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Underway seawater and atmospheric measurements of volatile organic compounds in the Southern Ocean

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S1: Description of the blanks

High purity British Technical Council approved (BTCA) "zero air" supplied by BOC Group plc is scrubbed by a hydrocarbon trap and used as the carrier gas for the SFCE. To test for the purity of this zero air carrier gas, it was passed through the Pt-catalyst. A small amount (less than 0.05 ppb) of VOCs was detected in this carrier gas. This is corrected for in the calculation of seawater concentration accounting for the VOCs in the dilution flow.

A number of different blanks were recorded daily on the ship and a Pt-catalyst blank was measured hourly. The Pt-catalyst blank consists of measuring ambient air scrubbed by a custom Pt-catalyst set to 450°C for 5 min every hour. The hourly automated measurement of Pt-catalyst blank was controlled by solenoid valves. The Pt-catalyst is expected to oxidize all VOCs to CO_2 and leave the humidity levels unaffected as shown previously (Yang and Fleming, 2019). Additionally, MilliQ water was measured daily followed by a "wet equilibrator blank". The "wet equilibrator blank" consisted of stopping the water flow into the SFCE and measuring zero air passed through the equilibrator coated in MilliQ water for 30 min. This was to allow purging of the gases from the walls of the equilibrator. Hence, the last 5 min of the wet equilibrator bank were used as a wet equilibrator measurement. Furthermore, a "humid air" blank was measured. This consisted of measuring the wet equilibrator air that was further scrubbed by the Pt-catalyst for 40 min. This blank was followed by a zero air measurement which consisted of directly measuring BTCA zero air scrubbed by a hydrocarbon trap. At every station, seawater from the deepest bottle on the rosette was measured (sampled from the CTD Niskin). This seawater coined here as "bottom seawater" was typically from 500−5000m depth, far below the mixed layer. For compounds that are produced in the mixed layer and consumed at depth (such as DMS) it may be expected that this seawater contains near zero amounts of VOCs.

These different blanks have advantages and disadvantages. Sample humidity is known to affect the measurement background and signal of the PTR-MS (de Gouw and Warneke, 2007; Wohl et al., 2019). The Pt-catalyst blank is the most suitable blank for the air measurements since it has the same humidity as the ambient air. A clear advantage of this blank is that it was measured hourly and enables to capture short term variability in the background. For example, a large change in background is typically observed after turning the PTR-MS off and on again, which occurred at the beginning of the deployment and on 07/03/19. Additionally, a higher number of blanks allows for a more precise determination of the true background.

The other blanks were all measured once per day, except the bottom seawater blank, which was measured as per availability. The Pt-catalyst blank could be used as a blank for the equilibrator headspace measurements for compounds that do not display a humidity dependence. However, this does not account for any possible contamination from the equilibrator. The wet equilibrator on the other hand may be overestimating any emission from the SFCE. This is because zero air spends twice as much time in the SFCE during a wet equilibrator blank compared to equilibrator headspace when measuring seawater. Additionally, any contamination by the coil is likely to be suppressed during the seawater measurement (Wohl et al., 2019). A blank that purely considers the effect of humidity on the signal is the humid air measurement. However, it also does not account for any possible contamination by the coil. The zero air carrier gas measurement is useful to capture any drift in the PTR-MS background. However, the zero air is much dryer than the Pt-catalyst blank. The benefit of the bottom seawater as a blank is that it is exposed to the SFCE the same way as the underway seawater and thus accounts for any possible contamination from the coil. However, using the bottom seawater as a blank would lead to an underestimation of the seawater concentration if the deep concentration is >0.

On ANDREXII, for compounds that display a near zero humidity dependence of the background (acetone, isoprene, DMS), the Pt-catalyst blank is used as a blank. For compounds that do display a humidity dependence of the background (acetaldehyde, methanol), humid air or the wet equilibrator was used as a background for the SFCE headspace measurements (see Table 1).

S2: Daily normalized concentration

Table S1: Average diurnal change in acetaldehyde, acetone and isoprene seawater concentrations and airside mixing ratios. The hourly concentration is normalised by the average concentration of the corresponding day.

solar hour of day	acetaldehyde daily normalised seawater concentration	acetaldehyde daily normalised air mixing ratio	acetone daily normalised seawater concentration	acetone daily normalised air mixing ratio	isoprene daily normalised seawater concentration	isoprene daily normalised air mixing ratio
0	0.788675	0.776747	0.995097	0.974841	0.943956	0.926846
1	0.814159	0.872506	1.023879	0.931819	0.94083	0.945539
2	0.867075	0.714347	1.007151	0.955947	0.953883	0.911663
3	0.910626	0.643516	0.96519	0.968363	0.982217	0.837849
4	0.837073	0.654276	0.942302	0.996761	0.980161	1.080864
5	0.793929	0.693675	0.936027	0.981523	0.996149	1.044377
6	0.760484	0.817866	0.916124	0.975197	0.987399	0.964475
7	0.800622	0.879388	0.91814	0.977652	0.967868	0.95186
8	0.867686	0.797183	0.942331	0.880796	0.928248	1.018882
9	0.996176	1.1813	0.917628	0.929205	1.007334	0.910476
10	0.843284	1.143173	0.928064	1.032775	0.986988	1.080667
11	1.094314	1.681464	0.945101	1.102935	1.018838	1.405764
12	1.171157	1.287594	1.00346	1.044295	1.053715	0.886844
13	1.568916	1.413326	1.069712	1.09462	1.100622	0.9531
14	1.332422	1.615852	1.03397	0.950218	1.030993	1.009859
15	1.350397	1.413706	1.043292	1.04865	1.05734	1.003888
16	1.265919	1.444674	1.082216	1.138299	1.002782	1.291885
17	1.150155	1.446171	1.06375	1.055577	1.001323	1.049174
18	1.166623	0.956746	1.025235	1.057446	1.036747	1.354458
19	1.027749	1.162019	0.976317	0.994014	0.980945	1.150238
20	0.989716	1.054761	0.971302	0.996036	0.963933	1.134235
21	1.082239	1.107551	1.010829	0.945843	0.9931	0.825963
22	0.960864	1.057073	0.99395	0.956057	0.967383	0.830455
23	0.872243	0.86164	0.991981	0.960849	0.951282	0.882022