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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Comprehensive Atmospheric Modeling of Reactive Cyclic Siloxanes and Their Oxidation Products" *by* Nathan J. Janechek et al.

Anonymous Referee #2

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The authors develop an emissions inventory of siloxanes, which they then model in CMAQ. They find that the spatial concentrations of parent and oxidized products are different. They also assess seasonality and vertical gradients of siloxanes. For the most part, the analysis is technically sound, although I do have some critiques. The manuscript is well composed, and advances understanding of the atmospheric impacts from personal care products. Overall, my recommendation is for publication of this paper with some revisions.

General Comments

1. As I understand from Page 5, the authors' construct their inventory using methods described by McLahlan et al. (2010), which are mainly based on antiperspirant sales.

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Discussion paper

Yet, the first sentence of the manuscript mentions that siloxanes are also present in sealers, cleaning products, and silicone products. To what extent are the authors' underestimating emissions by only considering antiperspirant sales? MacKay et al. (2015) suggest that antiperspirants only account for ~70% of D5 consumption in personal care products in Canada. Buser et al. (2014) report per capita D5 emissions of 190 mg/person/d, yet the emissions used in this study are ~30% lower. This is confusing, since Buser et al. also forms the basis of this study's emissions estimate (Page 5, Line 11). Table S2 (which I really liked, and think warrants inclusion in the main text rather than in supplemental), shows a wide range of per capita siloxane emissions. It is not clear that the authors' emissions are central estimates compared with the prior literature. Some text justifying the authors' selection of the emissions estimation technique would be helpful.

2. The authors' estimate D4 and D6 emissions by ratio to D5 from Chicago measurements (Page 5). However, there appears to be significant variability in in D4/D5 and D6/D5 emission ratios in the literature (Table S2). Tang et al. (2015) highlight that the emissions of D4 and D6 from personal care products are 1-2 orders of magnitude smaller than D5. Whereas the ratio used in this study for D6 is about an order of magnitude lower than for D5, and the ratio for D4 is only a factor of 3 lower. Again, it is not clear that the authors' emissions of D4 and D6 are central estimates compared with the prior literature, and some justification on why the authors' chose Chicago emission ratios would be helpful.

3. In the abstract, the authors' highlight that siloxanes have a high dependence on population density. I think it is important to mention that while this looks like the case for D5, it appears to be less so for D4 and D6. For D4 and D6, the model exaggerated urban-rural contrasts in Figure 3, and half the data points in Figure 4 were off by an order of magnitude compared to observations.

Specific Comments

Introduction

4. Page 1, Line 24. Where does the 4.5 x 10ˆ5 kg/y produced number come from? Citation needed.

5. Page 3, Lines 4-7. First mention of the DEHM and BETR models, and should be spelled out/described here, rather than later in the manuscript.

Methods

6. Page 4, Line 20. Is there a reference for the meteorology used that the authors' can cite? If not, what settings were used to generate the meteorological fields in WRF?

7. On Page 4, Line 25, kOH values are reported for parent molecules. However, it's not clear if oxidation products react away as well, and if this is taken into account.

8. Page 5, Lines 9-14. It is not clear why the authors' chose the methodology they did for estimating D4, D5, and D6 emissions, given the range of literature values shown in Table S2. Some justification here is needed.

9. Page 5, Line 25. What version of the NEI are 2004 emissions based on? Also, satellite trends of NO2 have shown significant decreases over the U.S. from 2005-2011 (Russell et al., 2012). By using an inventory that is 5-7 years out-of-date between the model and observations, how would modeling results be affected if NOx emissions were lowered (especially with respect to Figure 2)? Also, what biogenic emissions inventory (and version) is used?

Results

10. Page 7, Line 17. It is not clear why the authors' state that rural and remote locations follow an OH-induced seasonal pattern when the statistical relationships find only wind speed of significance (Page 8, Line 4). Suggest revising this statement here and in the conclusions section.

11. Section 3.4. Given the large discrepancies in model and observations for D4 and

D6 (see Comment 3), especially in rural locations (Figures 3 and 4), Figures 5 and 6 seem like a stretch. I suggest removing these figures and section, which can be done without any loss to the main findings of the manuscript.

Tables and Figures

12. I found Tables 2 and 3 hard to follow. The point on the relationship with population could be better made with a scatter plot with population on the x-axis, and D4/D5/D6 concentrations on the y-axis. Also, how is population determined for sites located in parks?

13. Figure 3. Would be helpful to include in the caption the year and region of the sampling, for readers unfamiliar with the Yucuis et al. study. Also, state abbreviations in the figure labels would be helpful.

14. Figure 4. The flow of this figure was confusing to me at first. It may help to put all the CMAQ vs. measured concentration plots in one column, and other model comparisons in the right column. Also, it would help to label the horizontal resolution of each model, for readers who may be unfamiliar with BETR and DEHM.

15. Figure 8. I think this figure could benefit from having the same x-axes. The vertical concentration gradients do not appear as sharp for o-D5 than for the parent molecule, which is instructive.

Minor Comments

16. Page 2, Line 17. References listed here look misplaced.

References

Mackay, D., and I. van Wesenbeeck (2014), Correlation of Chemical Evaporation Rate with Vapor Pressure, Environ Sci Technol, 48, 10259-10263, doi:10.1021/es5029074.

Russell, A. R., L. C. Valin, and R. C. Cohen (2012), Trends in OMI NO2 observations over the United States: effects of emission control technology and the economic recession, Atmos Chem Phys, 12, 12197-12209, doi:10.5194/acp-12-12197-2012.

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