

## ***Interactive comment on “Missing OH Reactivity in the Global Marine Boundary Layer” by Alexander B. Thames et al.***

### **Anonymous Referee #1**

Received and published: 13 November 2019

This paper presents OH reactivity measurements from the ATom aircraft project, providing a substantial dataset in the under-studied marine boundary layer which will no doubt help to improve our understanding of the global oxidation capacity. A comparison of measured OH reactivity with modelled OH reactivity in this region seems to demonstrate that there is missing OH reactivity and the authors attribute this to an ocean source of short-lived reactive gases. As well as a number of minor comments, I have a few queries on the analyses performed to demonstrate that the missing OH reactivity in the MBL is statistically significant. Once these questions have been addressed, I am suggesting this manuscript is published in ACP.

Pg 1, line 36: Define OHR

Pg 1, line 38: Calculated or modelled OH reactivity?

C1

The amount of ‘missing’ reactivity often depends on the completeness of the individual OH sinks that were measured alongside. Although not the primary focus of this paper, it would be informative to know if the OH reactivity budget could be closed in the boundary layer over land?

Pg 3, paragraph 3: Given the sparsity of MBL OH reactivity observations, I suggest the authors expand their discussion (in section 4 on the earlier Mao et al study) to include the Pfannersill et al study which reports higher MBL OH reactivities and higher missing OH reactivities than observed during ATom.

Table 2: Was NO<sub>2</sub> measured during the project? If it was, but was not used to constrain the model, could the authors provide a comment on the level of agreement between measured and modelled NO<sub>2</sub>?

Pg 5, line 140: ‘background signal’ I presume the authors mean the ‘OH offline’ signal? As it reads, however, this ‘background signal’ may be confused with kbackground.

Pg 5, line 141: Did the ratio of the flow of carrier gas to the flow of ambient air vary with altitude? If it did, the authors should comment on the impact impurities in the carrier gas may have at high and low altitudes respectively. Could a change in the flow ratios explain the observed pressure dependence presented in Fig 2?

Pg 5, line 148: what NO concentration do the authors class as ‘high NO’?

Pg 5, line 156: Do the authors expect the low molecular weight VOCs present in the PAM chamber to form particles?

Pg 5, line 159: What do the authors mean by ‘media’

Pg 6, line 198: Was a pressure dependent background applied to all the OH reactivity data?

Pg 7, line 209: ‘..only 0.2 s<sup>-1</sup>’ vs Pg 6, line 187: ‘0.25 – 0.3 s<sup>-1</sup>’

Pg 7, section 2.3: How are photolysis rates treated in the model?

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Pg 9, line 279: 'Some extreme outlier points were removed.' the authors should comment on the approach they chose to remove data – was this data flagged as potentially having a problem?

Pg 9, line 287 and figure 4: Some of the OH reactivity data measured above 10 km do not match the model calculated OH reactivity exactly. Why?

Pg 9, line 292: Do the authors expect ambient HO<sub>2</sub> to make it into the flow tube without being lost on inlet lines? Given the fast rate coefficient employed in the model for the reaction of CH<sub>3</sub>O<sub>2</sub>+OH, did CH<sub>3</sub>O<sub>2</sub> not contribute a significant sink for OH?

Pg 10, line 309: 4 km is much higher than the MBL and for ATom 3 there seems to be statistically significant missing OH reactivity up to 6 km (fig 5). Was there any evidence of long-range transport of pollution in these regions that could contribute to OH reactivity (and missing OH reactivity) during these flights?

Pg 10, line 321: The authors should also comment of the 8 – 12 km data in figure 6. Some of these points also lie above the red dashed line. The number of 8 – 12 km points lying above the line is less than in the 0 – 4 km data, but is this simply because the 10 – 12 km data was set to match the modelled reactivity? I suggest that this analysis is conducted on 8 – 10 km data only and also 0 – 2 km and 2 – 4 km separately.

Pg 11, fig 7: I don't think the trend in missing reactivity with latitude is best illustrated by figure 7. Do the authors see a reasonable correlation if they plot missing reactivity vs latitude in a scatter plot?

Pg 11, line 339: The authors should make it clear which figure these data have been included in.

Pg 12, line 367: What were the typical NO concentrations during the campaigns? Table 3: I presume that the reactions from line 3 onwards apply to both Case 1 and Case 2? As the Table is set out, however, it currently looks like only 1 reaction ( $X + OH = XO_2$ )

C3

is added for Case 1. If ' $XO_2 + NO = HO_2$ ' is included as a reaction, shouldn't ' $HO_2 + NO = OH$ ' also be considered?

Pg 13, line 392: I think the authors mean 'missing' reactivity here.

Pg 13, 405 onwards: To determine the source strength, both the lifetime and the ambient concentration of the two species needs to be considered. So, although the calculated concentration of the alkane is ~43 times greater than the calculated concentration of the sesquiterpene, the lifetime of the alkane is ~43 longer, so the source strength to maintain the calculated concentrations of both species should be the same.

Pg 13, line 407: the Travis et al., 2019 is missing from the reference list.

Pg 13, line 412: 's<sup>-1</sup>' - superscript '-1'

Pg 13, line 413: '~0.5 ppb' or '0.26 ppb'?

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-866>, 2019.

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