³ batch of MilliQ water was used to dissolve the pure standards and it was also syphoned into the sampling bottles. A MilliQ blank has been subtracted from the measurements of the evasion calibration curves. The same three air displacement micropipettes (20-200 mm³, 100-1000 mm³, 0.5-5 cm³) with plastic tips were used for this dilution. All volumetric flasks were class A volumetric glassware. The SFCE was typically purged with MilliQ water for at least 30 min before starting measurement. The solubilities of the VOCs at 20 °deg-C used to compute the expected mixing ratio are presented in table E1.

Line 305-310: Are the solubilities known to a level of accuracy that allow for 5 significant figures? If not, perhaps the uncertainty should be clarified.

Suggestion accepted

The precision of the purging factor depends on the precision of the solubility measurement. Since solubilities are reported in this paper to two significant figures, purging factor is reported here to two significant figures as well. For freshwater, computed purging factors assuming full equilibration and equal zero air: water flows are: 1.00015 for methanol, 1.00111 for acetone, 1.00225 for acetaldehyde, 1.063 for DMS, 1.184 for

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320 benzene, 1.2109 for toluene and 2.5768 for isoprene. The same computation in seawater gives the following purging factors: 1.00015 for methanol, 1.00122 for acetone, 1.0025 for acetaldehyde, 1.0875 for DMS, 1.221 for benzene, 1.2655 for toluene and 2.961 for isoprene. We see that PF varies from being insignificant (~ 1) for highly soluble VOCs to quite large ($\gg 1$) for the sparingly soluble gases. To compute the expected headspace

Line 354: "100cm³ n: 100cm³" should this be restated as "air and water at equal flow rates of 100 cm³ at 20 C"?

Suggestion accepted.

370 Air and water at equal flow rates of 100 cm³ at 20 °C are ~~The air to water ratio of 100 cm³ n:100 cm³~~ is chosen to allow for a reasonably long equilibration time, large surface area for exchange, and so high signal while satisfying the air flow requirements of the PTR-MS. They are also chosen such that the stripping of the soluble

Line 370: Peristaltic pumps are notoriously bad actors in dissolved gas sampling, and require assiduous attention to maintain constant flow over time. Would you recommend another pump, perhaps a magnetically coupled stainless steel gear pump, to others?

Thank you very much for your recommendation. We are looking forward to taking your recommendation on board.

Line 376: "Our aim is to build an equilibrator that fully equilibrates for the very soluble OVOCs". This sentence succinctly describes the manuscript. Consider if it can be placed somewhere in the abstract or introduction (perhaps around line 93).

Suggestion accepted. This sentence has been moved from line 376 to line 96.

95 In this paper we extend the application of the segmented flow coil equilibrator (SFCE). ~~In this paper, we present a segmented flow coil equilibrator (SFCE) that~~ is adopted from the designs used by Xie et al. (2001) and Blomquist et al. (2017) for measurements of carbon monoxide and DMS, respectively. We couple this equilibrator to a PTR-MS with the settings optimised for measurement of VOCs in the water phase. Our aim is to build an equilibrator that fully equilibrates for the very soluble OVOCs.

Line 516: Hollow cathode DC plasma discharge

Suggestion accepted.

To measure the VOC concentrations, we use a commercially available high sensitivity Proton-Transfer-Reaction Mass Spectrometer (de Gouw & Warneke, 2007; Lindinger & Jordan, 1998). Briefly, water vapor is ionised in a Hollow cathode DC plasma discharge~~hollow cathode~~. The hydronium ions react with sample air in the drift tube.

Line 528: Instead of (H₂¹⁸O⁺)H₂O (which would be m/z 39) you probably mean (H₂¹⁶O)H₃O⁺.

Indeed. Suggestion accepted.

water clusters. In practice, such water dimmers are monitored at m/z 37 (i.e. isotopic hydronium water cluster (H₂¹⁶O⁺)H₂O) as a percentage of the primary ion count, accounting for isotopic abundance (Blake et al. 2009):



Line 530: A great deal is written here about how much effort is put into managing humidity to achieve consistent results. Getting a handle on these relationships is a crucial aspect for achieve maximal PTR-MS performance and is both widely recognized and documented from a very early point in the PTR-MS methods arrival. The implementation as described basically has a PTR-MS with a heated inlet and vacuum system, in a conditioned space aboard a ship, drawing a gas/water mixture through a temperature controlled coil (the SFCE) at 20C. The vapor pressure of water at this temperature is around 17 torr. The flow rate of water vapor through the PTR-MS ion source was essentially constant (3 sccm). One might surmise these measurements benefited from an extremely predictable and stable input of water relative to air quality and biogeochemical measurements. How much variation in drift tube humidity was there? Can you show us a plot of % m/z 37 over time? How about %m/z 55? What's the return of this tweaking vs running the PTR-MS in a more conventional manner?

Thank you for this comment. Figure 1 shows a timeseries of the drift tube humidity as monitored as a fraction of m/z 21 during the deployment in the Canadian Arctic. The figure shows the drift tube humidity while measuring equilibrator headspace, outside air and zero air from a gas cylinder.

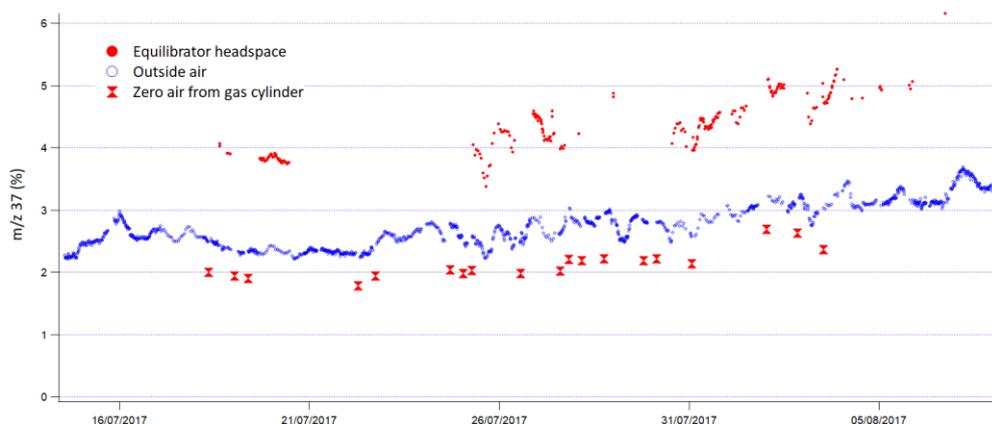


Figure 1: Timeseries of the drift tube humidity during the deployment in the Canadian Arctic when measuring outside air, equilibrator headspace and zero air from a gas canister.

Figure 1 shows that the equilibrator headspace humidity (as indicated by m/z 37) was almost always less than 5% of the m/z 21 signal.

Unfortunately, we did not monitor m/z 55, but we expect it to be very small given the small amount of m/z 37 monitored already.

Figure 2 shows the effect of varying the drift tube voltage on the abundance of the water hydronium cluster. The figure shows that at decreasing drift tube voltage, the abundance of hydronium water clusters increases.

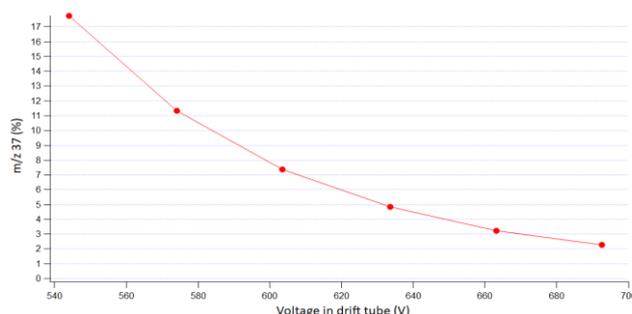


Figure 2: Abundance of water hydronium cluster in the drift tube as a function of the drift tube voltage.

An abundance above 5% of m/z 37 is undesirable. In a more recent deployment, the drift tube voltage was set to 640V which equates to 147 Td.

Line 544: "ionization by water clusters is lower energy and ..."

Suggestion accepted.

(Warneke et al. 2001). On the other hand, this process decreases the proton affinity difference between the primary ion and the VOC and thus the excess energy released on proton transfer reaction ionisation by the water cluster is softer and hence. This leads to less fragmentation for example of isoprene in the drift tube (Schwarz et al. 2009); (ii) humidity in the drift tube leads to non-collision rate limited reactions; (iii) large water

Line 544-560: *Running the instrument at 160 Td is unusual, as is the water flow (5 sccm) and discharge current (3mA). Most investigators report a sweet spot between 100 and 140 Td, with resulting uncertainties in the range of 5-25% RSD. While discharge conditions are not as commonly reported (to my dismay), the latest HS-PTR-MS user manuals up to 2011 (the last I have access to) suggest water flow rates between 6-15 sccm and discharge of 4-6 mA. While it does have the effect of reducing the abundance of hydrated clusters in the drift tube, it also decreases the reaction time and greatly increases fragmentation, both of the target analytes and of higher mass molecules, from whom the fragment ions can then interfere with the measurements. There are basically two selection criteria of the PTR-MS method (1) Only molecules with a proton affinity higher than water are detected (2) Those protonated ions can be uniquely detected at a specific m/z ratio either directly or by some signal deconvolution. By operating the PTR-MS in this configuration, it's likely that those conditions are only true for a select set of compounds. I would surmise that performance with monoterpenes, acetic acid, and anything with a terminal hydroxyl group to be especially problematic. The high degree of fragmentation of isoprene observed here is emblematic of these operating conditions. The authors should emphasize that in seeking to suppress cluster formation in the drift tube, they are making substantial performance trade-offs in other areas.*

Many thanks for these thoughts. This is helpful for our future research. The discharge current and the water flow were operated at bespoke settings following recommendations by the manufacturer. We suspect their motivation is to extend the lifetime of the source. We acknowledge

that the high drift tube voltage does lead to some fragmentation of compounds such as isoprene. However, our main focus is measurement of the very small OVOCs that do not tend to fragment. We also acknowledge that the high drift tube voltage does affect the sensitivity of the instrument as it reduces the reaction time in the drift tube. The effect of this should be captured in the gas phase calibrations. As mentioned before, in more recent deployments, the PTR-MS drift tube voltage has been set to 640V. Please see below on how the manuscript was changed upon your recommendation.

Clearly, excessive water clustering in the drift tube is undesirable. To keep the water dimer to be < 5% of the primary ion count when measuring headspace equilibrator, the PTR-MS drift tube was operated at 160Td (700V, 2.2 mBar and 80°C in the drift tube). The water vapor flow into the source was set to 5 cm³/min, the source current at 3 mA and the source valve to 35%. At these settings, the amount of hydronium water clusters is below 1% when measuring dry zero air and the amount of O₂⁺ ions is below 0.7% of the primary ion counts. Residual water cluster measured during dry canister measurement is due to unionised water vapor from the hollow cathode entering the drift tube (Warneke et al. 2001). The disadvantage of this high drift tube voltage are increased fragmentation and a reduced reaction time in the drift tube leading to overall lower sensitivity. In this case these were trade-off worth considering since the focus of these measurements are small and generally not fragmenting molecules. The decrease in sensitivity is captured through regular gas phase calibrations. The interested reader looking to do the same measurements should feel free to adapt those settings to their requirements.

Line 570-603: I'm a bit confused: how much of the background signal of OVOCs are being attributed to humidity and how much do you think is from OVOCs in the water can? Can you comment on the background signal of these other OVOCs over time? Water held under dynamic vacuum preferentially degases, so one would expect any dissolved gases to be removed from the water can after a prolonged period of PTRMS operation, especially in a warm instrument cabinet on a rocking ship, turning over the water. Reviewing several years of my own PTR-MS datasets, I see elevated backgrounds immediately after the instrument is turned on after service/water can fills, but they quickly recede to a stable signal (usually a few hundred CPS) with an extremely weak relationship between m/z 37 and m/z 45 or m/z 63.

Suggestion accepted. Our results show that for all compounds, except DMS and acetaldehyde, the backgrounds seem independent of sample humidity – i.e. all of the VOC background is coming from the source H₂O reservoir. When measuring dry synthetic air, all of the background can be attributed to VOCs in the water can. Synthetic air measurement for DMS or acetaldehyde is typically below 0.25 ppb. The contribution of sample humidity for both compounds is around 0.6 ppb as seen in fig. B1. A few sentences have been added here for clarity.

During this experiment, the source water flow in the PTR-MS was kept constant, and the ~~in this experiment,~~ zero air measurement has been subtracted ~~thus to removing~~ remove the contribution to the VOC signals from the PTR-MS source water reservoir. ~~During the experiment, the water flow into the source has been kept constant.~~ Variations in the measured background are thus due to the sample humidity alone. These results suggest that using zero air (e.g. bypassing the SFCE) as the background could lead to overestimations of dissolved DMS and acetaldehyde measurements under similar PTR-MS settings.

Line 651: I suggest calling Appendix E: "Compilation of published solubilities for methanol, acetone, and acetaldehyde".

Suggestion accepted.

Appendix E: ~~Compilation of published solubilities for methanol, acetone and acetaldehyde~~ ~~Compilation of experimentally determined solubilities for methanol, acetone and acetaldehyde~~

Table 3: (and throughout). For consistency, I suggest sticking with nmol/dm³ throughout and using scientific notation for isoprene instead of pmol dm⁻³. i.e. $9.96 \times 10^{-3} \pm 1.25 \times 10^{-3}$ nmol dm⁻³)

Suggestion accepted.

Table 2: Precision and limit of the detection of the seawater VOC measurements (6 min average).

	measurement precision 1σ	Limit of detection
methanol (nmol dm ⁻³)	6.52	19.56
acetaldehyde (nmol dm ⁻³)	0.17	0.51
acetone (nmol dm ⁻³)	0.44	1.32
DMS (nmol dm ⁻³)	0.0069	0.0207
isoprene (nmol dm ⁻³)	0.58×10^{-3}	1.74×10^{-3}
benzene (nmol dm ⁻³)	0.0043	0.0129
toluene (nmol dm ⁻³)	0.0042	0.0126

Figure 3 (a): Typo “assuming” not “assuning”.

Suggestion accepted.

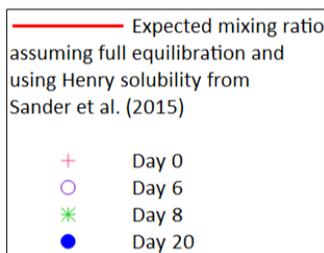


Figure 4: I suggest either using all black or using some color variation. It's hard to tell the 1:1 line and the fit to the measurement lines.

Suggestion accepted. The figure has been changed to all black and the dash size of the fit to the measurement has been increased to make it easier to distinguish from the 1:1 line.

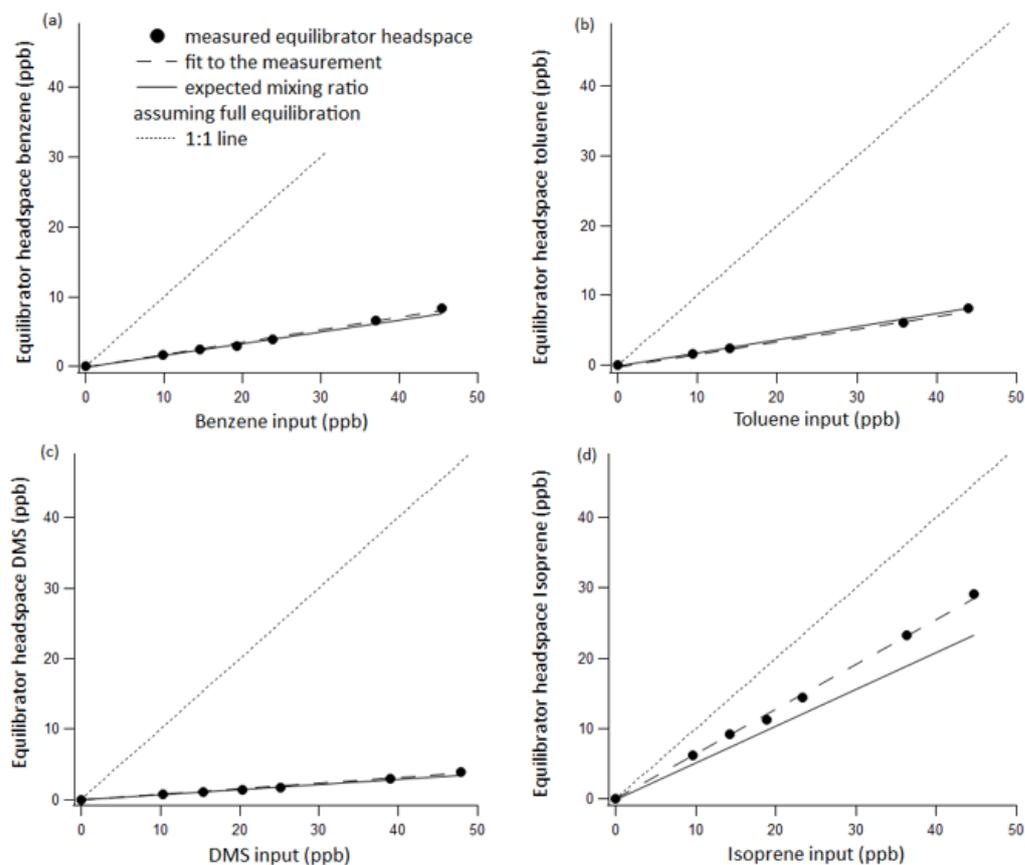


Figure 4: Invasion calibration curves for benzene (a), toluene (b), DMS (c) and isoprene (d) where a known amount of standard gas is added to the zero air carrier gas while measuring VOC-free Milli-Q water. Error bars were too small to display, but the noise associated with the measurement was found to be 0.0084 and 0.0044 ~~ppb~~ for DMS and Isoprene respectively and 0.015 and 0.013 ~~ppb~~ for benzene and toluene respectively. This was calculated as the std. dev. of 10 consecutive water blank measurements. A 1:1 line is included in 4 to illustrate the role of the water phase in absorbing these compounds.

Figure 5: This plot and caption could use some clarification. This is a comparison of range solubilities observed with the SFCE-PTR-MS system and values predicted from literature. The meaning of the numbers in the legends (1-44) of Figure 5 are not immediately clear. To help, each line could be "Ref. x" (x=1-44), with "This work" as the thick red line and "S. P. Sander" as the thick blue one. In the caption, please write what you want the reader to take away from this demonstration. It seems like you are seeing lower solubility than the literature values.

Suggestion accepted. The figure legend and figure description have been modified according to the reviewer's comments.

