Response to Reviewers

We thank both reviewers for their constructive comments and suggestions. Our responses to the reviewers' comments are indicated in blue italics. The revised manuscript follows.

Reviewer 1

General Comments

This is a strong paper. The methodology is of high quality, the discussion of the results is insightful, and the paper is very well written. Large scale modeling of the atmospheric fate of cVMS has been previously conducted by others using similar methods and the general principles governing atmospheric fate of these chemicals have been discussed. The major technical innovations in this paper are:

- A higher spatial resolution, which allows a better description of concentrations in large urban areas.

- The inclusion of oxidation products in the model, which allows the concentration fields of the products to be explored.

The major contributions of this paper to understanding are:

- A more thorough discussion of how cVMS emission patterns and properties affect the horizontal, vertical and temporal variability in concentrations of cVMS and their primary oxidation products. The horizontal and temporal variability for cVMS has been discussed earlier, but not in this depth. The vertical variability for cVMS is novel, as is the discussion of the cVMS oxidation products.

- A comparison of the model results is made with a larger and more diverse set of measurements than has been presented previously attempted, lending more confidence to the modeling, in particular for D4 and D6.

A disappointment with this paper is that more effort was not devoted to exploring the atmospheric fate of the cVMS oxidation products. Although these model data represent one of the major technical innovations of the work, the vast majority of the discussion is devoted to discussing the native cVMS.

Response: The additional work on atmospheric fate of the oxidation product is work in progress. More detailed work on the oxidation fate requires semivolatile aerosol partitioning of the cVMS to be coded into the CMAQ model. We felt that the work was of sufficient contribution to the field to publish in two stages – one focusing on gas phase concentrations (the paper in question) and a followup paper that includes aerosol partitioning of the oxidation product. The aerosol yield information is just becoming available in the published literature now (in 2017) and would have been premature at the time of submission (in 2016).

Specific Comments

Page 2, line 4: Here the authors take sides in an ongoing infected scientific/political debate. They support this position by citing papers representing just one side of the debate. This is unnecessary and does not contribute to the credibility of their work.

Response: We have revised this section (p. 2, lines 2-14) by shortening it and referring the reader to a list of major regulatory screenings, reviews, and recent articles on the subject.

Page 2, lines 16-17: Here several references are given for work that was published in just one paper, even though that one paper is expressly stated at the beginning of the sentence.

Response: The additional citations, which contain measurement comparison to the DEHM or BETR models, have been removed. These papers are referenced later as examples of model-measurement comparisons.

Page 2, lines 24-27: I am surprised by the selection of information presented here, given that the second author has published simulations that give much more detailed insight into the latitudinal gradients, urban-remote gradients, seasonal patterns and sensitivity to processes and parameterizations on a hemispheric scale.

We have tried to modify this paragraph (p. 2, line 23 – p.3, line 8) to improve it along the lines of the reviewer comment.

Page 3, line 4: McLachlan et al. (2010) had no measured data from summer and autumn. Incorrect citation.

Response: We have separated citations (p. 3, lines 20-22) for McLachlan et al. (2010) and Krogseth et al. (2013) to remove confusion of which work corresponds to which period. We have changed our definition of the seasons to match those defined in the respective papers. The paper now states McLachlan et al. (2010) covering late spring and Krogseth et al. (2013) covering late summer.

Page 4, line 26 and paragraph that follows: It is not clear how dry deposition was modeled. Were the surfaces considered to be infinite sinks? Is this a reasonable assumption for the cVMS? I am not aware of evidence showing that cVMS are rapidly degraded on surfaces, except on soil when it is very dry. cVMS have log octanol-air partition coefficients of about 4-6, which suggests that surface media have a limited ability to soak up cVMS and that a partitioning equilibrium between the atmosphere and surfaces would be reached quickly. In this case, assuming that surfaces are infinite sinks would be a poor assumption. While I doubt that this will modify the conclusions of this study, it is important that the assumptions made in modeling deposition are clearly stated and justified.

