

Interactive comment on “Oxygenated volatile organic carbon in the western Pacific convective centre: ocean cycling, air–sea gas exchange and atmospheric transport” by Cathleen Schlundt et al.

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Response to the referee#1 Mingxi Yang

We thank Mingxi Yang (MY) for the intensive work on our manuscript and the helpful comments. We appreciate his effort to improve our manuscript.

MY: This is a really interesting paper that describes a set of oxygenated volatile organic compound (OVOC) measurements in surface ocean/lower atmosphere of the western Pacific. The authors explored relationships between seawater OVOC concentrations and phytoplankton groups as well as types of dissolved organic matter. They also

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constrained 1) the contribution of air-to-sea flux on the oceanic OVOC budget, 2) the contribution of sea-to-air flux on the atmospheric OVOC budget, and finally 3) the contribution of boundary layer OVOCs to the upper troposphere (relevant for HO_x cycling).

The number of data points is somewhat limiting (especially the atmospheric OVOC concentrations, which are necessary for the flux calculation), but the analysis is sound and the data interpretation seems reasonable. I think the paper is publishable after minor revisions.

Specific comments: p.2 Line 6-31. To be more precise, the authors should specify the sources and sinks of individual OVOC compounds in these 2 paragraphs, rather than always using the term “OVOCs”.

Authors: We have changed the text to give some specific examples of different OVOCs for the different sources and sinks. For instance: “OVOCs, such as acetone and acetaldehyde, are involved in the production of reactive nitrogen compounds, such as nitrogen dioxide (NO₂, involved in ozone production), peroxyacetic acid (HNO₄), and nitric acid (HNO₃), and they are precursors of peroxyacetyl nitrate (PAN), a persistent harmful pollutant (Folkins and Chatfield, 2000; Fischer et al., 2014). OVOCs, such as acetone, are a source for hydrogen oxide radicals (HO_x), which is of special importance for the upper troposphere (UT), where the concentration of a main precursor, namely water vapor, is much lower than at the Earth surface (Singh et al., 1995; Wennberg et al., 1998; Müller and Brasseur, 1999). Furthermore, OVOCs, such as acetone, acetaldehyde and propanal, can contribute to particle formation in the atmosphere, resulting in albedo enhancement (Blando and Turpin, 2000). . . .” However, most of the OVOCs have the same or similar sources; thus, we kept often the term OVOCs to keep the sentences simple. We hoped that providing the appropriate references would aid in this. Furthermore, acetone and methanol are the most well studied OVOCs and the literature refers mainly to these two compounds. There were less specific publications about e.g. butanone or butanal compare to acetone and methanol. MY: p.3 line 4-10. The ‘either. . .or’ scenario doesn’t completely hold due to photochemical destructions

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of OVOCs, for example. This paragraph also feels disconnected from the neighboring paragraphs. Can probably just move it to Section 3.2.2. Authors: Indeed, the OVOCs are not only distributed in the atmosphere as indicated by the “either...or” scenario, but can also be destroyed and produced. Thus, we rewrote the first sentence (and subsequent sentences). However, we think it should stay in the introduction, in order to give some background on the region as a transport pathway to the UT. We added another sentence linking this paragraph to the beginning of the Intro, to underline the importance of OVOCs as an UT HOx source. .

MY: p.4 line 5-19. Did the authors thoroughly test the effect of using potassium carbonate as the drying agent – that it doesn’t cause any loss/contamination in OVOCs?

Authors: We tested a couple of different methods to dry the sampling gas stream to avoid blocking our cryotrap. We tested different cold traps, such as ethanol mixed with dry ice or frozen water mixed with different salts. However, these cold traps were not cold enough to freeze the water fast enough without losing the OVOCs. The OVOCs dissolved immediately in the water when it condensed in the water trap. We also tried Nafion. However, ketones like acetone were trapped in Nafion. Only potassium carbonate showed good reproducibility without losing significant amounts of OVOCs. We had to pretreat the K₂CO₃ before use by flushing it with helium for 20min. When the K₂CO₃ got too wet OVOCs were trapped again, so we had to replace the trap after around 5 measurements. We now give more details about this trap in the text.

MY: Out of curiosity, in this setup how much of each OVOC compounds is purged out from the water phase after 20 minutes approximately?

Authors: We never did a full sparge of the samples to see how long it took to purge approximately 100%. It took too long and flooded the lines with too much water. We did repeated tests for reproducibility of the signal with the same standard concentration at different sparging times. Therefore, we have confidence in the measurements, but cannot answer what percent was sparged i in 20 mins.

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MY: The fact that the water standards were prepared in Milli Q water while the actual samples were seawater will likely create a small bias in the measurement (due to the effect of salinity on gas solubility, and thus purging efficiency).

Authors: We discussed this at length during the time of setting up our system. We tested adding our standard solution to seawater (SW) vs. MilliQ (MQ) several times. The seawater standards were never very repeatable/precise. For example, after sparging both SW and MQ for approx. 3 days, the blanks in seawater were at least double the MQ blanks. Eventually, the uncertainty in our calibrations was larger than the possible systematic problem of the salting out effect. We could control our MQ blanks better and had much better reproducibility, so we decided to use MQ and take the highest uncertainties.

MY: Given the analytical errors and reproducibility stated, what are the limits of detections for these compounds in seawater?

Authors: The detection limit of all OVOCs was around 0.06 nmol L⁻¹. We added this info in the text.