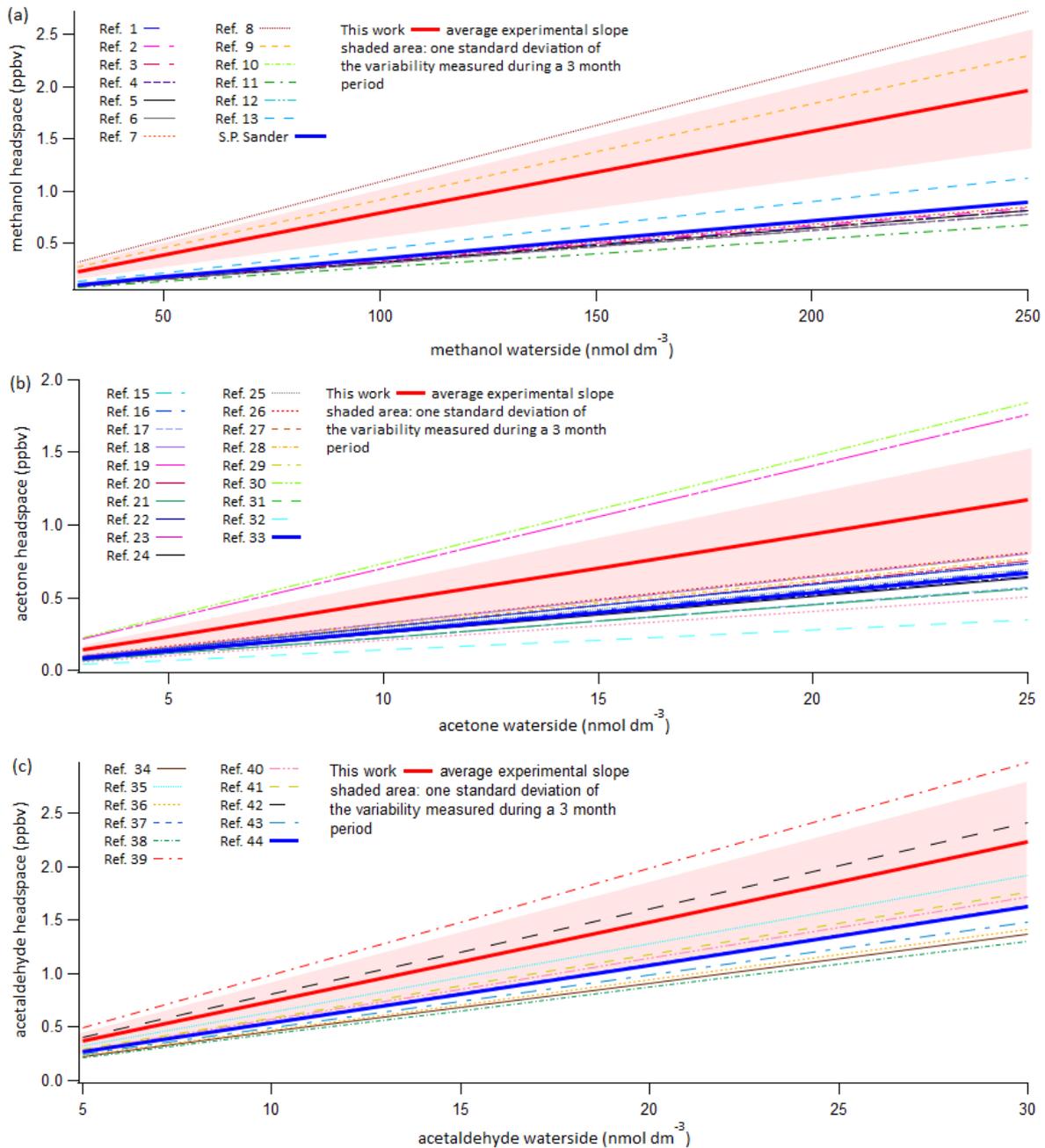


Figure 54: This is a Evasion calibrations of OVOCs. comparison of range solubilities observed with the SFCE PTR-MS system and values predicted from literature. Displayed are the average experimentally determined slopes of 14 calibration curves of methanol (a) and acetone (b) and 11 calibration curves of acetaldehyde. The figure shows that in the SFCE, These calibrations suggest possibly lower solubility of these compounds is observed than compared to literature values. (c). Shaded area indicates one sigma standard deviation of the variance in the slope during this three-month period. Average experimentally determined calibration slope for methanol, acetone and acetaldehyde were 0.00786 ± 0.00115 ppb ppbv nmol⁻¹ dm³, 0.0469 ± 0.0145 ppb ppbv nmol⁻¹ dm³ and 0.0743 ± 0.0190 ppb ppbv nmol⁻¹ dm³. Plotted along this are the predicted slopes using all experimentally determined solubilities as listed in R. Sander (2015). The recommended solubility by S. P. Sander et al., (2015) is plotted as a solid thick line in dark blue. The key to the figure is listed in the appendix, listing an in-text reference followed by the dimensionless water over air Henry solubility and the predicted slope using the experimentally determined solubility. For full reference of the cited solubilities, please refer to R. Sander (2015).

Figure 7: Can this be remade as a full page plot? The horizontal axis is extremely tight.

If size is an issue, plot gases of similar magnitude on the same subplot and use the right axis. I suggest adding to the x axis "Sample Date & Time (HH:MM DD/MM/YYYY)".

Comments applied with thanks. To address the reviewer's comments, the horizontal axis range has been reduced to make it appear less tight. Additionally, the figure size was increased by approx. 30%. The horizontal axis has been labelled accordingly.

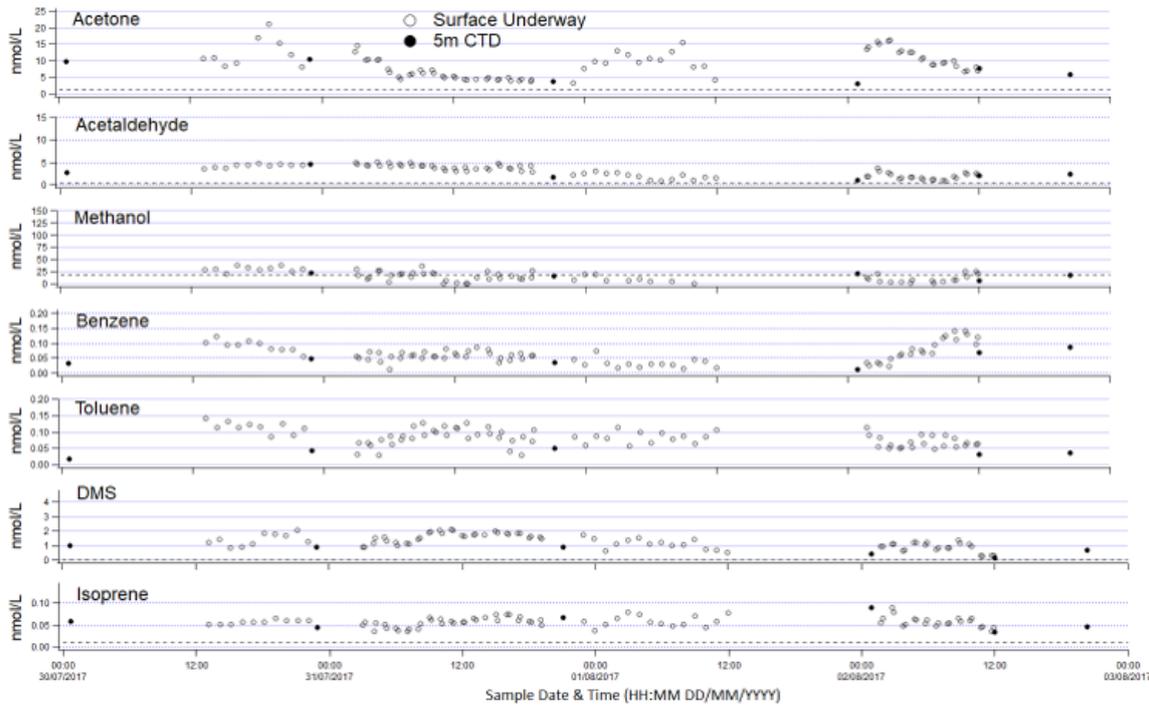


Figure 7: Selection of VOC measurements made from the ship's build in underway surface water supply (open symbols) and discrete samples from 5m rosette (closed symbols). The dotted line represents the limit of detection.

Figure B-1: Are there error bars (like the caption says) in these plots? They are not rendering on my printer or pdf.

Suggestion accepted.

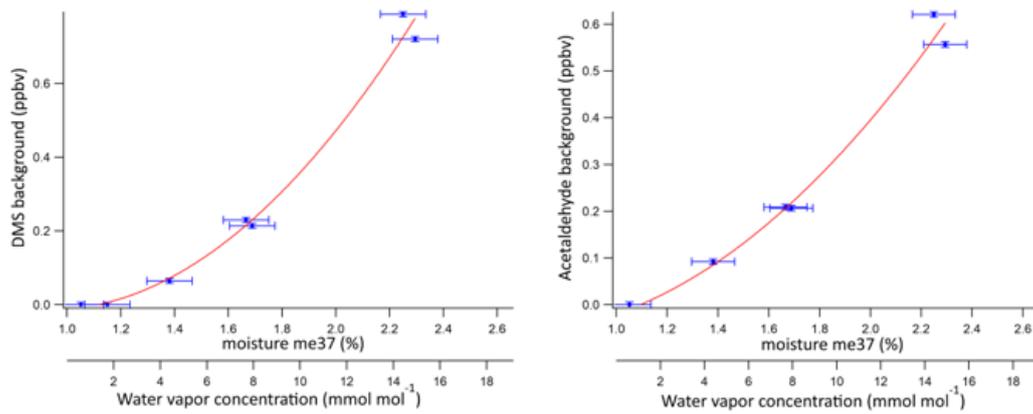


Figure B1: Background dependence of DMS (a) and acetaldehyde (b) signal on the humidity in the sample air. Error bars represent the standard deviation of ten consecutive blanks.

Reply to Reviewer 2 comments for: Segmented flow coil equilibrator coupled to a Proton Transfer Reaction Mass Spectrometer for measurements of a broad range of Volatile Organic Compounds in seawater

Many thanks for the thoughtful comments from this anonymous reviewer. Please see our responses below. Reviewer comments are in italic and replies in normal font. The changes to the manuscript are presented as figures taken from the manuscript with the changes made indicated by red track changes.

References: Please check the form of references shown in the text. For example, "Blando & Turpin, 2000" (page 1, line 28) should be shown as "Blando and Turpin, 2000", and "de Bruyn, Clark, Senstad, Barashy, & Hok, 2017" (page 2, line 43) should be shown as "de Bruyn et al., 2017".

Suggestion accepted.

Page 2, line 35 Please add the suitable references.

Suggestion accepted.

Current estimates of air–sea VOC fluxes and the cycling of VOCs in the oceans have been limited in part by our ability to measure these compounds in [the surface seawater phase](#). [For example global budgets for acetone highlight the uncertainty of oceanic emissions](#) (Fischer [et al.](#), [Jacob, Millet, Yantosca, & Mao](#), 2012). [A more recent sensitivity analysis of this model stresses the importance of accurate oceanic mixed layer concentrations on the global acetone budget, especially in the Southern Hemisphere](#) (Brewer [et al.](#), 2017).

Page 3, line 88 The response time of 10 min is only for isoprene, not for the other compounds such as acetone, methanol and so on.

Suggestion accepted.

to PTR-MS to measure four different VOCs at a time (Williams [et al.](#), 2004). A bubbling-type equilibrator has also been developed for underway measurements of a range of dissolved VOCs with PTR-MS (Kameyama [et al.](#), 2010). The large volume of the bubbling equilibrator (i.d. 15.2 cm, height 100 cm) makes it very bulky and
90 creates a long response time ([up to 18-19 min e.g. for methanol](#)~~about 10min~~). Moreover, the high-water flow requirement of this type of equilibrator ($1 \text{ dm}^3 \text{ min}^{-1}$) is also less suitable for discrete measurements.

Page 3, line93-102 Those explanations itself are generally well, but not suitable in introduction section. I assume that those sentences could be removed.

Suggestion accepted. This explanation has been moved to section 2.1.

The design of our SFCE is shown in Fig. 1. The SFCE is coupled to PTR-MS for measurement of methanol, acetone (2-propanone), acetaldehyde (ethanal), dimethyl sulphide (DMS), isoprene (2-methyl-1,3-butadiene), benzene and toluene (methyl benzene). These gases cover a large ~~solubility~~ range of solubilities (see Sect. 4.2.13.2). ~~This, demonstrates demonstrating~~ the versatility of the SFCE. ~~Though, t~~ The main advantage of this equilibrator lies in its design. Briefly, the segmented flow allows for a large surface area for gas exchange, ample equilibration time, and so a high degree of equilibration. The simple headspace and water separation system allows for rapid drainage of the sampled water as well as separation of the headspace from water without spray or droplet formation. This ~~reduces the~~enables a fast response time ~~to below 1 min~~. Due to the ease of changing the water sample intake and low water flow ($100\text{ cm}^3\text{ min}^{-1}$), the equilibrator can conveniently be used for both continuous underway and discrete measurements. The equilibrator is entirely made up of commercially available Polytetrafluoroethylene (PTFE) tubing and fittings, which should minimise adsorptive loss and make

4

the equilibrator relatively inexpensive and easy to replicate. The constant flow of water and smooth surfaces should also reduce bio fouling and facilitate occasional cleaning.

Page 10, line 334 Ionized toluene should be found in not only m/z 93 but also m/z 79 depending on the drift tube voltage. Did the authors find the fragmentation of toluene? m/z 79 is used to identify benzene amount, therefore, the authors need to care of existence of the fragmentation.

Suggestion accepted. A sentence highlighting this uncertainty has been added to the manuscript.

fragment ion m/z 41 and 39 respectively. This is in general agreement with Schwarz et al., (2009). This fragmentation ratio increases with increasing drift tube voltage (see appendix). It is possible that some of the mass 79 measured here contains a contribution from fragmenting toluene. However, because the gas standard contains both it is not straightforward to evaluate the magnitude of this interference.

Page 11, line 354 What is the ratio of “100 cm³n:100 cm³” here? Maybe typo?

Suggestion accepted. The “n” here is used to emphasized that this is a normalized mass flow delivered by a mass flow controller. This has been highlighted on page 4, line 115-116.

Segmented flow coil equilibrator coupled to a Proton Transfer Reaction Mass Spectrometer for measurements of a broad range of Volatile Organic Compounds in seawater

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Abstract. Here we present a technique that utilises a segmented flow coil equilibrator coupled to a Proton Transfer Reaction-Mass Spectrometer to measure a broad range of dissolved volatile organic compounds and gases. ~~Due to its relatively unique design composed of a segmented flow~~ large surface area for gas exchange, small internal volume, and smooth headspace-water separation ~~ion~~, the equilibrator is highly efficient for gas exchange and has a fast response time (under 1 min). The system allows for both continuous and discrete ~~and continuous~~ measurements of volatile organic compounds in seawater due to its ~~ease of changing sample intake~~ and low sample water flow (100 cm³ min⁻¹) and the ease of changing sample intake. The equilibrator setup is both relatively inexpensive and compact. Hence it can be easily reproduced and installed on a variety of oceanic platforms, particularly where space is limited. ~~As a result of its~~ The internal area of the equilibrator is smooth and unreactive surfaces. Thus, the segmented flow coil equilibrator is expected to be less sensitive to biofouling and easier to clean than membrane-based equilibration systems. The equilibrator described here fully ~~equilibrates for gases that are similarly soluble or more soluble than toluene,~~ and can easily be modified to fully equilibrate for even less soluble gases. The method has been successfully deployed in the Canadian Arctic. ~~Here,~~ Some example data of underway surface water and Niskin bottle measurements in the sea ice zone are presented to illustrate the efficacy of this measurement system.

1 Introduction

30 Volatile organic compounds (VOCs) are present ubiquitously throughout the atmosphere (Heald et al., 2008) and play important roles in the chemistry of ozone chemistry (Monks, 2005) and OH concentrations (Lewis et al., 2005) as well as in particle formation (Blando ~~and~~ Turpin, 2000). For example, acetone, acetaldehyde and methanol particularly affect the oxidative capacity of the remote marine atmosphere (Lewis et al. 2005). The oxidation products of dimethyl sulphide (DMS) and isoprene are important particle precursors

35 in the marine atmosphere that may affect cloud formation and ~~the albedo effect of the planet~~the Earth's radiative balance (Charlson, ~~Lovelock, Andreae, & Warren et al.~~, 1987; Claeys et al., 2004). Benzene and toluene are organic pollutants typically emitted from anthropogenic sources, e.g. by ship traffic (Saeed ~~and~~ Al-Mutairi, 1999). The oceans play an important role in controlling atmospheric VOC concentrations by exchanging VOCs with the atmosphere (Carpenter et al., 2012).

40 Current estimates of air-sea VOC fluxes and the cycling of VOCs in the oceans have been limited in part by our ability to measure these compounds in ~~the surface seawater phase~~. For example global budgets for acetone highlight the uncertainty of oceanic emissions (Fischer ~~et al.~~, ~~Jacob, Millet, Yantosca, & Mao~~, 2012). A more recent sensitivity analysis of this model stresses the importance of accurate oceanic mixed layer concentrations on the global acetone budget, especially in the Southern Hemisphere (Brewer et al., 2017).

45 Only a small number of methods allow for in situ quantification of VOCs. For example, derivatisation methods have been used, which require the synthesis of toxic chemicals to determine aldehyde concentrations in seawater with detection by high performance liquid chromatography (Zhu ~~and~~ Kieber, 2018). Such methods are not suitable for measuring a large number of samples. Most methods of detection require the analyte to be in the gas phase, necessitating an adequate extraction or equilibration device.

50 ~~Previous~~Some waterside dissolved gas concentration measurements have ~~primarily~~ been made using purge and trap (PT) systems coupled to Gas Chromatograph – Mass Spectrometers (de Bruyn, ~~Clark, Senstad, Barashy, & Heket et al.~~, 2017). This method is sensitive enough to allow detection in seawater (quantification down to nmol dm^{-3}) but requires manual handling and is often more suitable for discrete measurements. A Gas Chromatograph - Mass Spectrometer has been coupled to a PT system to measure benzene and toluene amongst other compounds (Huybrechts ~~et al.~~, ~~Dewulf, Moerman, & Langenhove~~, 2000). Others have coupled PT systems to a Gas Chromatograph - Flame Ionisation Detector to measure isoprene (Exton, ~~Suggett, Steinke, & McGinity et al.~~, 2012), ethanol, and propanol in seawater (Beale et al., 2010). ~~However, t~~These setups are only suitable for discrete samples with a sample treatment time of under 2h and care must be taken to avoid wall adsorption and desorption effects in the setup. A ship-based PT Gas Chromatograph - Mass Spectrometer has been used to measure a broad range of VOCs in discrete surface water samples with a three-hour frequency; ~~t~~. ~~However t~~this required two people and represented a considerable workload (Schlundt et al., 2017). Some purge and trap systems have been automated to allow for underway measurements of halocarbons, DMS, and isoprene semi-continuously every ca. 30 minutes (Andrews et al., 2015). ~~Extracted or equilibrated air from seawater contains a large amount of water vapour, which potentially affects the VOC detection. Thus, a dryer is often used to reduce the humidity in the sample air. Measurement of very reactive/sticky gases such as methanol or acetone is problematic using this method due to adsorption and desorption on the dryer or tubing~~ (Beale, Liss, Dixon, & Nightingale ~~et al.~~, 2011; Kameyama et al., 2010). ~~Additionally, the~~The fairly long measurement time ~~does not enable~~preclude high-resolution measurements ~~required for more reactive gases that display fine scale variability of these biologically reactive and short lived gases~~. This highlights the need for continuous, fast, and automated measurement techniques that do not require pre-treatment.

