

## ***Interactive comment on “Isotopic constraints on the role of hypohalous acids in sulfate aerosol formation in the remote marine boundary layer” by Qianjie Chen et al.***

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### **Responses to Referee #2**

We thank Referee #2 for the helpful comments. Please find our responses below.

1. First, in paragraph 230, the fractional contributions are discussed rather than the concentration. Later in the manuscript, the authors address the concentration but it may be worth mentioning the rationale for describing fractional contribution rather than amount here.

**Response:** Thanks for this suggestion. We separated the “Result” section (Sect. 4) and “Discussion” section (Sect. 5) in the manuscript. For the “Result” section, we

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showed only the observations of concentrations and isotopes and primary modeling results (without HOX contribution). Based on these results, we calculated the fractional contribution of sulfate formation from HOX and  $[HOX]_g$ , which is now described in the “Discussion” section. In paragraph 230, all the fractional contributions shown are obtained directly from the GEOS-Chem model, which does not include the fractional contribution from HOX and  $[HOX]_g$  mixing ratio.

**Additional changes to the manuscript:** Add “Based on the modeled fractional contributions to the sulfate burden from each oxidant except HOX, and knowledge about reaction rate constants of “HOX + S(IV)” reactions and Henry’s law constants of HOX, we calculate the amount of HOX needed to explain the discrepancy between  $\Delta^{17}O_{mod}(nssSO_4^{2-})$  and  $\Delta^{17}O_{obs}(nssSO_4^{2-})$  in Sect. 5.2.4.” to Line 234 in Section 4.2.

2. Second, dark OH reactions (from nitrogen reactions on aerosol surfaces, e.g. Fuchs et al., 2013 doi:10.1038/ngeo1964) has recently been described as an important nighttime oxidation pathway that is typically not considered in chemistry and aerosol models. What would the implications be here and can it be ignored?

**Response:** Thanks for raising this interesting question. High nighttime OH concentrations have been observed in forests (Faloona et al., 2001) and urban areas (Lu et al., 2014). The mechanism behind this is still unknown. Possible explanations include unimolecular reactions of isoprene-derived peroxy radicals (Fuchs et al., 2013) and an additional ROX production process from VOCs and additional recycling ( $RO_2 \rightarrow HO_2 \rightarrow OH$ ) (Lu et al., 2014).

In the offline aerosol version of GEOS-Chem that we used in this study, nighttime OH concentration are set equal to zero, so that nighttime oxidation of S(IV) by OH does not occur in the model. However, as the gas-phase reaction “ $SO_2 + OH$ ” is relatively slow compared to aqueous S(IV) oxidation, adding this dark OH production mechanism will be negligible. In our sensitivity study of doubling OH concentrations shown in Sect. 5.2.1, the fraction of sulfate produced by OH oxidation increases only from 20 % to 27

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% globally. In addition, we think this dark OH production can be ignored in our study because most of our samples are from remote marine boundary layer where isoprene and VOCs abundance are low.

**Changes to the manuscript:** Add “A diurnal variation as a function of solar zenith angle is applied to OH concentrations and photolytic loss rates of  $H_2O_2$  in the model.  $NO_3$  is set to be zero during daytime.” to Line 172 in Sect. 3.

Add “Thus, doubling OH concentrations has an insignificant effect on  $\Delta^{17}O_{mod}(nssSO_4^{2-})$ . The nighttime OH concentrations observed in forests and urban areas (Faloona et al., 2001; Lu et al., 2014) should have insignificant effects on our model results as most of our samples are collected in the remote MBL where isoprene and VOCs abundance are low. Our sensitivity study with doubled OH suggests additional nighttime sources of OH are not able to resolve the modeled overestimate of  $\Delta^{17}O(nssSO_4^{2-})$  observations.” to Line 277 in Sect. 5.2.1.

3. Third, how realistic is it that S(IV) + HOX results in no pH change in clouds (paragraph 420) and although this is the treatment used in the model, what are the difficulties associated with changing both cloud pH and the fraction of S(IV) + HOX at the same time?

**Response:** We do not have “S(IV) + HOX” reaction in the model. Adding “S(IV) + HOX” reaction in the model will probably decrease cloud pH, which will result in decreases in the fractional contribution of  $O_3$  relative to  $H_2O_2$  ( $f_{O_3}/f_{H_2O_2}$ ) (Line 422). Thus, the HOBr concentration calculated by assuming no change in pH is likely an overestimate (Line 432). We do not have enough information to estimate the magnitude of pH change after adding “S(IV) + HOX” reaction.

For a follow-up study, we are implementing “S(IV) + HOX” reaction in the model. The cloud pH will change in accordance with the additional sulfate produced via “S(IV) + HOX” reaction, as cloud pH in the model is a function of sulfate and other ion concentrations.

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**Changes to the manuscript:** Add “The magnitude of the potential decrease in cloud pH can only be obtained after adding the “S(IV) + HOX” reactions in the model, which will be done in a follow-up study.” to Line 422.

#### Reference

Faloona, I., Tan, D., Brune, W., Hurst, J., Barket, D., Couch, T.L., Shepson, P., Apel, E., Riemer, D., Thornberry, T. and Carroll, M.A.: Nighttime observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy, *J. Geophys. Res.: Atmospheres*, 106(D20), pp.24315-24333, 2001.

Fuchs, H., Hofzumahaus, A., Rohrer, F., Bohn, B., Brauers, T., Dorn, H.P., Häseler, R., Holland, F., Kaminski, M., Li, X. and Lu, K.: Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, *Nature Geoscience*, 6(12), pp.1023-1026, 2013

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