Response: Cyclic siloxane dry deposition in CMAQ 4.7.1 is handled as an infinite sink. A deposition velocity is calculated using Pleim m3dry method that takes into account mixing and turbulence, molecular properties, and land type (Byun et al., 1999). The deposition velocity is multiplied by a concentration to calculate the amount deposited. This is consistent with how other species are treated in CMAQ. The Methods section (p. 5, lines 26-30) has been updated to reflect this.

A paragraph (p. 10, line 32 – p. 11, line 7) has been added to the Results and Discussion section describing that gas concentrations may be underpredicted due to the assumption that surfaces are treated as infinite sinks for deposition. We also explain that based on logK_{OA} *and log* K_{AW} *values, we would expect the influence to be minimized for the parent compounds since deposition is a minor process. For the oxidized species, the influence would be expected to be larger but surface degradation of the oxidized species is unknown. We also found similar or lower log*K_{OA} *values for other CMAQ deposition species.*

Page 6, line 31 and elsewhere: The literature cited by the authors discusses other sources of cVMS emissions besides personal care products. For instance, Brooke et al. (2009c) list emissions of residuals in PDMS as being twice as important as personal care products for emissions of D4 to air.

Response: We had already acknowledged non-personal care product sources in the introduction but have rephrased the section in question (p. 8, lines 10-13) to add the details from the UK risk assessment (Brooke et al., 2009a, b, c). The Brooke et al. (2009 a,b,c) emission estimates for Europe indicate the major source of D4 to the air is from residual PDMS while D5 and D6 is from personal care product use.

Page 8, lines 20-22: This assumption depends on the number of measurements that were conducted and the time period over which the measurements integrated. A handful of very short measurements can well give a non-representative picture of "typical" summer concentrations. I suggest that the authors provide some information on the number and length of the measurements.

Response: Yucuis et al. (2013) measurement details have been added to paper (p. 10, lines 3-6).
Chicago, IL: 16 measurements, 12 h, 8/13 – 8/21
Cedar Rapids, IA: 4 measurements, 24 h, 6/29, 7/2, 7/14, 7/26
West Branch, IA: 5 measurements, 30 – 47 h, 7/6, 7/15 – 7/22
A caveat (p. 10, lines 8-9) about the representativeness of the Yucuis et al. (2013) measurements has been added.

p. 10, lines 18-20: Why are hourly modeled data compared with daily measurements when it is clear that the different time scales makes the comparison difficult? I suggest that you integrate the modeled data into 24 h periods so that a direct comparison can be made.

Response: Thanks, we agree that it makes the most sense to average CMAQ data to 24-hour intervals. Table 2 and Section 3.3.3 of the text have been updated.

p.11, lines 10-16: Why did the authors not compare the levels of the oxidation products instead of comparing the levels of their precursors? The concentrations of the oxidation products of the cVMS have been calculated, and it should be possible to calculate them for SO2 as well. Given that one of the innovations of this work was the modeling of the cVMS oxidation products, I do not understand why these data are not used.

Response: In summary, we thank the reviewer for this excellent suggestion, but defer its implementation until future work for the reasons stated below. Furthermore, our rationale for looking at the precursor ratios is explained: because of the similar oxidation kinetics with OH, we believe that looking at precursor ratios is a useful conceptual model, particularly for the aerosol science community, which has given considerable investigation to the sulfur oxidation process. Furthermore, this conceptual model ties in nicely with experimental measurements of the precursor ratio (SO2/cVMS) and the aerosol ratio (S/Si), which for example was available in Bzdek et al. (2014).