70 Two types of equilibrators are commonly used for continuous measurements of dissolved gases. One type allows for direct exchange between the carrier gas and the water, while the other uses a membrane to

extract gases. Directly exchanging equilibrators such as the Weiss-style showerhead equilibrator (Johnson, 1999) allow underway CO₂ measurements with a <35 minute frequency. This has been used widely to measure
75 CO₂ and short lived halocarbons (Arévalo-Martínez et al., 2013; Butler et al., 2007). However, spray generated from the showerhead lengthens the equilibrator's response time for highly soluble gases, making it less suitable for high frequency measurements of highly soluble VOCs such as methanol (Kameyama et al., 2010). Membrane equilibrators avoid spray formation and allow for selective diffusion. Hollow fibre membranes have previously been used for measurement of dissolved CO₂ (Hales et al., Takahashi, & Bandstra, 2005; Sims et al., 2017) and DMS (Tortell, 2005; Yang, Blomquist, Fairall, Archer, & Huebert et al., 2011). They have previously been used to extract volatile compounds from the water phase continuously (Tortell, 2005). By using a hydrophobic membrane, the amount of water vapor in the detector can be reduced. For example membrane inlet mass spectrometers have been used to measure DMS and inorganic gases in seawater with a measurement frequency of more than once per minute (Tortell, 2005). Underway measurements of seawater DMS
85 concentrations have been made with a 1 minute frequency using a Chemical Ionisation Mass Spectrometer (CIMS) coupled to a porous Teflon membrane (Saltzman et al., de Bruyn, Lawler, Marandino, & McCormick, 2009). One disadvantage of membrane equilibrators is that the equilibration efficiency could be affected by biological growth on the membrane surface (biofouling), especially in biologically productive areas where some VOCs are known to have strong sources.

90 Extracted or equilibrated air from seawater contains a large amount of water vapour, which potentially affects the sensitivity of VOC detection and could cause condensatation in the sample tube. Thus, a dryer is often used to reduce the humidity in the sample air for measurements of gases including DMS and CO₂. Measurement of very soluble/sticky gases such as methanol or acetone is problematic with this approach due to gas adsorption and desorption on the dryer or tubing material (Beale et al., 2011; Kameyama et al., 2010). Thus the effect of high sample humidity needs to be considered in the design of the measurement system.

The choice of detector that the equilibrator is coupled to is crucial as well. Proton Transfer Reaction - Mass Spectrometry (PTR-MS) is a widely used tool that allows high-frequency (0.1–1s) measurement of a broad range of trace gases in the atmosphere (Lindinger and Jordan, 1998; Blake et al., 2009). It is similarly suitable for high-resolution ship-based measurements of VOCs. Efforts have been made to quantify methanol, acetone,
100 and acetaldehyde in discrete water samples using a membrane system coupled to PTR-MS (Beale et al., 2011). This represents a significant advance over the methods described above as there is no need for sample pre-treatment and the setup does not contain reactive surfaces. Others have used a purge and trap system coupled to PTR-MS to measure four different VOCs at a time (Williams et al., 2004). A bubbling-type equilibrator has also been developed for underway measurements of a range of dissolved VOCs with PTR-MS (Kameyama et al., 2010). The large volume of the bubbling equilibrator (i.d. 15.2 cm, height 100 cm) makes it very bulky and
105 creates a long response time (up to 18-19 min e.g. for methanol about 10min). Moreover, the high-water flow requirement of this type of equilibrator (1 dm³ min⁻¹) is also makes it less suitable for discrete measurements.

In this paper we extend the application of the segmented flow coil equilibrator (SFCE). In this paper, we present a segmented flow coil equilibrator (SFCE) that is adopted from the designs used by Xie et al. (2001)
110 and Blomquist et al. (2017) for measurements of carbon monoxide and DMS, respectively. We couple this

115 equilibrator to a PTR-MS with the settings optimised for measurement of a broad range dissolved VOCs in humid equilibrator headspace in the water phase. The main aim is to build an equilibrator that fully and rapidly equilibrates for the very soluble OVOCs (Oxygenated Volatile Organic Compounds, in this paper referring to methanol, acetone and acetaldehyde). The main advantage of this equilibrator lies in its design. Briefly, the segmented flow allows for a large surface area for gas exchange, ample equilibration time, and so a high degree of equilibration. The simple headspace and water separation system allows for rapid drainage of the sampled water as well as separation of the headspace from water without spray droplet formation. This reduces the response time to below 1 min. Due to the ease of changing the water sample intake and low water flow ($100 \text{ cm}^3 \text{ min}^{-1}$), the equilibrator can conveniently be used for both continuous underway and discrete

120 measurements. The equilibrator is entirely made up of commercially available Polytetrafluoroethylene (PTFE) tubing and fittings, which should minimise adsorptive loss and make the equilibrator relatively inexpensive and easy to replicate. The constant flow of water and smooth surfaces should also reduce bio-fouling and facilitate occasional cleaning. The equilibrator is described in detail in Sect. 2.1. The effect of humidity on the dissolved gas measurements by the PTR-MS A consideration with using PTR-MS for measurement of dissolved gases is the effect of humidity on the measurement calibration. A discussion on how this is addressed can be found is described in Sect. 2.2 and in the Supplementary material. The computation of dissolved VOC concentrations is described in Sect. 3.2. A consideration in making seawater VOC measurements is the difficulty in getting an accurate background, or blank. Hence ~~the~~ choice of blanks, or backgrounds for dissolved VOC background concentration measurements is discussed and described in Sect. 4.3.1. ~~The computation of dissolved and expected VOC concentrations is described in Sect. 3.2.~~ We assess the performance of the SFCE coupled to -PTR-MS system in Sect. 4, focusing in particular on the equilibration efficiency (Sect. 4.2), and response time (Sect. 4.3) and limit of detection (Sect. 4.4). Installation of the SFCE on a ship along with some sample data from an Arctic cruise is presented in Sect. 5. ~~The final consideration with using PTR-MS for measurement of dissolved gases is the effect of humidity on the measurement calibration. A discussion on how this is addressed can be found in Sect. 4.1 and in the appendix.~~

135

2 System description

2.1 Segmented flow coil equilibrator

The design of our SFCE is shown in Fig. 1. The SFCE is coupled to PTR-MS for measurement of methanol, acetone (2-propanone), acetaldehyde (ethanal), dimethyl sulphide (DMS), isoprene (2-methyl-1,3-butadiene), benzene and toluene (methyl benzene). These gases cover a large ~~solubility~~ range of solubilities (see Sect. 4.2.13.2). ~~This demonstrates demonstrating~~ the versatility of the SFCE. ~~Though, the~~ main advantage of this equilibrator lies in its design. Briefly, the segmented flow allows for a large surface area for gas exchange, ample equilibration time, and thus a high degree of equilibration. The simple headspace and water separation system allows for rapid drainage of the sampled water as well as separation of the headspace from water without spray or droplet formation. This reduces the enables a fast response time to below 1 min. Due to the ease of changing the water sample intake and low water flow ($100 \text{ cm}^3 \text{ min}^{-1}$), the equilibrator can conveniently be used for both continuous underway and discrete measurements. The equilibrator is entirely made up of commercially

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185 available Polytetrafluoroethylene (PTFE) tubing and fittings, which should minimise adsorptive loss and make the equilibrator relatively inexpensive and easy to replicate. The constant flow of water and smooth surfaces should also reduce biofouling and facilitate occasional cleaning.

190 In our setup, the SFCE takes approximately equal, continuous flows of high purity zero air ($100 \text{ cm}^3 \text{ n min}^{-1}$, where n indicates normalised mass flow at 0°C , 1 atm; controlled by a Bronkhorst mass flow controller) and unfiltered seawater ($95\text{--}100 \pm 5 \text{ cm}^3 \text{ min}^{-1}$, controlled by a peristaltic pump, Watson Marlow 120 S/DV with 8 cm long Pumpsil platinum cured silicone tubing 4.4 mm i.d.). We used either Ultra-low VOC zero air (Praxair) scrubbed by a hydrocarbon trap or BTCA grade zero air (BOC) oxidized by a custom-made Platinum-catalyst (heated to 450°C) as the zero air carrier gas for the SFCE. Complete oxidation of VOCs in the custom made PT-Catalyst has been demonstrated previously for both dry air and air that is fully saturated with water at 20°C (Yang and Fleming, 2019). ~~(Yang & Fleming, 2018).~~

200 The seawater is supplied-pumped either from the ship's underway water system or, in the case of discrete measurements, via 900 cm^3 glass sample bottles ~~in the case of discrete measurements~~ (Sect. 5.12.2). The carrier gas and water meet in a ~~PTFE-Teflon~~ tee piece (4 mm inner diameter), which naturally leads to the formation of distinct segments of carrier-gas/zero air and water. The segments travel through a coiled, 10 m long PTFE tube (outer diameter 6.35 mm, wall thickness, 1.19 mm). Each segment of carrier gas or water is approximately 1.5 cm long, giving an approximate total surface of exchange of 82 cm^2 in the coil. The coil is immersed in a water bath kept at a constant temperature of 20°C . The residence time in the 10 m tube is approx. 0.6 min. Laboratory measurements indicate that regardless of the initial water temperature ($0\text{--}25^\circ\text{C}$), the water exiting the equilibrator has a temperature of $20 \pm 1^\circ\text{C}$. Keeping the temperature essentially constant has the benefit of (i) simplifying calibrations/calculations of aqueous concentration, and (ii) in the case of cold, high latitude seawater samples, increasing the VOC signal in the headspace as warming to 20°C reduces the gas solubility. A rapid biological response to this warming is not expected ~~due to the very short residence time~~ in the segmented flow coil due to the very short residence time of 0.6 min.

210 In the initial design, after equilibration in the coiled segmented flow tube, the carrier-gas-analyte-equilibrated air-water mixture is separated in a 200 cm^3 PTFE jar (Saville). Here, the sample gas mixture is going/travels/goes towards the PTR-MS and the seawater is-drained away rapidly via a U-shaped drain (Fig. 1B). The U-shaped drain prevents intrusion of lab air and prevents the equilibrated-gas/sample air from escaping via/through the water drain. We estimate a response time of about 2 minutes with the PTFE jar as the air-water separator. This is due to a combination of its sizable internal volume and the production of water-droplets/sea spray inside of the jar due to the falling droplets. The latter, which buffered the headspace to step-changes in seawater concentration in the case of highly soluble gases. After the Arctic-Arctic field deployment, the PTFE jar was found to slightly outgas some VOCs (see Sect. 4.3.1 for further information) and was replaced with a PTFE tee piece (Swagelok, outer diameter: 12.7 mm, wall thickness 1.6 mm). This modification improved the system response time to less than 1 minute by greatly reducing the volume of the air-water separator and allowing for a smooth separation of the equilibrated air-water mixture headspace and water segments without droplet formation (see Sect. 4.34). ~~This also allows for~~ the entire SFCE ~~to~~ consist of readily available PTFE tubing

and fittings ~~routinely~~ used routinely for air sampling ~~and are thus not expected to interact with these compounds~~. See Fig. 1 for these two designs.

225 ~~At the exit of the equilibrator~~On the top end of the air-water separator, the humid headspace ~~air~~ (100 cm³n min⁻¹) is diluted with dry zero air (20 cm³n min⁻¹, same as the carrier gas, controlled by another Bronkhorst mass flow controller). This prevents condensation in the ~2 m PTFE tubing between the equilibrator and the heated (80°C) inlet of the PTR-MS (Fig. 1). ~~This facilitates installation on board as detector and equilibrator can be within approx. 5m from each other.~~The SFCE system is operated at a slight overpressure (~~measured to be~~ approx. 0.024 mbar above atmospheric pressure) in order to reduce the likelihood of lab air contamination (e.g. 230 due to leaks). A vent is installed upstream of the PTR-MS to avoid pressurizing the detector. The vent flow is typically ~20 cm³ min⁻¹ – the residual between the carrier gas flow (100 cm³n min⁻¹), the dilution flow (20 cm³n min⁻¹), as well as the PTR-MS intake flow (~100 cm³ min⁻¹).

235 The entire SFCE system fits on a bench space of about 40 cm by 40 cm (see ~~appendix~~Supplementary material). ~~Importantly, t~~The SFCE is designed such that a failure of an individual component does not result in a catastrophic over- or under-pressurization of the system. For example, if the carrier gas is stopped (e.g. gas supply runs out), the PTR-MS simply measures lab air via the vent and the water is drained from the SFCE as usual. If the water flow from the underway sampling stops, the peristaltic pump will simply pump lab air into the equilibrator. These unexpected failures can be easily identified as lab air has typically much higher concentrations of VOCs than ~~marine air or equilibrator headspace gas~~sample air~~equilibrator headspace in a~~ 240 marine environment. If the PTR-MS fails, the headspace ~~gas~~air gas simply exits via the vent and/or the top of the U-shaped drain.

Due to the smooth surfaces and constant and complete water renewal, the equilibrator should not be very prone to biofouling. The lack of a membrane for gas exchange means that the degree of equilibration should not vary significantly even if there is some biofouling. To clean the SFCE if necessary, the seawater intake and the water drain pipe are connected to a 10% HCl solution for 10 min. During this ~~operation~~procedure, the PTR-MS is disconnected to sample lab air and the gas flow is stopped. A flow of HCl thus covers all the parts of the equilibrator that are normally exposed to seawater. To resume measurement of ambient seawater, the flow of HCl is stopped and the carrier gas flow is started to drain the HCl safely into the recirculated solution. The equilibrator is typically rinsed with seawater before resuming measurement.

250 2.2 PTR-MS operation

255 Equilibrator headspace mixing ratios were initially computed using compound specific rate constants of the reaction between the VOC in question and the hydronium ions in the drift tube of the mass spectrometer (Yang et al., 2013; Zhao and Zhang, 2004). Pre and post cruise dynamic gas phase calibrations using a gravimetrically prepared VOC gas standard (Apel-Riemer Environmental Inc., Miami, Florida, USA, 517 nominal volume mixing ratio of 500 ppbv for acetaldehyde, 490 ppbv-methanol, 512 ppbv-acetone, 491 ppbv-isoprene, 527 ppbv DMS, 500 ppbv-benzene, 483 ppbv-toluene) and two Bronkhorst mass flow controllers agree within 15% of the computed mixing ratios for all VOCs except isoprene. Isoprene was found to fragment significantly where 17% of the isoprene molecules are found at the primary ion (m/z 69) and 30% and 53% were found at

260 the fragment ion m/z 41 and 39 respectively. This is in general agreement with Schwarz et al. (2009). This fragmentation ratio increases with increasing drift tube voltage (see Supplementary material). It is possible that some of the mass 79 measured here contains a contribution from fragmenting toluene. However, because the gas standard contains both compounds, it is not straightforward to evaluate the magnitude of this interference.

265 The PTR-MS measurements can be affected by humidity. Our use of a dilution flow lowers the humidity in the sample gas by 20% and thereby reduces the measurement sensitivity to humidity. To check for the effect of humidity on the PTR-MS measurement, gas calibrations were carried out at different humidities using three Bronkhorst mass flow controllers. To produce carrier gas air at different humidities, a flow of moist air saturated in humidity at 20°C is generated by passing zero air through a wetted SFCE and diluted by varying amounts of dry zero air directly from a gas canister cylinder. This mixture is scrubbed by the Pt-catalyst (-which does not appear to change the humidity levels) and then added to the flow of VOC gas standard.

270 The signal of most VOCs monitored is independent of the sample humidity. However, isoprene, benzene and toluene show a weak humidity dependence in their gas phase calibrations. Changing the humidity in sample air from completely dry to nearly saturated in humidity at 20°C, the abundance of isoprene primary ion increases by 33% (see Supplementary material). This is because the hydronium water clusters do not cause isoprene fragmentation upon ionisation (Schwarz et al., 2009). The opposite is observed with benzene and
275 toluene where primary ion abundance was found to decrease by 12% and 18% respectively over same humidity range. This is because the humidity makes ionisation less efficient (see Supplementary material). In fact, hydronium water clusters have a lower ionisation energy, thus ionising benzene and toluene less effectively (de Gouw and Warneke, 2007; Warneke et al., 2001); see Supplementary material. The humidity dependant slopes from the gas phase calibrations were used to correct the measured equilibrator headspace mixing ratios. For a
280 more detailed discussion on the settings of the PTR-MS during deployment, the computation of VOC mixing ratios in the PTR-MS, and the effects of humidity on the signal amplitude and background, please see the Supplementary material. We note that our use of a dilution flow lowers the humidity in the sample gas by 20% and thereby reduces the measurement sensitivity to humidity.

2.2 Field deployment

285 The SFCE has been field tested on a three week research cruise in the Arctic for measurements of underway surface water and discrete samples from depth profiles (Sect. 5). For underway measurements, seawater from the ship seawater supply was continuously piped into an open topped PTFE beaker fixed in the sink and allowed to overflow. The seawater was pulled by the peristaltic pump into the SFCE from the bottom of this beaker. This is to buffer pressure variations and so variable flow rates in the underway water supply, which
290 could affect instrument response (Sect. 4.2). The open topped beaker also allows marine debris to diffuse and escape from the top, rather than clogging the SCFE intake. Since there are no membranes, small particles that do enter the SCFE simply pass through the 4 mm inner diameter tube and are drained away.

295 Discrete water samples from the ship's rosette were collected in 900 cm³ ground stopper glass sample bottles via Tygon tubing. Sample bottles were rinsed three times and overfilled without introducing bubbles to avoid air contamination. To measure discrete samples, the underway measurement was stopped, and the PTFE

300 ~~water intake tube was simply moved from the seawater intake to each sample bottle (water flow stopped during changeover). Water was pumped from the bottom of the 900 cm³ sample bottles, while minimizing agitation. The top 5 cm of the discrete water sample was not measured because of the possibility of air contamination. Sampling time per bottle was under 9 min. The analysis of about eight discrete samples including blank measurements (Sect. 3.1) is typically finished within two hours of sample collection. This should be fast enough to avoid sample degradation of even the most reactive VOCs (Beale et al., 2011). To verify that the seawater supplied by the ship's underway water supply is uncontaminated, we sampled at every station from 5m depth. The underway and rosette samples are compared in Sect. 5.~~

305 ~~3 Derivation of Dissolved VOC concentrations from SFCE/PTR-MS measurements~~ ~~Derivations of dissolved VOC concentrations~~

The PTR-MS measures VOC mixing ratios (in ~~ppb~~ppbv) in the headspace of the equilibrator. Below we discuss how to convert these mixing ratios to dissolved ~~waterside-gas~~ concentrations (in nmol dm⁻³). Headspace equilibrator VOC mixing ratios are converted to ~~ppb~~nmol dm⁻³ using the ideal gas law as stated in Eq. (1):

$$\frac{n}{V} = \frac{P}{R * T} \quad (1)$$

310 Where n (mol) represents the quantity of matter, V (dm³) represents the volume of gas, P (Pa) represents the pressure, $R = 8.314$ (m³ Pa K⁻¹ mol⁻¹) ~~represents the gas constant of 8.314~~ and $T = 293.15$ (K) ~~represents the temperature in the segmented flow tube of 293.15 K~~. A conversion factor of 0.001 is applied to convert from m³ to dm³.

