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Interactive comment on "Underway seawater and atmospheric measurements of volatile organic compounds in the Southern Ocean" *by* Charel Wohl et al.

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Many thanks for the thoughtful comments from this reviewer. The reviewer has been able to provide thought provoking comments which in our opinion improved the manuscript. 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 in red font colour.

The authors mention that, to their knowledge, these are the first reported seawater measurements for methanol, acetone and acetaldehyde. Even for DMS and isoprene the Southern Ocean is highly undersampled which, for all 5 compounds, increases

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errors when running global atmospheric models and using no (or very sparse) data from the Southern Ocean. This fact highlights the importance of these measurements presented in the manuscript, which I think the authors are aware of. However, I suggest to even highlight this importance in the introduction section adding a paragraph about the Southern Ocean and its influence on the atmospheric chemistry, highlighting the importance of this work.

Suggestion accepted, please see below.

L74: Models indicate that over the Southern Ocean and globally, DMS (Tesdal et al., 2016) and isoprene (Carslaw et al., 2013) emissions are important for cloud formation and the albedo of the planet. The Southern Ocean is highly under-sampled for DMS and isoprene which increases errors when running global atmospheric models and using no (or very sparse) data from the Southern Ocean. To give an appreciation of the sensitivity of the models to these emissions, Woodhouse et al. (2013) calculate a 4-6 % change in global CCN for a 10 % change in DMS flux (relative to Kettle and Andreae (2000)) in the Atlantic sector of the Southern Ocean for December. Variations in CCN concentrations show clear seasonal trends with highest concentrations typically observed in austral summer (Kim et al., 2017a) thus suggesting, amongst others, a role of biological productivity in formation of CCN over the Southern Ocean.

2.1.1: Calibrations. Do the authors have any scientific explanation why isoprene, the most insoluble compound within the 5 compounds presented, is the only compound not achieving fully equilibration using the presented setup?

The reason for incomplete equilibration of isoprene is discussed in detail in a manuscript describing the technique used to make these measurements (Wohl et al., 2019). To briefly recap, the degree of equilibration depends on solubility of the compound due to the dependance of the air sea exchange onstant on solubility (Liss and Slater, 1974). Less soluble compounds are expected to equilibrate slower.

2.2.3: The authors mention the light driven contamination in the seawater measure-

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ments of acetone, acetaldehyde and isoprene and I am confident that they solved this issue. However, for me it is not clear what exactly causes this issue. Perhaps the authors could state clearly if they think it is coming from contamination of the material exposed to high sunlight intensity or from photochemical production in the water flowing through the tube. Both facts seem reasonable, however, if it is the material shouldn't you see these variations also when measuring outside air? Did you experience similar issues in former cruises or tests?

For us it also remains unclear what exactly caused this issue. When sunlight was shining directly at the equilibrator through the window, VOC levels measured with the PTR-MS/SFCE immediately increased to unrealistically high levels. When we closed the blinds, the measured VOC levels greatly decreased and the change was again immediate. A large reduction in the VOC levels was also observed when shielding the air-water separating tee from direct sunlight. The residence time of sample air in this air-water separating tee was on the order of half a minute.

Concerning the outsie air sampling line: the residence time in the air sampling tube was short at approximately 6 s. Most of the 90 m long air inlet tube was also shielded from direct sunlight. We have not experienced issues on former cruises with Teflon air inlets. And our only previous deployment of the SFCE (Wohl et al. 2019) at sea was in a windows-less lab. Photochemical productions of isoprene and carbonyl compounds at the sea surface microlayer has been observed before (Brüggemann et al., 2018; Ciuraru et al., 2015). It's possible that similar reactions were taking place on the water surfaces inside of the SFCE. However such photochemical productions were not evident in the air measurement because the air sampling tube was usually dry and the air residence time was much shorter.

A few sentences have been added to the manuscript:

The exact cause of this light-driven contamination in the SFCE system is unclear. Photochemical production of isoprene and carbonyl compounds at the sea surface micro-

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layer has been observed before (Brüggemann et al., 2018; Ciuraru et al., 2015). It could be that similar reactions were taking place on the water surfaces inside of the SFCE.

Figure 3: Data is shown for 2 weeks before and after dealing with this issue. First, the cruise started only one week before the issue was dealt with, which leads to second, do the two subsets of data have about the same number of measurements? Please check. Additionally, the authors state that daytime values prior to 04/03/19 were not used. However, it seems, that night time data shown in Figure 3 is consistently (for all three compounds) lower than data prior to 04/03/19 shown in Fig. 5a, 7a, and 8a. (i.e. Figure 3, acetone seawater night time values “2 weeks before”: âĹij6 nM; Figure 7, average acetone seawater values shown prior to 04/03/19: âĹij7-9nM). Please check.

Indeed, the cruise started one week before the issue was dealt with. This has been corrected in the text of the manuscript. Bespoke analysis was carried out on 5 min averaged data, where each hour of measurements would contain seven 5 min averaged datapoints. The hourly bins before the SFCE was protected from light contain between 8 and 24 5 min averaged datapoints. The hourly bins after the SFCE was protected from light contain between 30 and 81 5 min averaged datapoints. Generally the fewest datapoints were for daytime measurements, due to operations during daytime.

Thank you for pointing out this inconsistency which has been corrected for in the updated manuscript.

l. 309 / Table 2: The authors mention the positive skewness (mean: 0.053, median: 0.045) in the isoprene ambient air mixing ratio which they explain by biology and wind driven emissions as well as the very short atmospheric lifetime. I totally agree. However, this skewness is not at all discussed in the DMS section although the skewness is way higher (mean: 2.6, median: 1.39). DMS has a longer atmospheric lifetime and is more soluble than isoprene.

The reviewer appears to be referring here to ambient air DMS mixing ratios, while citing

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values of the DMS seawater concentrations. The DMS ambient air mixing ratios do not display a strong positive skewness. Therefore we assume that the reviewer refers to the DMS seawater concentrations. The suggestion has been accepted and this skewness is discussed in a little bit more detail. See below. The campaign mean seawater concentration of DMS was 2.60 nmol dm-3 and the median was 1.39 nmol dm-3. This illustrates the positive skewness of the DMS seawater concentrations due to episodic high concentrations of DMS.The highest DMS seawater concentrations were observed near the Antarctic Peninsula upwelling region (around 28/02/19, up to 7.55 nmol dm-3) and east of the South Sandwich Islands (around 13/03/19, up to 24.44 nmol dm-3). Chlorophyll a was also elevated in those regions.

Technical corrections: l. 11: delete “and” after “compounds” Suggestion accepted. l. 27: missing full stop after “outgassing” Suggestion accepted. l. 288: “As shown in Fig. 1 and Fig. 2 . . .” Suggestion accepted. 292: “chlorophyll a” Suggestion accepted. l. 441: “dependent” Suggestion accepted. l. 452: remove “in” Suggestion accepted. l. 518: add “,” after “isoprene” Suggestion accepted. ll. 726-730: check reference Reference checked and corrected. typo Figure caption 1: double use of “data” Typo corrected. Figure 2a: right y-axis: remove “(PSU)” Suggestion accepted. Figure 2b: left y-axis “μg dm-3” Suggestion accepted.Figure caption 5: “. . .and time series of chlorophyll a.” Typo corrected.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2020-2/bg-2020-2-AC2-supplement.pdf

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