We had not thought of examining the oxidation product concentration ratios, and we will explore that in our subsequent work that includes true aerosol partitioning of the oxidation products. It is complex to do (because of the different compartments that S(IV) and oxidized cVMS partition to). This complexity would require considerable additional word count in methods and results and discussion to accommodate. We anticipate oxidized cVMS to partition between gas phase, aerosol phase, and cloud droplets. Sulfur has the same phase partitioning issues, plus it can exist in different levels of dissociation (H2SO4, HSO4-, SO4--). So while such a ratio is likely possible, multiple ratios for different compartments would need to be considered – i.e., aerosol, cloud droplet, gas phase.

p.12, line 11: Has this been proven? It seems like a reasonable assumption, but I did not find proof for it in the paper.

Response: Thank you for the correction, as the statement has not been proven, but is rather an assumption. We have rephrased (p. 14, line 18) to state that we hypothesize increased model errors due to uncertain D4 and D6 emission rates.

Figures 1 and 2: The concentration intervals represented by the different colors are inconsistent. Could you not use a consistent logarithmic scale?

Response: Both figures now use a logarithmic scale, however the range is different from Figure 1 to 2 – so a given color does still indicate one concentration for cVMS and another for o-cVMS. We prefer to have separate scales in order to visually show concentration variability for each compound. While this may lead to confusion about relative concentrations, the fact that cVMS concentrations are much higher is noticeable throughout the paper, including in the abstract and in tables such as Table 1.

Figure 3: Information should be provided about the time period (dates) for which model data were collected and for which measured data were collected.

Response: The relevant details have been added to the now Figure 4 caption and the corresponding text.

References

Brooke, D., Crookes, M., Gray, D., and Robertson, S.: Environmental Risk Assessment Report: Decamethylcyclopentasiloxane, Environment Agency of England and Wales, Bristol, UK, 2009a.

Brooke, D., Crookes, M., Gray, D., and Robertson, S.: Environmental Risk Assessment Report: Dodecamethylcyclohexasiloxane, Environment Agency of England and Wales, Bristol, UK, 2009b.

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Yucuis, R. A., Stanier, C. O., and Hornbuckle, K. C.: Cyclic siloxanes in air, including identification of high levels in Chicago and distinct diurnal variation, Chemosphere, 92, 905-910, doi:10.1016/j.chemosphere.2013.02.051, 2013.

Reviewer 2

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. 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.

Response: The authors acknowledge the emissions section was a bit confusing as written. We have reworded (p. 6, lines 12-17) it to:

> *"The U.S., Canadian, and Mexican per capita emission rates of D5 provided by personal communication (van Egmond, 2013) and previously used and reported in McLachlan et al. (2010) was adopted for this study. Briefly, as reported in McLachlan et al. (2010), D5 emission rates were derived from country specific market share based on antiperspirant sales data combined with D5 consumption data from antiperspirant plus 10% to account for other sources. A table of many available cVMS emissions rates from multiple methods are represented in Table S2, and a wide variation exists."*

For D5, we adopted the per capita emissions from van Egmond (2013) and our only work was to grid according to population density at the model's horizontal resolution. For D4 and D6, we used the measurements of Yucuis et al. (2013) to establish D4/D5 and D6/D5 emission ratios.

McLachlan's method calculated D5 emissions from antiperspirant usage plus 10% to account for other sources. They then used antiperspirant sales data to calculate each countries market share. They combined each countries market share with their estimate of D5 consumption to get an emission.

The main reasons we used the emission values that we did use are (i) our modeling work started in 2013 and the values were the most recently available at the time, to our knowledge; (ii) we *thought that country-specific values were important to include for our study; and (iii) the emissions had previously been used in the DEHM model, facilitating comparison.*

We have removed the Buser et al. (2014) citation from the emissions methodology section. It was included because it includes work on emissions and reports the U.S. D5 emission value from the McLachlan et al. (2010) work, but it is perhaps misleading because we are not taking any of the Buser et al. (2014) values for incorporation into our model runs.