315 The degree of equilibration for each gas in the ~~SFCCFE~~ was determined experimentally and is presented in Sect. 4. ~~23~~. For compounds that fully equilibrate in the equilibrator, the following Eq. (2) is used to compute the measured dissolved gas concentrations:

$$C_w = (C_a - C_{a_0}) * H * PF * 1.2 \quad C_w = C_a - C_{a_0} * H * PF * 1.2 \quad (2)$$

320 Where C_w (nmol dm⁻³) represents the dissolved ~~waterside-gas~~ concentration, C_a (~~ppb~~ppbv) represents the measured headspace mixing ratio, C_{a_0} (~~ppb~~ppbv) represents the background mixing ratio (see Sect. ~~43~~.1), H represents the dimensionless liquid-over-gas form of Henry solubility (see Sect. ~~43~~.2.1), PF represents a purging factor (see ~~appendix Supplementary material and, sect. 4.2.1 text below~~), a factor of 1.2 is applied to account for the dilution of these gases in the headspace of the equilibrator.

325 Equilibrator headspace is laden with water vapour and humidity is known to influence the PTR-MS measurement (de Gouw and Warneke, 2007). For a more detailed discussion on the settings of the PTR-MS during deployment, the computation of VOC mixing ratios in the PTR-MS, and the effects of humidity on the signal amplitude and background, please see the appendix Supplementary material.

For compounds that partially equilibrate, the mean calibration curve estimated from liquid standards diluted in MilliQ water (S in μppbv nmol⁻¹ dm³) was used to determine measured waterside dissolved gas concentrations after subtraction of the background;

(3)

$$330 \quad C_w = (C_a - C_{a_0}) * \frac{1}{S} \quad C_w = C_a - C_{a_0} * 1S$$

This is more suitable than Eq. (2) as the Henry solubility and the purging factor do not apply for partially equilibrating gases. Technically, using a freshwater calibration curve to calculate gas concentrations in seawater will introduce an uncertainty (nominally within 120%) due to the effect of salinity on gas solubility. Of all the VOCs studied here, the highly insoluble isoprene is the only one that does not completely equilibrate in the SFCE. The salting out effect of isoprene seems small relative to the uncertainty in the isoprene calibration curves (Sect. 4.2.23.2) and is thus neglected here.

3.1 Estimation of the background and system blank

340 The ideal system blank for seawater VOC measurements would be VOC-free seawater. However, we have been unable to generate or obtain seawater that is free of methanol, acetone or acetaldehyde due to the high solubility and ubiquity of these gases. Additionally, it is debatable which seawater may be free of methanol, acetone or acetaldehyde due to a lack of understanding in the cycling of these compounds. The choice of background is most important for the soluble VOCs (methanol, acetone, acetaldehyde) as the ratio of background to signal can be quite high and the background can be variable. For example, for acetone the average signal to background ratio during field testing for three weeks was 1.62 with a background standard deviation of 26%. Below, we discuss three different approaches at estimating the background of the seawater VOC measurements.

350 First, direct measurements of carrier gas zero air (i.e. bypassing the SFCE) are used to track any drift in the internal PTR-MS background. This simple method of blanking was used by e.g. Yang et al., (2013). Since humidity is known to affect the background of some of the measured compounds (de Gouw & Warneke, 2007) (see appendix), we do not expect bypassing the equilibrator with zero air to give the most representative blanks for all seawater VOCs because (i) zero air has a much lower humidity than the equilibrator headspace; (ii) it does not account for any possible contamination within the equilibrator.

355 Second, at every sampling station, water from the bottom of the water column was collected and measured. Here we define the bottom water as the deepest water sample provided by the rosette, which was between 290 m and 1700 m (well below the mixed layer). For certain VOCs that are only produced in the

surface ocean and rapidly consumed at depth (such as DMS), it might be expected that their concentrations in deep water to be close to zero. However, there is insufficient field data to know whether this is the case for all the VOCs monitored here. Measurements of methanol and acetone in the north Atlantic show that their concentrations do decrease below the mixed layer (Williams et al., 2004) but do not necessarily go to zero. Similarly, depth profile measurements showed acetone concentrations near the detection limit (0.3 nM) at 200 m (Beale, Dixon, Arnold, Liss, & Nightingale, 2013), while methanol and acetaldehyde concentrations at depth did not decrease as rapidly. We note that for these measurements a flow of dry nitrogen was used as a background which may be an underestimation of the true system blank for acetaldehyde (see appendix). The chief advantage of using the bottom water measurement as the background is that the headspace gas has the same properties (humidity, temperature, exposure to the equilibrators) after equilibration as the headspace equilibrated with surface water and has been through the same collection protocol as the surface water samples.

The final blank we determined was the “wet equilibrator” blank. This consisted of stopping the water flow into the equilibrator and purging the wet equilibrator (that had been coated with bottom seawater) with zero air for 20 min. During this blank measurement, humidity in the headspace remained constant as small water droplets remained inside of the coil and were not substantially dried by the zero air. During the Arctic cruise, the wet equilibrator blank consistently resulted in the lowest blank reading on the PTR-MS for all VOCs except for methanol and acetone as a result of a contamination (discussed below). Thus, in practice the wet equilibrator blank seems to be the best surrogate for a “true” water blank for almost all VOCs measured here.

The 200 cm³ jar used for separating the headspace from the seawater after equilibration is made from PTFE, and thus was not expected to cause any contamination. However, we found that the empty equilibrator blanks of methanol and acetone were about 0.2 ppb higher than their deep water blanks during the Arctic cruise. The most plausible explanation for this seems to be an emission of methanol and acetone from the PTFE jar itself, which is suppressed during the water measurement. During the three-week field deployment, we observed a strong correlation between zero air and bottom water measurements ($R^2=0.92$ methanol, $R^2=0.69$ acetone), suggesting the concentrations of these VOCs at depth are either uniform or very small. Because of the contamination as described above, we report seawater acetone and methanol concentrations from this cruise using bottom water as a blank; these concentrations should thus be viewed as lower limit estimates. After the cruise, we replaced the PTFE jar with a PTFE tee fitting (Swagelok) and this contamination greatly decreased.

We find that ultrapure MilliQ water or bottom seawater water is typically free of the less soluble compounds such as DMS, toluene, benzene and isoprene. This is confirmed by good agreements between the wet equilibrator blanks and the MilliQ/ bottom seawater measurements. The agreements also suggest that our system is not affecting the measured concentrations of these compounds e.g. through cell lysis. The concentrations of methanol, acetone, and acetaldehyde measured in the MilliQ water are much higher than those in seawater and are highly variable. Thus, we conclude that MilliQ water is not free of these gases (see appendix). Similarly, we found that tap water or bottled drinking water is typically not free of methanol, acetone, and acetaldehyde, likely due to slow leakage of these compounds from the piping or plastic container.

3.2 Estimation of equilibration efficiency

430 As a brief recap, for gases that appear to fully equilibrate in the SFCE, seawater concentrations (C_w) are computed from the equilibrator headspace mixing ratio (C_a) using the dimensionless Henry solubility constant (H) (R. Sander, 2015). Headspace equilibrator mixing ratios are converted from ppb to nmol dm^{-3} using the ideal gas law and the dilution of equilibrator headspace is accounted for by multiplying measured equilibrator mixing ratios by 1.2 (Sect. 3, Eq. (2)).

435 Where possible, values for Henry solubility recommended by S. P. Sander et al., (2015) were used for this calculation as those were deemed most reliable. These values represent freshwater solubilities and are converted to seawater solubilities accounting for salting-out effects (Johnson, 2010). Values of the dimensionless Henry solubility (water over gas) in freshwater and seawater as well as the references for the solubility are displayed in Table 1.

440 Two methods are used to assess the equilibration efficiency of the SFCE: evasion and invasion. In evasion experiments, liquid standards of methanol, acetone and acetaldehyde were prepared by serial dilution of the pure solvent in the same batch of MilliQ water. Aliquots of pure, undiluted methanol (For spectroscopy Uvasol) and acetone (HPLC standard) were dispensed using volumetric pipettes. A 1 cm^3 volumetric flask was used to aliquot pure acetaldehyde ($>99.5\%$, A.C.S. Reagent). Subsequent dilutions utilised a volumetric pipette and volumetric flask. Liquid standards of Isoprene and DMS were prepared gravimetrically airtight each day. A syringe pump (New Era Pump Systems) was used to dynamically dilute DMS and isoprene standards in a flow of MilliQ water. For this calibration, the flow of MilliQ water is measured at the drain.

445 For evasion experiments, a solubility-dependent fraction of dissolved VOCs is transferred into the gas phase during the equilibration process. Thus, the final dissolved concentration will be somewhat lower than the initial concentrations. To account for the removal of a fraction of these gases from the waterside during equilibration, a purging factor (PF) based on mass conservation is applied. The PF is the ratio between the waterside concentration before and after complete equilibration in the coil. The derivation of this compound specific purging factor is presented in the appendix. At equal air and water flow rates, it simplifies to:

$$PF = \frac{C_w(\text{before equilibration})}{C_w(\text{after equilibration})} = 1H + 1 \quad (4)$$

455 For freshwater, computed purging factors assuming full equilibration and equal zero air: water flows are: 1.00015 for methanol, 1.00111 for acetone, 1.00225 for acetaldehyde, 1.063 for DMS, 1.184 for benzene, 1.209 for toluene and 2.568 for isoprene. The same computation in seawater gives the following purging factors: 1.00015 for methanol, 1.00122 for acetone, 1.0025 for acetaldehyde, 1.075 for DMS, 1.221 for benzene, 1.255 for toluene and 2.961 for isoprene. We see that PF varies from being insignificant (≈ 1) for highly soluble VOCs to quite large ($\gg 1$) for the sparingly soluble gases. To compute the expected headspace mixing ratio during waterside calibrations (i.e. evasion experiments) assuming full equilibration, the known waterside concentrations are divided by the purging factor. For such evasion experiments, the equilibration efficiency is calculated as the measured headspace mixing ratio divided by the expected headspace mixing ratio assuming full equilibration.

460

We also tested the uptake of gaseous VOCs into the water phase (i.e. invasion). This is especially useful for gases such as benzene and toluene, as we were unable to generate liquid standards of these compounds due to their toxicity. During invasion experiments, a flow of VOC gas standard was diluted to varying degrees with VOC free zero air using mass flow controllers. This diluted VOC gas standard was then equilibrated with essentially VOC-free Milli-Q water. This assumption is acceptable as we used relatively high carrier gas-VOC mixing ratios (up to 50 ppb) and the Milli-Q water is essentially free of DMS, benzene, toluene and isoprene (Sect. 3.1). The headspace equilibrator mixing ratio is measured and compared to the expected mixing ratio at full equilibration. Calculation of the expected mixing ratios at full equilibration during invasion experiments is presented in the appendix. For invasion experiments, the equilibration efficiency is calculated as the observed change in mixing ratio over the expected change in mixing ratio.

4 System-SFCE testing performance

4.1 Estimation of the background and system blanks for seawater VOC measurements

The ideal ~~system blank~~ background, or blank, for seawater VOC measurements would be VOC-free seawater. However, we have been unable to generate or obtain seawater that is free of methanol, acetone or acetaldehyde due to the high solubility and ubiquity of these gases. Additionally, it is debatable whether any natural seawater may be free of methanol, acetone or acetaldehyde as there is a lack of knowledge about the cycling of these compounds. The choice of background is most important for these soluble OVOCs (~~methanol, acetone, acetaldehyde~~) as the ratio of background to signal can be quite high and the background can be variable. For example, for acetone the average signal to background ratio during the three-week Arctic field testing campaign for three weeks (Section 5) was 1.62 with a background standard deviation of 26%. Below, we discuss three different approaches at estimating the background of the seawater VOC measurements.

First, direct measurements of zero air ~~carrier gas zero air~~ (i.e. bypassing the SFCE) were used to track any drift in the internal PTR-MS background. This simple method of deriving a blank was also used by Yang et al., (2013). Since humidity is known to affect the background of some of the measured compounds (de Gouw and Warneke, 2007) (see Supplementary material), we do not expect bypassing the equilibrator with zero air ~~to~~ This approach might not give provide the most representative of ~~blanks~~ backgrounds for all seawater VOCs because (i) zero air has a much lower humidity than the equilibrator headspace and humidity could affect the backgrounds of some of the measured compounds (de Gouw and Warneke, 2007) (see Supplementary material); (ii) it does not account for any possible contamination within the equilibrator.

Second, at every sampling station, bottom water (i.e. the deepest water collected by the rosette, which was between 290 m and 1700 m, well below the mixed layer) ~~water from the bottom of the water column was collected and measured.~~ Here we define the bottom water as the deepest water sample provided by the rosette, which was between 290 m and 1700 m (well below the mixed layer). For some VOCs that are thought to be only produced in the surface ocean and rapidly consumed at depth (such as DMS), it might be expected that their concentrations in deep water to be close to zero. However, there is insufficient field data to know whether this is the case for all the VOCs monitored here. Measurements of methanol and acetone in the north

500 Atlantic show that their concentrations do decrease below the mixed layer (Williams et al., 2004) but do not
necessarily go to zero. Similarly, depth profile measurements showed acetone concentrations near the
detection limit ($0.3 \text{ nmol}^{-1} \text{ dm}^3$) at 200 m (Beale et al. 2013), while methanol and acetaldehyde concentrations
at depth did not decrease as rapidly. We note that for these measurements a flow of dry nitrogen was used as a
background which may be an underestimation of the true system blank (see Supplementary material). The chief
505 advantage of using the bottom water measurement as the background is that ~~the headspace gas~~ these samples
after equilibration ~~has~~ have the same properties (humidity, temperature, exposure to the equilibrator, and
collection protocol) after equilibration as the headspace equilibrated with surface water and ~~has been through~~
the same collection protocol as the surface water samples.

The final blank we determined was the “wet equilibrator” blank. This consisted of stopping the water
510 flow into the equilibrator and purging the wet equilibrator (that had been coated with bottom seawater) with
zero air for 20 min. During this blank measurement, humidity in the headspace remained constant as small
water droplets remained inside of the coil and were not substantially dried by the zero air. During the Arctic
cruise, the wet equilibrator blank consistently resulted in the lowest ~~blank~~-reading on the PTR-MS for all VOCs
except for methanol and acetone (as a result of a contamination, which is ~~discussed~~ below). Thus, in practice
515 the wet equilibrator blank seems to be the best surrogate for a “true” water blank for almost all VOCs measured
here. During the wet equilibrator blank, the bottom of the PTFE jar ~~or PTFE tee is filled with~~ contains
approximately 5 mL of residual seawater that is not readily flushed out; ~~i-~~in the case of the tee, ~~the water~~
leaves the tee ~~approximately immediately~~ there is essentially no residual seawater in the air-water separator.
During normal seawater measurement ~~of seawater~~, the residence time of zero air and seawater in the
520 equilibrator is approximately ~~10.6~~ min. The residence time of zero air ~~in the~~ during a wet equilibrator blank
measurement ~~doubles during the blank~~ is about 1.2 min.

The 200 cm^3 headspace jar used for separating the headspace from the seawater after equilibration is
made from PTFE, which should be inert. The manufacturer datasheet suggests that methanol and acetone are
525 amongst the most permeable gases in PTFE. The system is therefore at slight overpressure of approximately
 0.13 mBar and thus was not expected to cause any contamination from lab air. However, we found that the
empty equilibrator blanks of methanol and acetone were about 0.2 ppbv higher than their deep water blanks
during a cruise. The most plausible explanation for this seems to be outgassing or permeation of methanol and
acetone through the walls of the PTFE jar itself, which is suppressed during the water measurement. During the
530 three-week field deployment, we observed a strong correlation between zero air and bottom water
measurements ($R^2= 0.92$ methanol, $R^2= 0.69$ acetone), suggesting the concentrations of these VOCs at depth are
either uniform or very small. Because of the contamination ~~as described above~~, we report seawater acetone
and methanol concentrations from this cruise using bottom water as a ~~blank~~ the background; these
concentrations should thus be viewed as possible lower limit estimates. After the cruise, we replaced the PTFE
jar with a PTFE tee fitting (Swagelok) and this contamination greatly decreased.

535 We find that ultrapure MilliQ water or bottom seawater water is typically free of the less soluble
compounds such as DMS, toluene, benzene and isoprene. This is confirmed by good agreement between the
wet equilibrator blanks and the MilliQ/ bottom seawater measurements. This agreement also suggests that our

540 system is not affecting the measured concentrations of these compounds e.g. through cell lysis or rupturing. The concentrations of methanol, acetone, and acetaldehyde measured in the MilliQ water are during the Arctic cruise were much higher than those in seawater and were highly variable. Thus, we conclude that MilliQ water is not free of these gases (see Supplementary material). Similarly, we found that tap water or bottled drinking water is typically not free of methanol, acetone, and acetaldehyde, likely due to slow leakage of these compounds from the pipes, tubes and/or containers.

4.2 Estimation of equilibration efficiency

4.2.1 Experimental setup

545 As a brief recap, for gases that appear to fully equilibrate in the SFCE, seawater concentrations (C_w) are computed from the equilibrator headspace mixing ratio (C_a) using the dimensionless air over water Henry solubility constant (H) (R. Sander, 2015). Headspace equilibrator mixing ratios are converted from ppbv to nmol dm^{-3} using the ideal gas law and the dilution of equilibrator headspace is accounted for by multiplying measured
550 equilibrator mixing ratios by 1.2 (Sect. 3, Eq. (2)).

Where possible, values for Henry solubility recommended by S. P. Sander et al. (2015) were used for this calculation as those were deemed most reliable. These values represent freshwater solubilities and are converted to seawater solubilities by accounting for salting out effects (Johnson, 2010). Values of the dimensionless Henry solubility (water over gas) in freshwater and seawater as well as the references for the
555 solubility are displayed in Table 1-Table 4.