MY: Line 21-31. Was potassium carbonate used to dry the air samples too?

Authors: Yes. Also here we tested the possible loss and contamination of OVOCs. We used the same setup for air samples as for water samples to be consistent.

MY: p. 6, line 11-19. As discussed by Yang et al PNAS 2013 (www.pnas.org/content/110/50/20034.abstract), the Duce et al. 1991 parameterization probably underestimates airside diffusional resistance and thus overestimates total airside transfer velocity.

Authors: We tested our fluxes by comparing them to a newly computed flux using Johnson et al. (2010)’s recommendation for k_a (specifically Eqs. 10, 15, 16). The values are, on average, 20% higher (lower if fluxes are negative) using the new method. Since the values we report in the original manuscript are lower, they are a more conserva-

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tive estimate of the flux. We will keep these values but make a statement in the text reflecting this point and adding 20% to our uncertainty estimate.

MY: p. 10 line 24. If atmospheric OVOC input is important for the ocean mixed layer OVOC budget, some of the spatial variability/correlations in seawater OVOC can preassembly be in part explained by variability/correlations in atmospheric deposition fluxes of OVOCs?

Authors: We correlated also seawater OVOCs with OVOCs in the atmosphere and couldn't find any significant correlations. We assume that the variability in seawater and atmosphere due to the complex and different controlling factors in both spheres is too high to find similarities of marine and atmospheric OVOCs.

MY: Have the authors looked for correlations of OVOCs in air? By eye some of the compounds appear to strongly correlate.

Authors: That's a good point. We correlated the atmospheric OVOCs now and found significant correlation between acetone and propanal ($r^2 = 0.84$) and between acetone and butanal ($r^2 = 0.72$). We added this to the text in Section 3.2.1. We have been careful in the manuscript to not read too much into the fact that not all gases are correlated among each other, since atmospheric measurements have been taken less often (compared to oceanic measurements) and thus detecting significant correlation is more difficult. Therefore, one cannot exclude that the other gases are also controlled by the same factors, even though they do not show significant correlations

MY: p. 10 line 39-40. This sentence contradicts with what's stated in your abstract, that most of the OVOC fluxes were into the ocean. I'd pick a tone and stay with it.

Authors: MY is right that it sounds contradictory. We changed this sentence and the one in the abstract to make clear that we calculated, on average, a negative flux. Just to be clear, the fluxes were quite small, showing that the ocean and the atmosphere were near equilibrium for OVOCs.

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MY: Also, do the OVOC seawater concentrations, atmospheric concentrations, and air-sea fluxes vary diurnally? If so, it might provide further hints to the possible sources.

Authors: We compared the data we sampled in the night with the data from the day. However, we couldn't find significant differences between night and day datasets, probably do to different regions the day and night samples were taken. Unfortunately, we did not have 24h drift stations during the cruise to observe diurnal cycles of OVOCs at one place. It is worth to investigate this on the next cruise with drift stations.

MY: p. 11 line 23 (typo here, should be Section 2.8, not 2.6)

Authors: Thanks, we changed it.

MY: p. 12, line 31-33. This is reasonable, though it's still possible that some unmeasured oceanic hot spots upwind of the eastern region were contributing to the atmospheric OVOCs.

Author: MY is right that marine hot spots might have occurred at some distance to the cruise track and that we could not measure. , Given the high variability of the measured OVOCs in water, the existence of further hot spots is of course possible. We made a short statement to include this possibility. However, we think this is less likely, as these hotspots would need to be much larger than anything we did measure during the cruise in order to explain atmospheric mixing ratios 10 to 20 times larger than the ones resulting from the observed oceanic sources..

MY: p. 12, line 40. Are only positive sea-to-air fluxes used here (as implied by the omission of acetaldehyde), or do the average air-sea fluxes include both positive and negative fluxes? In the case of the former, this calculation would represent the maximum contribution to UT.

Authors: The fluxes we report are net fluxes, as they are computed using the net concentration gradient.

MY: More generally, I think the authors can benefit from differentiating between net

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vs. gross fluxes here (i.e upwards and downwards; see Yang et al. ACP 2014). Even in a case where the OVOCs are in air-sea equilibrium, molecules of OVOCs from the sea will still emit into the atmosphere and molecules of OVOCs in the atmosphere will still dissolve into the sea (just the two fluxes cancel out mathematically). It could be that the molecules of OVOCs in air and in water come from rather different sources. Long story short, to look at the upper-limit impact of ocean emissions on the UT, I think it'd be useful to do another FLEXPART model run prescribed with the gross emission fluxes ($= K * C_w$). Of course, for the ketones that have reasonably long lifetimes, some molecules of ketones in the atmosphere will have come from the ocean and vice versa.

Authors: We thank MY for this point and discussed it heavily, but finally came to the conclusion that using gross fluxes out of the ocean is not very realistic for determining atmospheric budgets. The only way that the gross flux could impact the UT OVOC budget is if the vertical transport out of the marine boundary layer would take place on shorter time scales than the two-way ocean-atmosphere exchange. However, this is unrealistic and such an assumption would bias our assessment of the amount of OVOCs that make it to the UT. Therefore, after giving this point considerable thought, we decided that the net flux is a better choice for determining a realistic impact of OVOCs on the UT.

MY: Figure 9. to make it easier for the readers, can the authors please stick to one timestamp format (either day of year or day/month)?

Authors: Thanks for the suggestion, we have changed the Figure.

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