To keep the work a manageable length, we argue for keeping Table S2 as a supplemental table. We suspect a large majority of readers will be more interested in the atmospheric chemistry and transport concepts published in the paper, while the minority of readers interested in the actual emissions (and their temporal-spatial variability) will inspect the supplement.

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.

Response: Ratios from Chicago were chosen to establish D4/D5 and D6/D5 ratios because Chicago represents a major North American metro area with cVMS measurements (added to p. 6, lines 18-19). Measurements from Toronto could also have been used in a similar way. Chicago was selected because of familiarity of the author team with the Chicago measurements. Bottom up construction of D4 and D6 emission ratios considering sector specific emissions (sealers, PDMS decomposition, industrial emissions, wastewater treatment, sewage sludge, etc.) was beyond the possible scope of our study.

Furthermore, in results and discussion (p. 10, lines 27-31, we have stated that the use of a wider dataset of atmospheric concentrations (for the emissions 'inversion') and consideration of non-personal care products is needed.

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.

Response: It is certainly possible D4 and D6 concentrations have important non-personal care sources and a possible reason observations were higher than modeled concentrations. We discuss this as a possible reason on page 10, lines 27-28 (Yucuis et al. comparison) and have added this to one of the reasons on page 11, lines 24-25 (Genualdi et al. comparison).

Specific Comments

Introduction

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

Response: This was the threshold for determining high production volume chemicals in the US. We have revised (p. 1, lines 25-26) this to follow the OECD definition of >1,000 tonnes per year and added the appropriate citation. The D4, D5, and D6 species are on this list.

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.

Response: Thanks, this has been fixed on page 2, lines 27-29.

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?

Response: The following WRF details have been added to the methods section on page 5, lines 8-11:

"WRF was run with time steps of 120 s, 30 vertical layers, Morrison double-moment microphysics scheme, RRTMG longwave and shortwave physics scheme, Pleim-Xiu surface layer, Pleim-Xiu land surface model with two soil layers, and ACM2 PBL scheme. Reanalysis nudging using North American Regional Reanalysis (NARR) data was performed every three hours."

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.

Response: Additional details on the handling of the oxidation species has been added (p.5, lines 16-21) to explain that the oxidation products are believed to undergo additional oxidation reactions (Whelan et al. 2004) but they will remain oxidized cVMS – and thus are correctly labeled in the mechanism scheme and in the figures. Their physical properties will change upon further oxidation, but details on the mechanism, kinetics, and properties are very limited. In our treatment, the first oxidation step is modeled; subsequent oxidation steps are not modeled.

Added text:

"Reactions of the oxidation products are not included in the model. In part, this is because information is limited on the kinetics of further oxidation and on the changes that this would cause for fate, transport, and properties. Whelan et al. (2004) modeled subsequent oxidation reactions, and chamber-based oxidation studies observe multiple substitution products likely due to multiple substitution reactions or auto-oxidation by internal rearrangement (Wu and Johnston, 2016). In the model, only the first oxidation is computed. The oxidation products are denoted o-D4, o-D5, and o-D6, and for calculation of physical properties relevant to deposition, the single OH substitution is assumed."

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.

Response: Please see the response to general comments one and two.

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?

Response: Emissions were calculated from NEI 2002, version 3, with on-road and point sources projected to 2004 using EGAS, the EPA's Point source and Economic Growth Analysis System. Biogenic emissions were from BEIS 3.13. The emission model details have been to page 6, line 33 – page 7, line 2. The impact on the results of the dated emission inventory is likely only relevant for SO2:Si ratios, as SO2 emissions have dropped sharply. Ozone levels have decreased, but the cVMS and o-cVMS do not interact directly with ozone in our simulations. The influence of ozone, NOx, and VOC changes on OH concentrations (which will influence cVMS and o-cVMS) is difficult to anticipate in size, direction, and timing.

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.