Two methods are used to assess the equilibration efficiency of the SFCE: evasion and invasion. In evasion experiments, liquid standards of methanol, acetone and acetaldehyde were prepared by serial dilution of the pure solvent in the same batch of MilliQ water. Aliquots of pure, undiluted methanol (For spectroscopy Uvasol) and acetone (HPLC standard) were dispensed using volumetric pipettes. A 1 cm^3 volumetric flask was
560 used to aliquot pure acetaldehyde ($\geq 99.5\%$, A.C.S. Reagent). Subsequent dilutions utilised a volumetric pipette and volumetric flask to prepare liquid standards ranging from 3 to $30 \text{ nmol}^{-1} \text{ dm}^3$ for acetone and acetaldehyde and 30 to $300 \text{ nmol}^{-1} \text{ dm}^3$ for methanol. Liquid standards of Isoprene and DMS were prepared gravimetrically airtight each day. A syringe pump (New Era Pump Systems) was used to dynamically dilute DMS and isoprene standards in a flow of MilliQ water. This yielded DMS standards of up to $7 \text{ nmol}^{-1} \text{ dm}^3$ and isoprene standards of
565 up to $2 \text{ nmol}^{-1} \text{ dm}^3$. For this calibration, the flow rate of MilliQ water is measured at the drain. For In evasion experiments calibrations, a solubility-dependent fraction of dissolved VOCs is transferred into the gas phase during the equilibration process. Thus, the final dissolved concentration will be somewhat lower than the initial concentrations. To account for the removal of the fractions of these gases from the seawater during equilibration, a purging factor (PF) based on mass conservation is applied. The PF is the ratio between the
570 dissolved gas concentration before and after complete equilibration in the coil. The derivation of this compound specific purging factor is presented in the Supplementary material. At equal air and water flow rates, it simplifies to:

$$PF = \frac{C_w(\text{before equilibration})}{C_w(\text{after equilibration})} = \frac{1}{H} + 1 \quad (4)$$

575 The precision of the purging factor depends on the precision of the solubility measurement. Since solubilities are reported in this paper to two significant figures, purging factor is reported here to two significant figures as well. For freshwater, computed purging factors assuming full equilibration and equal zero air: water flows are: 1.00 for methanol, 1.00 for acetone, 1.00 for acetaldehyde, 1.06 for DMS, 1.18 for benzene, 1.21 for toluene and 2.57 for isoprene. The same computation in seawater gives the following purging factors: 1.00 for methanol, 1.00 for acetone, 1.00 for acetaldehyde, 1.08 for DMS, 1.22 for benzene, 1.26 for toluene and 2.96
580 for isoprene. We see that PF varies from being insignificant (≈ 1) for highly soluble VOCs to quite large ($\gg 1$) for the sparingly soluble gases. To compute the expected headspace mixing ratio during ~~waterside calibrations (i.e. the evasion calibrations experiments)~~ assuming full equilibration, the known waterside concentrations are divided by the purging factor. ~~For such evasion experiments~~ Then, the equilibration efficiency is calculated as the measured headspace mixing ratio divided by the expected headspace mixing ratio assuming full equilibration.

585 We also tested the ~~uptake~~ absorption of gaseous VOCs into the water phase (i.e. invasion). This is especially useful for gases such as benzene and toluene, as we were unable to ~~generate~~ use liquid standards of these compounds due to their toxicity. During invasion experiments, a flow of VOC gas standard was diluted to varying degrees with VOC-free zero air using mass flow controllers. This diluted VOC gas standard was then equilibrated with essentially VOC-free Milli-Q water. ~~This~~ The assumption of no VOC in the initial water is ~~acceptable~~ reasonable as we used relatively high carrier gas VOC mixing ratios (up to 50 ppbv) and the Milli-Q water is essentially free of DMS, benzene, toluene and isoprene (Sect. 4.1). The headspace equilibrator mixing ratio is measured and compared to the expected mixing ratio at full equilibration. Calculation of the expected mixing ratios at full equilibration during invasion experiments is presented in the Supplementary material. For invasion experiments, the equilibration efficiency is calculated as the observed change in mixing ratio over the
590 expected change in mixing ratio.
595

Ideally we want to maintain ~~By maintaining~~ a stable equilibration efficiency of 100%. ~~This design~~ would maximise the signal to noise ratio and minimize the measurement uncertainty. This ~~would~~ may also reduce the need for frequent calibrations. Robust ~~dissolved gas~~ SFCE calibrations were not performed during the field testing presented here due to logistical constraints. Post-cruise calibrations were carried out on an
600 approximately weekly basis over several weeks, intended to be representative of the duration of the cruise. These calibrations were used to assess the equilibration efficiency of SFCE and uncertainties therein.

4.2.2 Equilibration efficiency of DMS and isoprene

605 Prior experimentations with a similar setup suggest that the 10 m segmented flow tube presented here is at least a factor of two longer than required for full equilibration of DMS (Blomquist et al., 2017). Hence we expect the ~~VOCs~~ soluble VOCs (methanol, acetone and acetaldehyde, DMS) to fully equilibrate due to their higher solubility and ~~gas phase control in gas exchange~~ (Liss and Slater, 1974). Figure 2 shows calibration curves for DMS and isoprene using liquid standards (i.e. evasion) over several weeks. The calibration curve for DMS

610 suggests full equilibration (Fig. 2a), where a ~5% underestimation of DMS in the mean is within the uncertainty of the solubility. The DMS calibration curves show very little noise and low weekly variability ($\pm 4\%$ std. dev.), suggesting that the SFCE-PTR-MS setup is very stable. The calibration curve for isoprene suggests 62% equilibration efficiency (Fig. 2b). A greater variability on a weekly basis ($\pm 14\%$ std. dev.) is observed in the isoprene calibration curves, likely due to incomplete (and hence less consistent) equilibration.

615 Results from the invasion experiments are displayed in Fig. 3 and confirmed that the equilibrator fully equilibrates for DMS, as the measured and expected gas phase mixing ratios of DMS match. The equilibration efficiencies of the less soluble gases benzene and toluene were found to be $94\pm 1\%$ and $95\pm 2\%$ respectively. The 5% difference is within the uncertainty of the solubility of these compounds, hence for computation of seawater concentrations we assume that these compounds fully equilibrate. This invasion experiment was also performed for the highly soluble OVOCs (methanol, acetone and acetaldehyde). These gases were found to be entirely absorbed into the water phase, leading to essentially noise in the measurements of headspace mixing ratios.

620 The equilibration efficiency of isoprene (the least soluble compound that we measure by far) of 69% from invasion is similar to that determined in the evasion experiments (62%) if we use the isoprene solubility from Karl et al. (2003) and the temperature dependence from Leng et al. (2013). We note that there is a large range in the values for isoprene solubility in the literature. Using the solubility values from Yaws and Yang (1992), or
625 Leng et al. (2013), or Mochalski et al. (2011) would result in a large and unexpected discrepancy in the equilibration efficiency of isoprene between the evasion and invasion experiments.

4.2.3 ~~call this section~~ 'Equilibration efficiency of OVOCs'

630 Both theoretical considerations (e.g. Liss and Slater, 1974) and experiments with varying air:water flow ratio (Sect. 4.25) indicate that the OVOCs should fully equilibrate within the SFCE. The average slope of 11 calibration curves for acetaldehyde and 14 calibration curves for methanol and acetone over a three-months period are shown in Fig. 4. Results are compared to the expected mixing ratio computed using every experimentally determined solubility listed in the compilation by R. Sander (2015). The measurements are also compared to the solubility recommended by S. P. Sander et al. (2015) which was chosen as a critical synthesis of published solubilities.

635 The experimentally determined calibration slopes for OVOCs are linear (typical R^2 above 0.95). Although, they are on average about 1.5 times higher than the solubilities recommended by S. P. Sander et al. (2015). Nevertheless, these experimental mean slopes are within the range of published solubility values. The relative standard deviation associated with the OVOC calibration curves (~25%) are much larger than that in the DMS calibration curves (4%), with the latter an indication for the stability of the PTR-MS/equilibrator system. On a weekly basis,
640 the calibration curves of individual OVOCs correlate with each other, and these OVOCs were diluted together from pure reagents. This suggests that most of the observed variability in OVOC calibration from week to week
645 might be due to errors or contamination in the serial dilution procedure. In order to ensure consistency with previous equilibrator setups (Kameyama et al., 2010), in this paper we report our dissolved gas concentrations using the recommended solubilities from S. P. Sander et al. (2015). Using the mean of our experimental dissolved gas calibrations would decrease the computed OVOC seawater concentrations by approximately 50%.

4.1 Effect of humidity on the PTR-MS measurements

Equilibrator headspace mixing ratios were initially computed using compound-specific rate constants of the reaction between the VOC in question and the hydronium ions in the drift tube of the mass spectrometer (Yang et al. 2013; Zhao and Zhang, 2004). Pre and Post cruise dynamic gas phase calibrations using a gravimetrically prepared VOC gas standard (Apel-Riemer Environmental Inc., Miami, Florida, USA, 517 ppb acetaldehyde, 490 ppb methanol, 512 ppb acetone, 491 ppb isoprene, 527 ppb DMS, 500 ppb benzene, 483 ppb toluene) and two Bronkhorst mass flow controllers agree within 15% of the computed mixing ratios for all VOCs except isoprene. Isoprene was found to fragment significantly where 17% of the isoprene molecules are found at the parent ion (m/z 69) and 30% and 53% were found at m/z 41 and 39 respectively. This is in general agreement with Schwarz et al., (2009). This fragmentation ratio increases with increasing drift tube voltage (see appendix).

The PTR-MS measurements can be affected by humidity. To check for the effect of humidity on the PTR-MS measurement, gas calibrations were carried out at different humidities using three Bronkhorst mass flow controllers. To produce carrier gas air at different humidities, a flow of moist air saturated in humidity at 20°C is generated by passing dry clean air through a wetted SFCE and diluted by varying amounts of dry air from a gas canister. The air is scrubbed by the Pt catalyst which does not appear to change the humidity levels and added to the flow of VOC gas standard. The signal of most VOCs monitored is independent of the sample humidity. However, isoprene, benzene and toluene show a weak humidity dependence in their gas phase calibrations. Changing the humidity in sample air from completely dry to nearly saturated in humidity at 20°C, the abundance of isoprene parent ion increases by 33% (see appendix). This is because the hydronium-water clusters do not cause isoprene fragmentation upon ionisation (Schwarz et al. 2009). The opposite is observed with benzene and toluene where parent ion abundance was found to decrease by 12% and 18% respectively over same humidity range. This is because the humidity makes ionisation less efficient (see appendix). In fact, hydronium-water clusters have a lower ionisation energy, thus ionising benzene and toluene less effectively (de Gouw and Warneke 2007; Warneke et al. 2001). The humidity dependant slopes from the gas phase calibrations were used to correct the measured equilibrator headspace mixing ratios. We note that our use of a dilution flow lowers the humidity in the sample gas by 20% and thereby reduces the measurement sensitivity to humidity.

4.2.4.2 Measurement sensitivity toward air:water flow ratio

Air and water at equal flow rates of 100 cm³ at 20 °C were The air to water ratio of 100 cm³:100 cm³ is chosen to allow for a reasonably sufficiently long equilibration time, large surface area for exchange, and so high signal while satisfying the air flow requirements of the PTR-MS. They were also chosen such that the stripping of the soluble compounds from the water phase during equilibration would be small (i.e. purging factor near 1). Additionally, the use of equal flows of air and water simplifies the calculation of waterside-dissolved gas concentrations. The water flow was not routinely monitored during the Arctic deployment and decreased by up to 20% due to aging of the peristaltic pump tubing. This could influence our measurement through at least (i) the equilibration time and hence the efficiency in the coil; (ii) the purging factor. To investigate the influence of these competing factors on the signal, an experiment was performed after the cruise measuring the same solution of liquid standard at different water flows into the equilibrator where-while keeping the air flow was kept constant (Fig. 52).

The signals of acetone, acetaldehyde, and DMS were found to be independent of the water flow into the equilibrator. These results provide strong experimental evidence that i) VOCs with solubility-solubilities that is greater than or similar to DMS do equilibrate in the coil, and ii) the gas flow does not remove a large fraction of these gases from the water phase during the equilibration process (i.e. purging). In contrast, the signal of isoprene was found to decline with decreasing water flow. As the water flow is decreased during in this experiment, the purging factor increased at a comparable rate to as the decrease in the isoprene headspace

690 mixing ratios ~~decreased.~~ This suggests that the change in purging factor is largely responsible for the change in the isoprene signal (Fig. 52). Consequently, compared to the soluble VOCs, for isoprene there is an additional uncertainty of ~20% that is due to the variable water flow during the cruise (see Sect. 4.45).

~~4.3 Equilibration efficiency~~

695 Our aim is to build an equilibrator that fully equilibrates for the very soluble OVOCs. By maintaining a stable equilibration efficiency of 100%, this design would maximise the signal to noise ratio and minimize the measurement uncertainty. This would also reduce the need for frequent calibrations. Robust waterside calibrations were not performed during the Arctic deployment due to logistical constraints. Post-cruise calibrations were carried out on an approximately weekly basis over several weeks, which is meant to be representative of the duration of the cruise. These calibrations were used to assess the equilibration efficiency of SFCE and uncertainties therein.

700 Prior experiments with a similar setup suggest that the 10 m segmented flow tube presented here is at least a factor of two longer than required for full equilibration of DMS (Blomquist et al., 2017). Hence we expect the OVOCs (methanol, acetone and acetaldehyde) to fully equilibrate due to their higher solubility and airside control in gas exchange (Liss and Slater, 1974). Figure 3 shows calibration curves for DMS and isoprene using liquid standards (i.e. evasion) over several weeks. The calibration curve for DMS suggests full equilibration (Fig. 705 3a), where a ~5% underestimation of DMS in the mean is within the uncertainty of the solubility. The DMS calibration curves show very little noise and low weekly variability ($\pm 4\%$ std. dev.), suggesting that the SFCE-PTR-MS setup is very stable. The calibration curve for isoprene suggests 62% equilibration efficiency (Fig. 3b). A greater variability on a weekly basis ($\pm 14\%$ std. dev.) is observed in the isoprene calibration curves, likely due to incomplete (and hence less consistent) equilibration.

710 Results from the invasion experiments are displayed in Fig. 4 and confirmed that the equilibrator fully equilibrates for DMS, as the measured and expected gas phase mixing ratios of DMS match. The equilibration efficiency of the less soluble gases benzene and toluene were found to be $94 \pm 1\%$ and $95 \pm 2\%$ respectively. The 5% difference is within the uncertainty of the solubility of these compounds, and so for computation of their seawater concentrations we assume that these compounds fully equilibrate. This invasion experiment was also 715 performed for the highly soluble OVOCs (methanol, acetone and acetaldehyde). These gases were found to be entirely absorbed into the water phase, leading to essentially noise in the measurements of headspace mixing ratios.

The equilibration efficiency of isoprene (the least soluble compound that we measure by far) of 69% from invasion is similar to what was measured in the evasion experiments (62%) if we use the isoprene solubility 720 from Karl et al., (2003) and the temperature dependence from Leng et al., (2013). We note that there is a large range in the isoprene solubility in the literature. Using the solubility values from Yaws & Yang (1992), Leng et al., (2013) or Mochalski et al., (2011) would result in a large discrepancy in the equilibration efficiency of isoprene between the evasion and invasion experiments, which we do not expect.

725 For the OVOCs, both theoretical considerations (e.g. Liss and Slater, 1974) and experiments with varying
air:water flow ratio (Sect. 4.2) indicate that they should fully equilibrate within the SFCE. The average slope of
11 calibration curves for acetaldehyde and 14 calibration curves for methanol and acetone over a three-months
period are shown in Fig. 5. Results are compared to the expected mixing ratio computed using every
experimentally determined solubility listed in the compilation by R. Sander (2015). The measurements are also
730 compared to the solubility recommended by S. P. Sander et al. (2015) which was chosen as a critical synthesis of
published solubilities.

The experimentally determined calibration slopes for OVOCs are very linear (typical R^2 above 0.95). However, in
the mean they are about 1.5 times higher than expected compared to the solubility recommended by S. P. Sander
et al. (2015). Nevertheless, these experimental mean slopes are within the range of published solubility values.
735 The relative standard deviation in the OVOC calibration curves (~25%) are much larger than that in the DMS
calibration curves (4%), with the latter an indication for the stability of the PTR-MS/equilibrator system. On a
weekly basis, the calibration curves of individual OVOCs correlate with each other, and these OVOCs were diluted
together from pure reagents. This suggests that most of the observed variability in OVOC calibration from week
to week is due to errors or contamination in the serial dilution procedure. In order to ensure consistency with
740 previous equilibrator setups (Kameyama et al., 2010), we report our waterside concentrations using
recommended solubilities from S. P. Sander et al. (2015). Using the mean of the experimental waterside
calibrations would decrease the computed OVOC seawater concentrations by approximately 50%.

4.34 Measurement response time

745 A series of liquid standards containing 20 nmol dm⁻³ acetone, 20 nmol dm⁻³ acetaldehyde and 200 nmol dm⁻³
methanol (Fig. 6) were analysed in order to determine the response and delay time of the equilibrator and to
test for any possible memory effect due to wall adsorption and desorption effects. Discrete samples were
swapped over rapidly and the water flow into the equilibrator was stopped briefly to avoid interference with
the measurement.

The residence time (0.6 min) in the equilibrator segmented flow tube was calculated from the flow of air and
water into the equilibrator and the volume of the segmented flow tube. The response time (e-folding time) of
750 the equilibrator response to the step change was calculated-estimated using the 8s PTR-MS measurements. ~~It
was calculated~~ to be 35, 33 and 33 s for methanol, acetone and acetaldehyde respectively. Thus, the response
time appears to be independent of the solubility of the compound and comparable to the residence time in
the SFCE. The rapid sharpness in the rate of increase/decrease in OVOC concentrations during upon water
change in this experiment also suggests that there was little no obvious 'carry over' or memory effect. While
755 the response time of the SFCE is less than 1 min, to reduce random noise and improve the precision of the
measurement, we typically average measured equilibrator headspace mixing ratios are typically averaged
over 6 min for both underway measurements and ~~the~~ discrete measurements, to reduce random noise and improve
the precision of the measurement.

4.45 Measurement precision and ~~l~~Limit of detection

760 The ~~analytical measurement~~ precision and the limit of detection (LOD) of this system are partly dictated by the
noise of the PTR-MS measurement. This in turn depends on the dwell time of the detector at a given mass and
thus the time the data are averaged over. Additionally, ~~it-the measurement precision depends on the factors~~
~~stated in Eq. (2), namely the strongly depends on the gas~~ solubility ~~of the compound, the purging factor and the~~
~~dilution flow~~. For isoprene, the ~~analytical measurement~~ precision depends ~~on the factors stated in Eq. (3), where~~
765 ~~an additionally consideration ions~~ the variability in water flow, ~~which adds 20% uncertainty~~. We compute the
~~measurement analytical~~ precision as the standard deviation ($1\text{-}\sigma$) of 10 consecutive 6 min wet equilibrator blank
measurements, which is then converted to a ~~waterside dissolved gas~~ concentration using Eq. (32) ~~for isoprene~~
and Eq. (23) ~~for isoprene the other VOCs~~. The ~~precision is therefore is results in~~ averaging ~~the noise~~ over 70
770 measurement cycles with a dwell time at each mass of 500 ms giving an effective dwell time of 3-5 s. The LOD is
defined as 3σ . The resulting measurement noise and limit of detection for each compound are displayed in table
2 for ~~6--min~~ ute averaged data. These values should approximately halve if the data are averaged ~~over to~~ 30
min ute intervals instead.

In the case of typically 900 mL discrete samples (see Section 5), the measurement time is limited by the water
flow rate. ~~Aa~~ larger water volume ~~should may~~ improve the ~~measurement analytical~~ precision by allowing for a
775 longer sampling and averaging time. This is especially relevant for the most soluble compounds including
methanol or acetone.

5 Field ~~measurements~~ deployment

2.2 Field deployment

780 The SFCE coupled to PTR-MS has been field tested on a three-week research cruise in the Canadian
Arctic. We d Underway surface water and depth profiles were measured ~~in the Canadian Arctic on board the Ice~~
Breaker CCGS Amundsen from mid-July until the beginning of August 2017. The ship travelled from Iqaluit to
Smith Sound and ended near Resolute (cruise track map in Supplementary material). ~~The SFCE has been field~~
~~tested on a three-week research cruise in the Arctic for measurements of underway surface water and discrete~~
~~samples from depth profiles (Sect. 5).~~ For underway measurements, seawater from the ship's pumped
785 seawater supply was continuously piped into an open-topped PTFE beaker fixed in the sink and allowed to
overflow. The seawater was pulled by the peristaltic pump into the SFCE from the bottom of this beaker. This
setup buffered pressure variations and hence variable flow rates in the underway water supply which could
have affected instrument response (Sect. 4.2.4). The open topped beaker also allowed marine debris to
overflow, rather than clogging the SGFCE intake. Since there are no membranes, small particles that do enter
790 the SGFCE simply pass through the 4 mm inner diameter tube and are drained away.

Discrete water samples from the ship's rosette were collected in 900 cm³ ground glass stoppered
sample bottles using Tygon tubing. Sample bottles were rinsed three times and overfilled without introducing
bubbles to avoid air contamination. To measure discrete samples, the underway measurement was stopped,
and the PTFE water intake tube was simply moved from the seawater intake to each sample bottle (water flow

795 ~~stopped during changeover). Water was pumped from the bottom of the 900 cm³ sample bottles, while~~
~~minimizing agitation. The top 5 cm of the discrete water sample was not measured because of the possibility of~~
~~air contamination. The sampling time per bottle was under 9 min. The analysis of about eight discrete samples~~
~~including blank measurements (Sect. 3.1) is typically finished within two hours of sample collection. This should~~
~~be fast enough to avoid sample degradation of even the most reactive VOCs (Beale et al., 2011). To verify that~~
800 ~~the seawater supplied by the ship's underway water supply is uncontaminated, we sampled at every station~~
~~from 5m depth. The underway and rosette samples are compared in Sect. 5.~~

~~The SFCE coupled to PTR-MS was used to measure underway surface water and depth profiles in the Canadian~~
~~Arctic on board the Ice Breaker CCGS Amundsen from mid-July until the beginning of August 2017. The ship~~
805 ~~went from Iqaluit to Smith Sound and ended near Resolute (cruise track map in appendix). A selection of data is~~
~~displayed in Fig. 7, but the full dataset will be presented elsewhere. Surface underway measurements were~~
~~made using the ship's main built-in underway water supply (3–4 m depth, inlet located at front starboard side of~~
~~the ship), whereas the discrete CTD measurements were from Niskin bottles at 5 m depth.~~

The SFCE coupled PTR-MS allows for continuous measurement of a breadth of VOCs at a high resolution.
810 Sample data presented in Fig. 7; contains 5 min measurements that are further averaged to hourly intervals.
The underway surface water measurements capture a larger variability range of concentrations (e.g. acetone
3.5–23 nmol dm⁻³) than discrete surface samples collected from the ship's rosette (e.g. acetone 2.9–10 nmol dm⁻³).
This highlights one of the benefits of underway measurements, as some of these compounds display
noticeable fine scale variability likely due to their short lifetime.

815 Contamination of the underway water supply relative to the CTD Niskin bottle has been observed for acetone
(Yang et al., 2014), probably due to the ubiquity of OVOCs and their wide application in shipboard science (e.g.
acetone for Chlorophyll extraction). Previous underway measurements of isoprene and DMS have found that
after switching the underway water supply on, the first few hours of data typically showed significantly higher
concentrations (Andrews et al., 2015). To verify that the seawater supplied by the ship's underway water supply
820 is uncontaminated, at every station the CTD Niskin bottle from 5m depth was sampled. For in our this particular
dataset on this Arctic cruise, underway measurements and discrete samples from 5 m depth do not show any
obvious ~~discernible~~ difference for most of the VOCs. This is confirmed by the fact that the average
concentration reported from the 5 m Niskin bottle (+/- 95% confidence interval of the mean) overlaps with the
average concentration measured from the ship's built-in underway water inlet 3h either side of the CTD
825 measurement (Table 3~~Table 3~~). Measurements below the limit of detection were included for all analysis to
avoid a biased mean. The DMS and toluene concentrations from the underway water inlet do appear to be
higher compared to measurements from the 5 m Niskin bottle. This could ~~possibly~~ be due to a contamination
of the underway water supply or perhaps due to ~~the~~ differences in sample depths between the underway
and CTD ~~data~~ measurements. ~~We observed~~ strong vertical gradients were observed near the surface for most
830 of the VOCs, which will be discussed in more detail in a future manuscript. The data presented here are

~~preliminary and~~ have not been corrected for this possible contamination. ~~Please note that the sample data presented here should not be used until further quality checking.~~

6 Conclusion and recommendations

835 This paper presents a ship-based equilibrator system coupled to a PTR-MS for measurements of a ~~breadth-wide~~
~~range~~ of ~~gases-VOCs~~ in seawater. Its main advantage lies in its unique design. The segmented flow gives a high
degree of equilibration due to surface renewal within each water segment (Xie et al., 2001), a large surface area
for gas exchange ~~as well as, and a long~~sufficient equilibration time. ~~We find~~It was found that ~~with a 10 m~~
840 ~~segmented flow tube, the SFCE~~ fully equilibrates for gases of similar or higher solubility than toluene. The
unique air-water separation system allows for rapid drainage of water without droplet formation, thus yielding
a high response time of less than 1 min even for the highly soluble OVOCs. Additionally, the SFCE can be used
for underway and discrete sampling due to the ease of changing the water intake and low water flow
requirements (100 cm³ min⁻¹). Since it consists entirely ~~out~~ of commercially available PTFE tubing, it can be
easily and relatively cheaply constructed and should have minimal wall adsorption effects. The smooth surfaces
and constant water flow make the equilibrator easy to clean and fairly resistant to biofouling. Finally, the SFCE
845 system is designed with multiple fail-safes, such that a failure of an individual component does not cause the
equilibrator/~~detector~~ to flood~~d~~ or over/under-pressurise.

The equilibrator can be used to measure compounds that only partially equilibrate (e.g. isoprene) but with
slightly higher uncertainty than for fully-equilibrating compounds. The ~~SFCCFE~~ could easily be optimised for
measuring these less soluble gases by making the segmented flow tube longer to allow more time for
850 equilibration or by adding an isotopically labelled standard. One of the considerations when measuring
dissolved gases with PTR-MS is the effect ~~of~~ humidity on the signal. ~~We have presented discussions on a~~
~~discussion is presented on~~ how to estimate the background of the water measurement and how to correct for
the effect of humidity on the ~~PTR-MS~~ signal ~~of the PTR-MS~~ (see ~~appendix~~Supplementary material). Further work
is being ~~carried out~~conducted to ~~identify~~obtain a more robust ~~estimate for OVOC~~-background ~~estimate~~ that
855 does not require deep seawater samples.

The SFCE-PTR-MS was used to measure methanol, acetone, acetaldehyde, DMS, isoprene, benzene and toluene
on board the Canadian ice breaker CCGE *Amundsen* during ~~the~~ Arctic spring ~~in 2017~~. A selection of the
underway measurements is presented here with a comparison to samples obtained from 5m Niskin bottles.

We envisage wide applications of this novel equilibrator such as deployment on further research cruises for
860 measurement of a ~~wide range~~breadth of gases. The SFCE ~~could~~can be coupled to other gas phase detectors
such as a CIMS (Saltzman et al., 2009), ~~The equilibrator can also be~~ incorporated into existing methods that
require fast response times, for example near-surface ocean profilers (Sims et al., 2017), ~~or~~. ~~The SFCE can also~~
~~be used to perform underway photochemical or surface microlayer reaction experiments. Finally, the method~~
865 ~~can be used to improve the measurements of dissolved gases in algae cultures, which currently rely on discrete~~
~~headspace sampling (Halsey et al., 2017).~~

7 Appendix:

Appendix A: PTR-MS Settings

To measure the VOC concentrations, we use a commercially available high sensitivity Proton Transfer Reaction Mass Spectrometer (de Gouw & Warneke, 2007; Lindinger & Jordan, 1998). Briefly, water vapor is ionised in a hollow cathode. The hydronium ions react with sample air in the drift tube. Here, gases with a proton affinity higher than water, including many VOCs, are ionised continuously usually without fragmentation. Hydronium ions are in large excess of the VOCs, which allows for application of pseudo-first order kinetics in the drift tube. Together with relatively well studied reaction rates between VOCs and hydronium ions (Zhao & Zhang, 2004) and mass spectrometer specific parameters (Yang et al. 2013), the mixing ratios of the VOCs can be fairly accurately computed without the need of an internal standard (Lindinger & Jordan, 1998). Nevertheless, reaction rate constants between VOCs and hydronium ions have a reported error margin of up to 50% (Blake et al. 2009; Ellis and Mayhew 2014). To correct for this, dynamic gas phase calibrations were carried out using a certified gas standard.

SFCE headspace is laden with humidity, which influences the PTR-MS measurement. Previous observations suggest that humidity in the sample affects drift tube kinetics through the formation of hydronium water clusters. In practice, such water dimmers are monitored at m/z 37 (i.e. isotopic hydronium water cluster ($H_2^{18}O^+ \cdot H_2O$)) as a percentage of the primary ion count, accounting for isotopic abundance (Blake et al. 2009):



Humidity has several effects on the measurement: (i) The additional water molecule stabilises the primary ion by sharing the positive charge thus increasing its proton affinity (Blake et al. 2009). For example benzene and toluene possess intermediate proton affinities and are ionised by the primary ion, but not the water cluster (Warneke et al. 2001). On the other hand, ionisation by the water cluster is softer and hence leads to less fragmentation for example of isoprene in the drift tube (Schwarz et al. 2009); (ii) humidity in the drift tube leads to non-collision rate limited reactions; (iii) large water clusters have different ion mobility, where (ii) and (iii) are not accounted for in the computation of the measured mixing ratio (Blake et al. 2009); (iv) sample humidity affects the backgrounds of some of the VOCs monitored (de Gouw & Warneke, 2007). (v) Some PTR-MS have a collision-induced dissociation (CID) chamber at the end of the drift tube in which the E/N is briefly raised to simplify the mass spectra and remove humidity induced clusters which leads to an overestimation of the true hydronium primary ion concentration in the drift tube and thus an overestimation of VOC concentrations (Blake et al. 2009). However, our PTR-MS instrument does not have a CID chamber. (vi) It is tempting to think of VOC protonation as a one way reaction. However the reaction is reversible and an increase in the water vapor concentration leads to increased reverse reaction which is strongly temperature dependant (Blake et al. 2009).

While the effect of changing humidity on the PTR-MS signal could in theory be corrected for based on complex parametrisations (Kameyama et al., 2010), keeping the sample humidity constant greatly simplifies the corrections. Partly because of this, we maintain a constant humidity in SFCE headspace (monitored at m/z of 37) by keeping the coil at 20°C. A dryer (e.g. Nafion) has been successfully used in the measurements of seawater

DMS (Blomquist, Huebert, Fairall, & Faloon, 2010) and would reduce many of the aforementioned measurement uncertainties. However Nafion dryers are known to remove very soluble/reactive OVOCs (Kameyama et al., 2010) and thus is not an option for our measurements.

905 Clearly, excessive water clustering in the drift tube is undesirable. To keep the water dimer to be <5% of the primary ion count when measuring headspace equilibrator, the PTR-MS drift tube was operated at 160Td (700V, 2.2 mBar and 80°C in the drift tube). The water vapor flow into the source was set to 5 cm³n/min, the source current at 3 mA and the source valve to 35%. At these settings, the amount of hydronium water clusters is below 1% when measuring dry zero air and the amount of O₂⁺ ions is below 0.7% of the primary ion counts.
910 Residual water cluster measured during dry canister measurement is due to unionised water vapor from the hollow cathode entering the drift tube (Warneke et al. 2001).

The PTR-MS is deployed in selective ion mode. Ions monitored at m/z 33, 45, 59, 63, 69, 79 and 93 were attributed to methanol, acetaldehyde, acetone, dimethyl sulphide, isoprene, benzene and toluene in accordance with previous mass assignments (Williams et al. 2001; Warneke et al. 2003). Propanal has previously
915 been shown to have a very minor contribution to m/z 59 (Beale et al., 2013). For methanol, we correct for the oxygen isotope interference by monitoring O₂⁺ in the drift tube and applying a theoretical isotopic distribution ratio, which is 0.076% of the O₂⁺ signal.

Appendix B: Humidity experiments and fragmentation experiments

To investigate the effect of humidity on the background, we measured clean synthetic air at different
920 humidities. VOC-free air saturated in humidity is generated by passing synthetic air (BTCA grade) over a wetted SFCE coated inside with MilliQ water and kept at 20°C in a water bath. The concentration of water vapor was calculated to be 22.9 millimole water vapor per mole of air. The water drain was capped for this experiment to balance out the pressure resistance provided by the Pt-Catalyst. This air is scrubbed with a Pt-Catalyst to oxidize all VOCs to CO₂. Efficiency of this catalyst at oxidizing VOCs in wet and dry air is demonstrated elsewhere (Yang and Fleming 2019) and it was found that the catalyst did not affect humidity levels. This flow of air saturated in
925 water at 20°C is dynamically diluted with dry zero air to generate VOC-free air at different humidities.

To verify that the measurement is not excessively affected by humidity at those settings, dynamic gas phase calibration curves were carried out at different humidity levels. Dynamic gas phase calibrations were carried out using mass flow controllers to dilute a flow of zero-VOC air at different moistures (BTCA air scrubbed
930 by Pt-catalyst) and a gravimetrically prepared standard gas in ultrapure N₂ with known amount of VOC (517 ppb acetaldehyde, 490 ppb methanol, 512 ppb acetone, 491 ppb isoprene, 527 ppb DMS, 500 ppb benzene, 483 ppb toluene, Apel-Riemer Environmental Inc., Miami, Florida, USA). The ratio between synthetic air and VOC standard in N₂ was typically more than 10:1, thus not significantly changing the matrix. During these experiments and during the Arctic field deployment, the abundance of water dimer was monitored at m/z 37
935 (representing (H₂¹⁸O⁺)H₂O) and calculated as a fraction of the primary ion while accounting for its specific transmission efficiency. Primary ion was monitored as the water isotope at m/z 21 and multiplied by the isotopic ratio of 500;

$$\%m/z\ 37 = \frac{cps(m/z\ 37)}{cps(m/z\ 21)} * 500 \quad (B1)$$

940 Measurement of zero-air at different humidities showed an exponential dependence of the DMS (m/z 63) and acetaldehyde (m/z 45) background to the humidity of the sample air (Fig. B1). The background of the other compounds presented here remained unaffected by humidity. For this analysis, dry zero air was subtracted as a system blank thus the Fig. B1 represents the additional background due to sample humidity. Here, a measured m/z 37 of 1% corresponds to dry canister air measurement. A m/z 37 between 1.4 and 2.0% corresponds to outside air measurements and m/z 37 of 2.2% corresponds to measurements of equilibrator headspace. The equilibrator headspace is nearly saturated in humidity as it is diluted by the dilution flow to reduce humidity.

950 Water vapor concentration and m/z 37 correlate linearly, thus both variables can be plotted on the same axis for comparison (Fig. B1). Lines of best fit for acetaldehyde and DMS background (in ppb) as a function of the additional hydronium water cluster in the drift tube due to sample humidity (in % m/z 37) was found to be;

$$ppbDMS = 0.351 - 0.789 \%m/z\ 37 + 0.425 \{ \%m/z\ 37 \}^2 \quad (B2)$$

$$ppbacetaldehyde = 0.0128 - 0.257 \%m/z\ 37 + 0.224 \{ \%m/z\ 37 \}^2 \quad (B3)$$

955 The flow of water vapor into the source was also varied while measuring clean dry canister air to simulate the influence of humidity induced water clusters on the background of the measurement. This indicated that the background of all the masses monitored changed and significantly increased for the soluble OVOCs (methanol, acetone, acetaldehyde). This is suggesting that the high background in the measurement of these compounds is due to residues of OVOCs in the water reservoir filled up with ultrapure water by the manufacturer. Thus highlighting the difficulty of obtaining OVOC free water.

960 The dynamic gas phase calibrations at different humidities showed that only calibration slopes of benzene, toluene and isoprene were humidity dependant (Fig. B2–Fig. B4). At the settings used, the calibration slopes of the other VOCs monitored did not vary with humidity. Benzene and toluene (Fig. B2 and Fig. B3) display humidity dependant calibration slopes because they possess intermediate proton affinities and are ionized by the primary ion but not by the primary ion water cluster (Warneke et al. 2001). The primary ion water cluster is more stable, because the additional water cluster stabilizes the positive charge (Blake et al. 2009).

965 For isoprene, the opposite effect is observed (Fig. B4) where the stabilising water cluster from humidity makes ionisation softer thus increasing the yield of the parent ion at m/z 69. Note that humidity dependant fragmentation of isoprene in PTR-MS has been observed before (Schwarz et al. 2009). Other masses that isoprene fragments can be found are m/z 39 and m/z 41.

970 To further investigate the fragmenting behaviour of isoprene, the same known amount of gas standard was measured at different voltages in the drift tube and ions at mass 41 and 69 were monitored (Fig. B5).

At lower voltages, the abundance of m/z 69 increases thus further supporting that isoprene is fragmenting in the drift tube. This fragmentation ratio was found to be very stable and vary by less than 5% over one month for twice weekly calibrations. The remaining isoprene molecules probably reside at m/z 39, which was found to be the dominant ion in this fragmentation (Schwarz et al. 2009). For the isoprene measurements presented here, the fragmentation ratio of isoprene at those settings is accounted for.

Appendix C: Map of the cruise track of the selection of data presented here

A map of the cruise track of the underway data presented here is shown in Fig. C1.