Response: The general behavior of the rural sites is established in section 3.2, with description of the month of maximum and minimum concentration (see also Figure S6). Due to the normalization, the regression is really testing the ability of seasonal variability in local OH to predict seasonal variability in cVMS. In other words, do sites with the highest winter:summer ratio of D5 also have the highest winter:summer ratio of local OH^{-1}*. The regression analysis says this is not the case. See Figure S8(B,D). The failure of the regression analysis to show predictive power of local OH ratios is different from the influence of regional OH on regional concentrations.*

However, the regression analysis is important, from our perspective, because of the way that it shows the combination of PBL height and wind speed (or rather the season-to-season variation in this) is a predictor of season-to-season variability in cVMS concentrations. See Figure S7(A,C). The text has been modified (p. 9, lines 13-15) to stress that the regression analysis is testing correlation in season-to-season variability across seasons and sites.

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.

Response: We would like to leave these figures in the paper. The assumptions behind them are well documented, and we have changed the text to stress that the figures in question are tied to the assumption of population density dependent emissions of D4, D5, and D6 (p. 13, lines 4-6). We feel that figures like this may help measurement scientists construct interesting sampling plans, and to establish preliminary sample times and air volumes necessary to get appropriate sample loadings. The fact that a model with population-dependent emissions and realistic spatio-temporal OH predicts these types of ratios is a valuable result. Future measurements may prove it wrong – and more D4 and D6 measurements and an emission inventory are needed.