Appendix D: Derivation of the purging factor

As mentioned in the main paper in Sect. 3.2, using equilibrator headspace mixing ratios, we compute waterside concentrations after equilibration in the coil. However, a solubility-dependent fraction of dissolved VOCs is transferred into the gas phase during the equilibration process. Thus the final dissolved concentration will be somewhat lower than the initial concentrations. To account for the removal of a fraction of these gases from the waterside during equilibration a purging factor (PF) based on mass conservation is applied. The PF is the ratio between the waterside concentration before and after complete equilibration in the coil:

$$PF = \frac{C_w(\text{before equilibration})}{C_w(\text{after equilibration})} \quad (D1)$$

, where;

$$(D2)$$

Here n is the total number of moles in the system and V_w is the volume of water. In the following demonstration, n_a and n_w are airside and waterside number of moles after equilibration and V_g is the volume of carrier gas. Thus n_a is the number of moles measured as equilibrator headspace mixing ratios. Hence;

$$(D3)$$

Combining and gives;

$$(D5)$$

Thus,

Combining Eq. (D5) and (D6) gives

Combining Eq. (D2) and (D7) with Eq. (D1) gives:

$$PF = 1 + 1H * VwVa \quad (D8)$$

At equal zero air/water flow rates, this is simplified to:

$$PF = \frac{Cw(\text{before equilibration})}{Cw(\text{after equilibration})} = 1H + 1 \quad (D9)$$

The expected mixing ratios during invasion experiments is calculated by combining Eq. (D4) and (D5);

(D10)

, where the total number of moles is the diluted VOC gas standard mixing ratio.

~~Appendix E: Compilation of experimentally determined solubilities for methanol, acetone and acetaldehyde~~

~~Appendix F: Photographs of the instrument setup~~

1030 8 Author contribution

CW and MY designed the equilibrator. CW carried out system performance tests. PN, AJ, DC and WS provided input to the method development. CW carried out the deployment on board with help from MY during installation. Collaboration with BE made these measurements in the Canadian Arctic possible. CW prepared the manuscript with contributions from all co-authors.

1035 9 Competing interest

The authors declare that they have no conflict of interest.

10 Acknowledgements

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Table 1: Dimensionless Henry solubility values (water over gas) in freshwater and seawater used to compute dissolved gas concentrations.

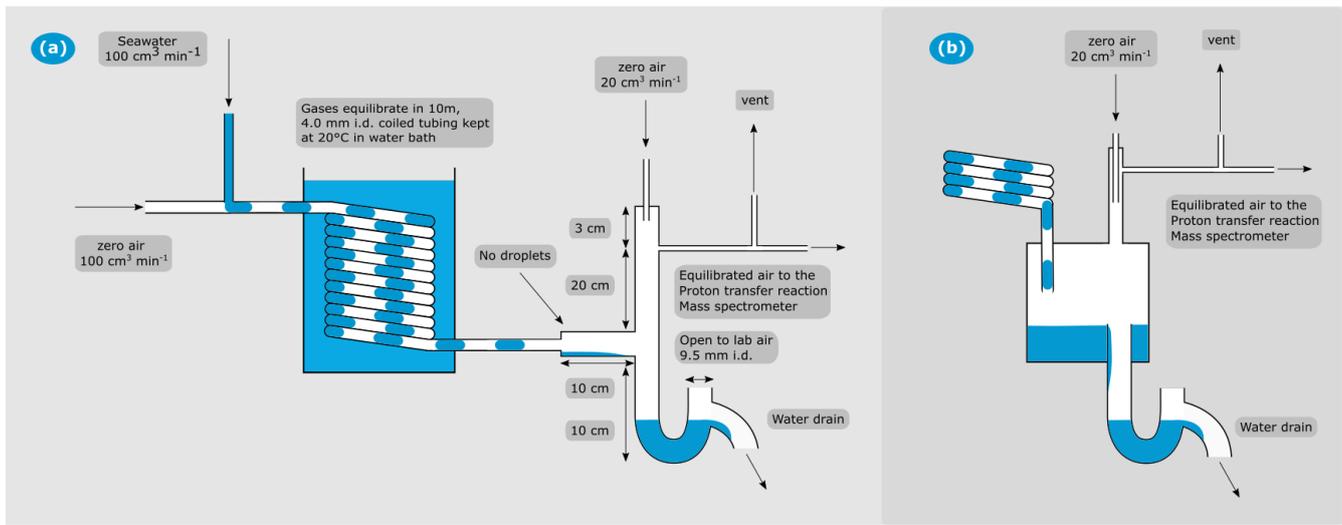
	Henry solubility at 20°C in freshwater	reference	Henry solubility at 20°C in seawater
methanol	6716	S. P. Sander et al., (2015)	6494
acetone	901	S. P. Sander et al., (2015)	819
acetaldehyde	444	S. P. Sander et al., (2015)	400
DMS	15.78	S. P. Sander et al., (2015)	13.28
benzene	5.44	Leighton and Calo, (1981)	4.52
toluene	4.77	McCarty and Reinhard, (1980)	3.92
isoprene	0.638	solubility from Karl et al., (2003) using temperature dependence from Leng et al., (2013)	0.510

1195 **Table 2: Analytical precision and limit of ~~the~~ detection of the seawater VOC measurements (6 min average).**

	measurement precision 1σ	Limit of detection
methanol (nmol dm ⁻³)	6.52	19.56
acetaldehyde (nmol dm ⁻³)	0.17	0.51
acetone (nmol dm ⁻³)	0.44	1.32
DMS (nmol dm ⁻³)	0.0069	0.0207
isoprene (nmol dm ⁻³)	0.58 *10 ⁻³	1.74 *10 ⁻³
benzene (nmol dm ⁻³)	0.0043	0.0129
toluene (nmol dm ⁻³)	0.0042	0.0126

Table 3: Average concentration measured for each compound from the 5m Niskin bottle and 3h either side of the Niskin measurement from the ship's build-in underway water inlet. Errors represent 95% confidence interval of this average.

	5m Niskin	Underway water inlet
methanol (nmol dm ⁻³)	17±6	15±6
acetone (nmol dm ⁻³)	7±2	8±2
acetaldehyde (nmol dm ⁻³)	3.8±1.2	3.8±1.0
DMS (nmol dm ⁻³)	0.90±0.16	1.51±0.38
isoprene (nmol dm ⁻³)	9.96*10 ⁻³ ±1.25*10 ⁻³	9.42*10 ⁻³ ±2.36*10 ⁻³
benzene (nmol dm ⁻³)	0.050±0.008	0.059±0.021
toluene (nmol dm ⁻³)	0.037±0.006	0.065±0.011



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Figure 1: A. Schematic of the segmented flow coil equilibrator coupled to PTR-MS. B. Schematic of the jar that was used during the field testing presented here ~~Arctic deployment~~ for headspace air-water separation. All other ~~connections~~ aspects of the SFCE were ~~kept~~ the same for the two designs.

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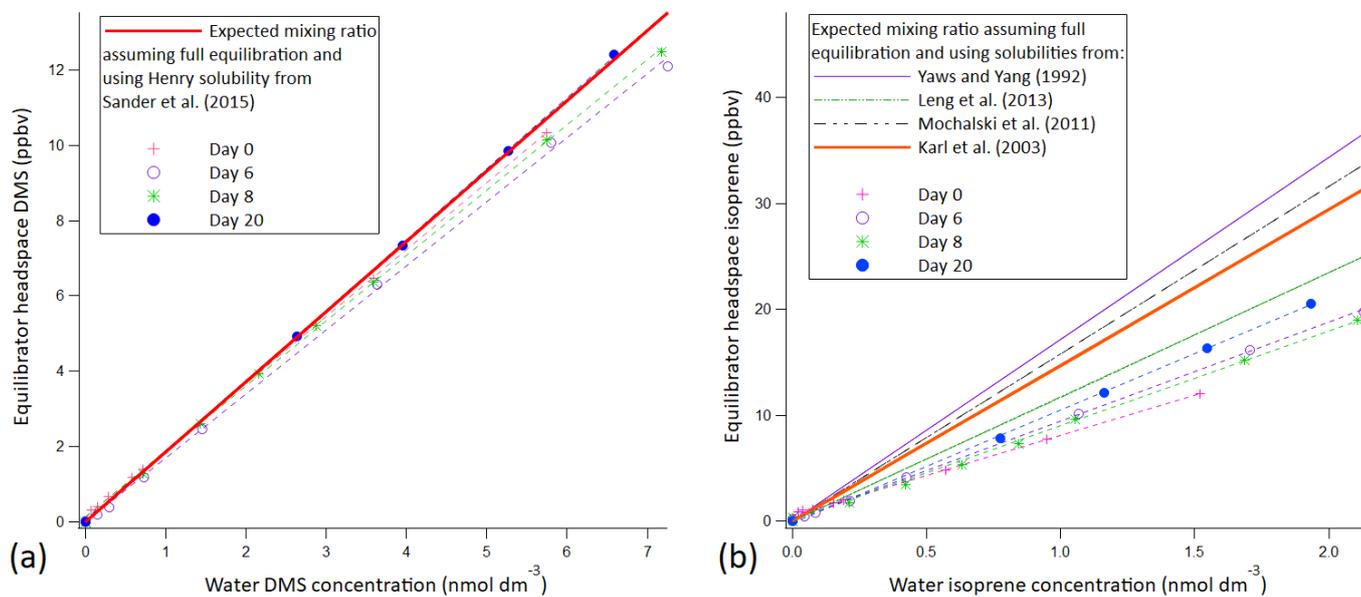


Figure 32: Waterside Dissolved gas Evasion calibration curves for DMS (panel a) and isoprene (panel b). Average slope of the experimental calibration curve was found to be $1.77 \text{ ppb nmol}^{-1} \text{ dm}^3 \pm 4\%$ and $9.12 \text{ ppb nmol}^{-1} \text{ dm}^3 \pm 14\%$ for DMS and isoprene respectively where errors represent standard deviation over a three-week period. Full equilibration slope was computed to be $1.87 \text{ ppb nmol}^{-1} \text{ dm}^3$ and $14.69 \text{ ppb nmol}^{-1} \text{ dm}^3$ for DMS and isoprene respectively (using S. P. Sander et al., (2015) for DMS solubility and Karl et al., (2003) solubility with Leng et al., (2013) temperature dependence). This suggests approximately 100% and 62% equilibration efficiency for DMS and isoprene respectively. Error bars are too small to display, but the noise associated with the measurement was found to be 0.006984 and 0.0005844 ppbv for DMS and Isoprene, respectively. This was calculated as the std. dev. of 10 consecutive water blank measurements.

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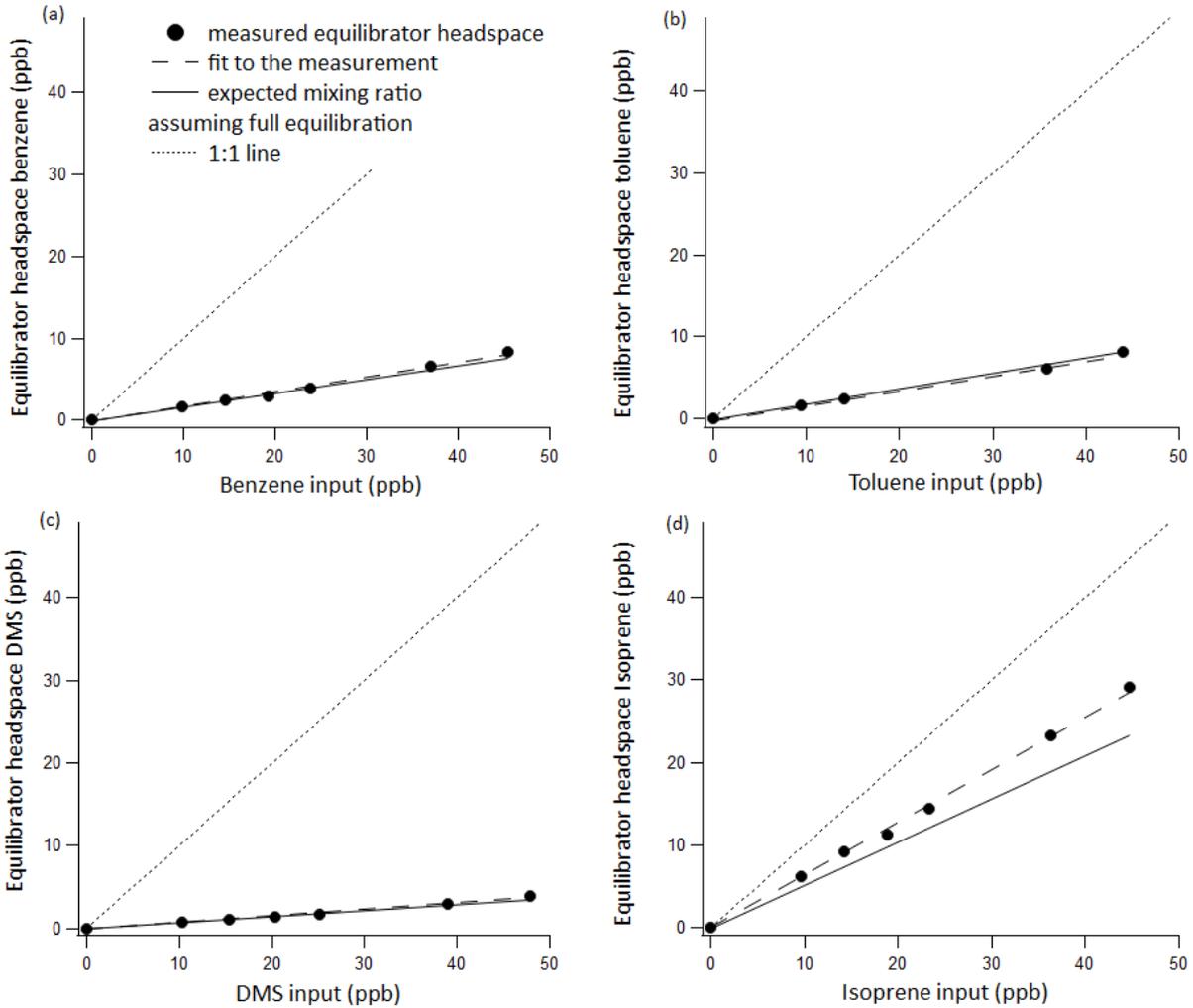


Figure 43: Invasion calibration curves for benzene (a), toluene (b), DMS (c) and isoprene (d) where a known amount of standard gas is added to the zero air carrier gas while measuring VOC-free Milli-Q water. Error bars were too small to display, but the noise associated with the measurement was found to be 0.0069 and 0.00058 ppbv, 0.0084 and 0.0044 ppb for DMS and Isoprene respectively and 0.04315

and ~~0.4243 ppb~~ 0.04243 ppbv for benzene and toluene respectively. This was calculated as the std. dev. of 10 consecutive water blank measurements. A 1:1 line is included ~~in 4-3-22~~ to illustrate the role of the water phase in absorbing these compounds.

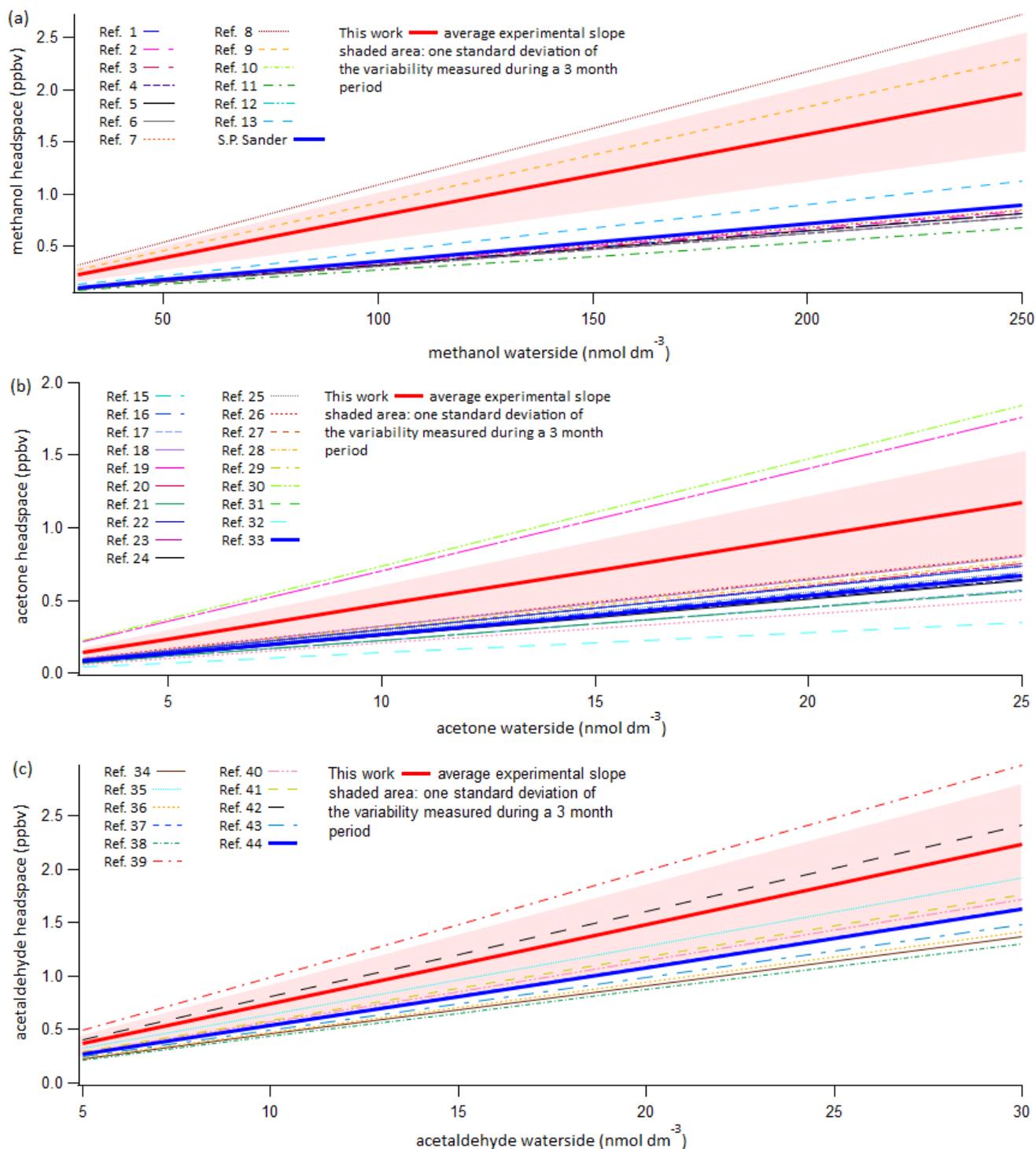


Figure 54: This is a Evasion calibrations of OVOCs. comparison of range solubilities observed with the SFCE PTR-MS system and values predicted from literature. Displayed are the average experimentally determined slopes of 14 calibration curves of methanol (a) and acetone (b) and 11 calibration curves of acetaldehyde (c). The figure shows that in the SFCE, These calibrations suggest possibly lower solubility of these compounds is observed than compared to literature values(c). Shaded area indicates one sigma 1σ standard deviation of the variance in the slope during this three-month period. Average experimentally determined calibration slope for methanol, acetone and acetaldehyde were 0.00786 ± 0.00115 ppb ppbv $\text{nmol}^{-1} \text{dm}^3$, 0.0469 ± 0.0145 ppb ppbv $\text{nmol}^{-1} \text{dm}^3$ and 0.0743 ± 0.0190 ppb ppbv $\text{nmol}^{-1} \text{dm}^3$. Plotted along this are the predicted slopes using all experimentally determined solubilities as listed in R. Sander (2015). The recommended solubility by S. P. Sander et al., (2015) is plotted as a solid thick line in dark blue. The key to the figure is listed in the a appendix table in the supplementary material, listing the an in-figure text reference followed by the dimensionless water over air Henry solubility in MilliQ water at 20°C and the predicted slope using the listed experimentally determined solubility. For full reference of the cited solubilities, please refer to R. Sander (2015).

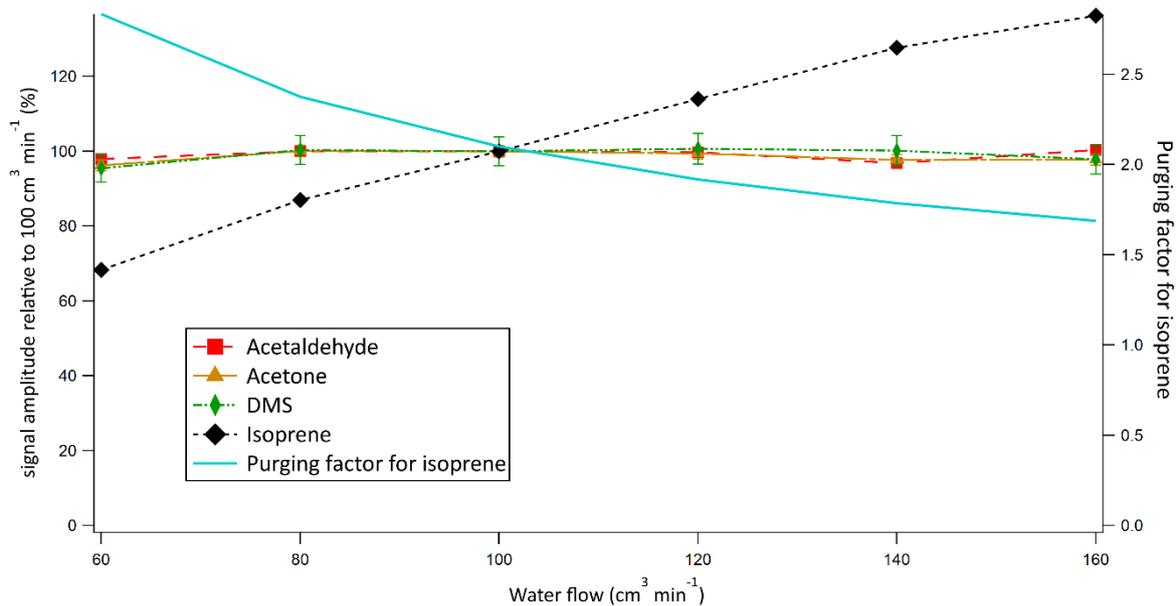
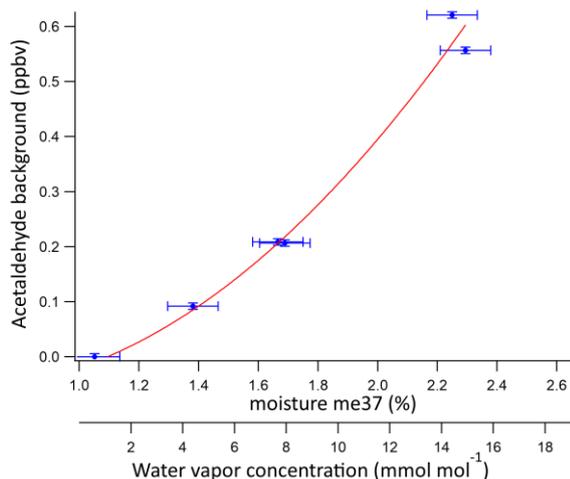
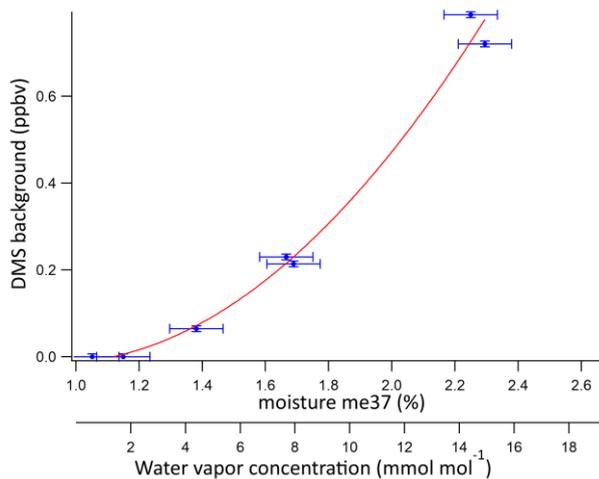


Figure 25: Relative signal as a function of water flow into the equilibrator. Error bars represent random error propagation where the initial error has been determined from the standard deviation of 10 consecutive 6 min blank measurements.

Figure 6: Instrument response to step changes in seawater OVOC concentration (step size: 20 nmol dm^{-3} acetone, 20 nmol dm^{-3} acetaldehyde, 200 nmol dm^{-3} methanol).



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Figure B2: (a) Benzene gas phase calibrations at different humidities and the dependency of the slope (b) and background (c) on the humidity. Error bars on the slope and intercept represent 95% confidence intervals of the linear regression.

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Figure B3: (a) Toluene gas phase calibrations at different humidities and the dependency of the slope (b) and background (c) on the humidity. Error bars on the slope and intercept represent 95% confidence intervals of the linear regression.

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Figure B4: (a) Isoprene gas phase calibrations at different humidities and the dependency of the slope (b) and background (c) on the humidity. Error bars represent 95% confidence intervals of the linear regression.

Figure B5: Ratio of the isoprene parent ion at m/z 69 to the fragment at m/z 41 as a function of drift tube voltage. Plotted along are the measured isoprene mixing ratio computed from the mass of each of the ions.

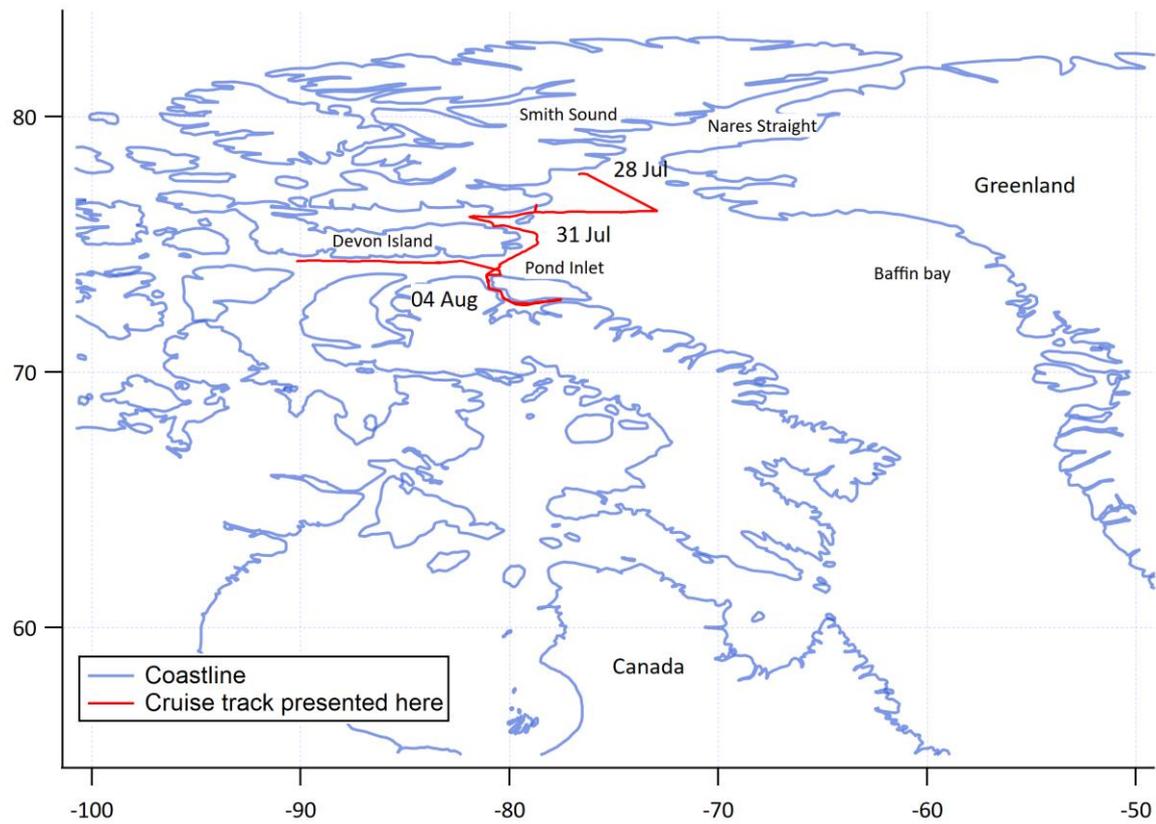


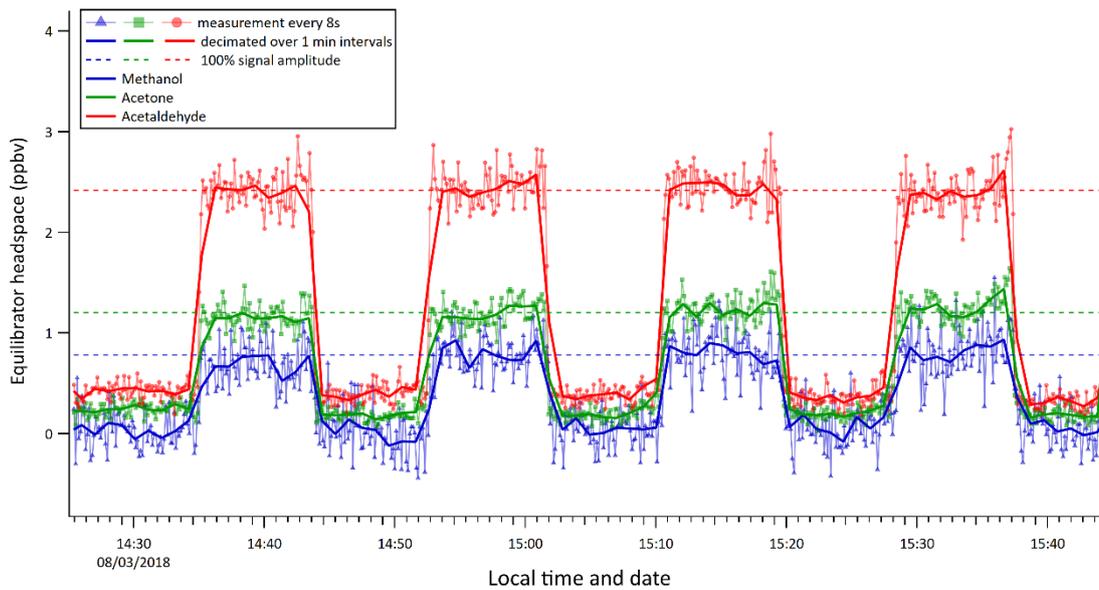
Table E1: Table listing experimentally determined Henry solubilities of methanol, acetone and acetaldehyde listed in R. Sander (2015) along with the in-text reference and the computed slope of the response in the equilibrator in $\text{ppb nmol}^{-1} \text{dm}^3$. For full reference of the cited solubilities, please refer to R. Sander (2015). Experimentally determined calibration slope for methanol, acetone and acetaldehyde were $0.00786 \pm 0.00115 \text{ ppb nmol}^{-1} \text{dm}^3$, $0.0469 \pm 0.0145 \text{ ppb nmol}^{-1} \text{dm}^3$ and $0.0743 \pm 0.0190 \text{ ppb nmol}^{-1} \text{dm}^3$.

Reference	Henry solubility	Predicted slope $\text{ppb nmol}^{-1} \text{dm}^3$
Methanol		
1. Li et al., (1993)	7378	0.00326
2. Snider and Dawson (1985)	7220	0.00333
3. Rytting et al., (1978)	7378	0.00326
4. Brunett et al., (1963)	7714	0.00312
5. Glew and Moelwyn Hughes (1953)	7430	0.00324
6. Butler et al., (1935)	7714	0.00312
7. Vitenberg and Dobryakov (2008)	7044	0.00341
8. St. Pierre et al., (2014)	2212	0.01090
9. Helburn et al., (2008)	2616	0.00919
10. Teja et al., (2001)	6716	0.00358
11. Zhou et al., (2000)	8882	0.00271
12. Gupta et al., (2000)	6678	0.00360
13. Altschuh et al., (1999)	5367	0.00448
14. S. P. Sander et al., (2011)	6715	0.00358
Acetone		
15. Benkelberg et al., (1995)	891	0.0269
16. Hoff et al., (1993)	878	0.0274
17. Zhou and Mopper (1990)	1060	0.0227
18. Guitart et al., (1989)	746	0.0322
19. Hellmann et al., (1987)	341	0.0703
20. Snider and Dawson (1985)	802	0.0299
21. Schoene and Steinhanses (1985)	1062	0.0226
22. Sato and Nakajima (1979)	933	0.0258

23. Vittenberg et al., (1975)	813	0.0295
24. Poulain et al., (2010)	946	0.0254
25. Ji and Evans (2007)	863	0.0278
26. Falabella et al., (2006)	744	0.0323
27. Strekowski and George (2005)	914	0.0263
28. Straver and de Loos (2005)	781	0.0308
29. Chai et al., (2005)	748	0.0321
30. Ayuttaya et al., (2001) (EPICS method)	325	0.0737
31. Ayuttaya et al., (2001) (static cell, linear form)	3.0587	5.93
32. Ayuttaya et al., (2001) (direct phase concentration method)	1725	0.0139
33. S. P. Sander et al., (2015)	901	0.0267

Acetaldehyde

34. Ji and Evans (2007)	527	0.0455
35. Straver and de Loos (2005)	374	0.0641
36. Marin et al., (1999)	510	0.0470
37. Benkelberg et al., (1995)	439	0.0547
38. Zhou and Mopper (1990)	552	0.0435
39. Guitart et al., (1989)	242	0.0991
40. Betterton and Hoffmann (1988)	419	0.0572
41. Snider and Dawson (1985)	408	0.0589
42. Vitenberg et al., (1974)	298	0.0991
40. Betterton and Hoffmann (1988)	419	0.0572
41. Snider and Dawson (1985)	408	0.0589
42. Vitenberg et al., (1974)	298	0.0804
43. Buttery et al., (1969)	487	0.0493
44. S. P. Sander et al., (2011)	444	0.0541



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Figure 6: Instrument response to step changes in MilliQ water OVOC concentration (step size: 20 nmol dm⁻³ acetone, 20 nmol dm⁻³ acetaldehyde, 200 nmol dm⁻³ methanol).

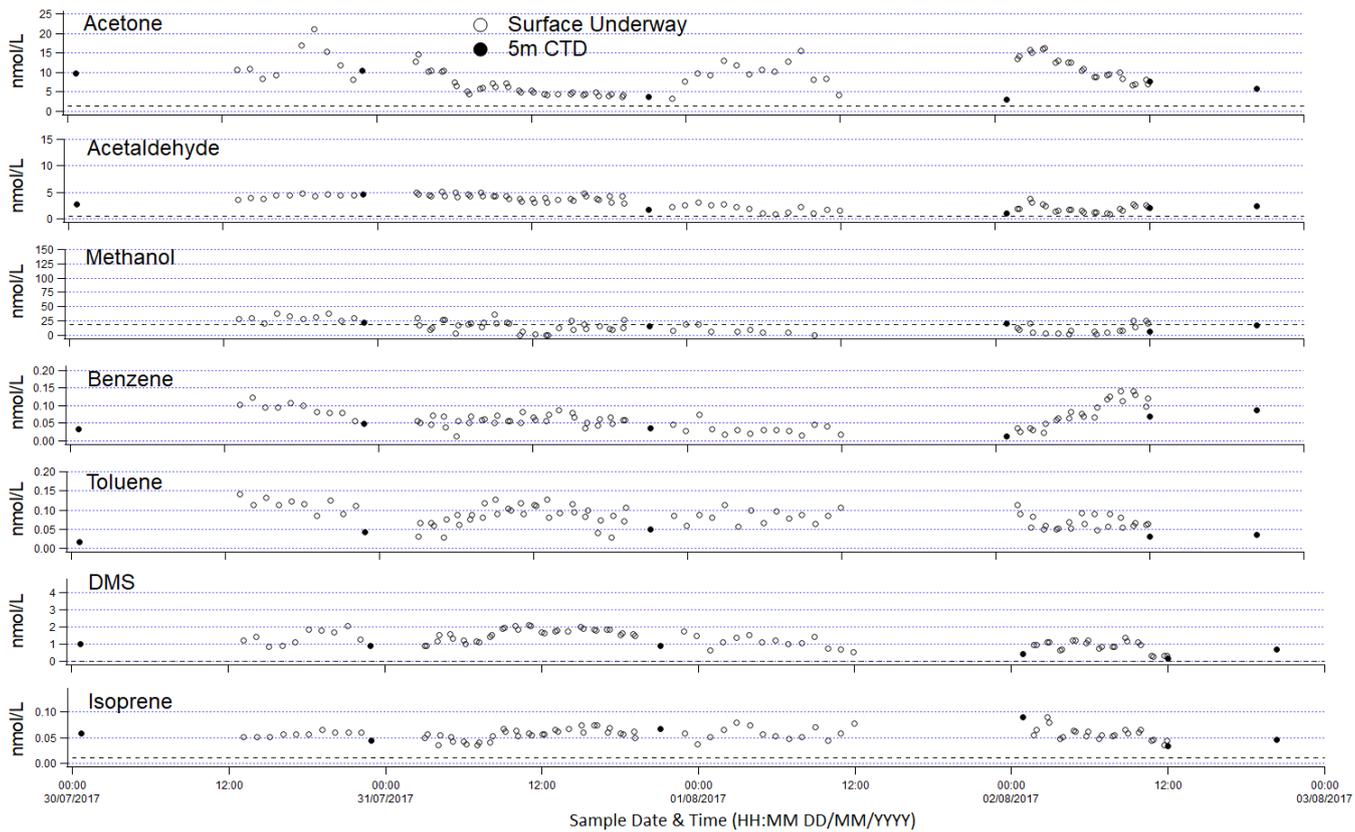


Figure 7: Selection of VOC measurements made from the ship's build in underway surface water supply (open symbols) and discrete samples from 5m rosette (closed symbols). The dotted line represents the limit of detection.

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Figure F1: a) Photograph of the instrument setup during deployment on the CCGS Amundsen with the jar trap. b) Photograph of the equilibrator in the laboratory post deployment with the PTFE tee fitting mounted to separate air and water at the end of the segmented flow tube.

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