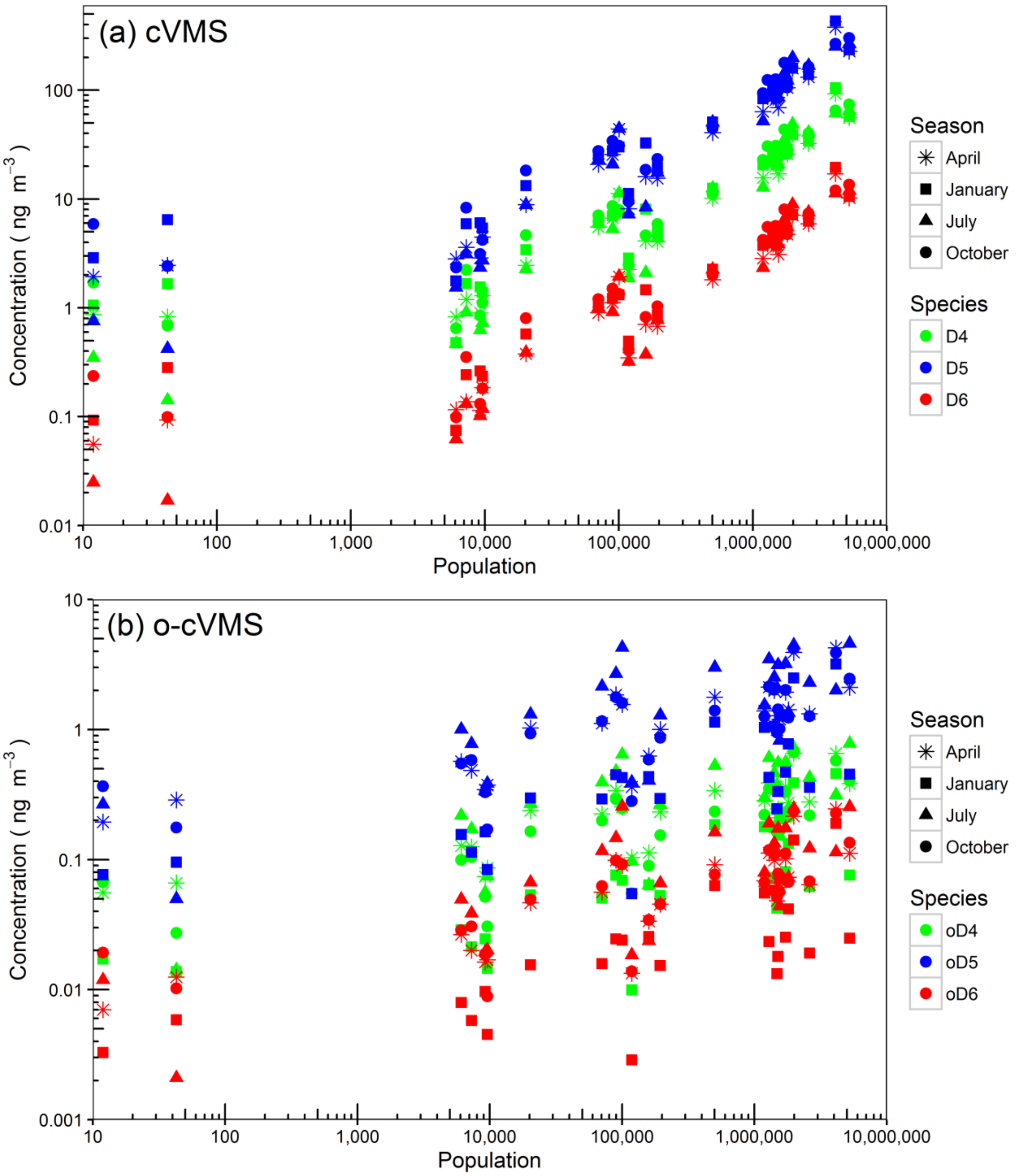
Tables and Figures

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?

Response: Thank you for the excellent figure suggestion. We have moved the tables to the supplemental section (now Tables S4 and S5), as we feel they may be useful references for monitoring study design. Population was determined from gridded population estimates detailed in the supplemental section. The population is that within the 36 km grid cell. For large metro areas that span multiple grid cells, the grid cell with highest population was used for analysis.

Population data was from population surrogates downloaded from EPA 2011 v6.0 Air Emissions Modeling Platform. This data is derived from census data, and therefore represents permanent population, and does not reflect seasonal visitors to tourist destinations. These details have been added to the paper on page 6, lines 31-33, and page 11, line 24.

Added following figure, now Figure 3:



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.

Response: Figure 4 has been updated with state labels and measurement details in the caption.

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.

Response: Figure 5 layout has been updated along with resolution details to figure caption.

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.

Response: Figure 9 has been edited to have consistent x-axes.

Minor Comments

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

Response: Citations have been removed.

References

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Comprehensive Atmospheric Modeling of Reactive Cyclic Siloxanes and Their Oxidation Products

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Abstract. Cyclic volatile methyl siloxanes (cVMS) are important components in personal care products that transport and react in the atmosphere. Octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), dodecamethylcyclohexasiloxane (D_6), and their gas phase oxidation products have been incorporated into the Community Multiscale Air Quality (CMAQ) model. Gas phase oxidation products, as the precursor to secondary organic aerosol from this compound class, were included to quantify the maximum potential for aerosol formation from gas phase reactions with OH. Four 1-month periods were modeled to quantify typical concentrations, seasonal variability, spatial patterns, and vertical profiles. Typical model concentrations showed parent compounds were highly dependent on population density as cities had monthly averaged peak D_5 concentrations up to 432 ng m^{-3}. Peak oxidized D_5 concentrations were significantly less, up to 9 ng m^{-3} and were located downwind of major urban areas. Model results were compared to available measurements and previous simulation results. Seasonal variation was analyzed and differences in seasonal influences were observed between urban and rural locations. Parent compound concentrations in urban and peri-urban locations were sensitive to transport factors, while parent compounds in rural areas and oxidized product concentrations were influenced by large-scale seasonal variability in OH.

1 Introduction

Cyclic volatile methyl siloxanes (cVMS) are present in a wide range of personal care and cosmetic products (e.g. hair products, lotions, antiperspirants, makeup, and sunscreens) as well as in sealers, cleaning products, and silicone products (Wang et al., 2009; Horii and Kannan, 2008; Dudzina et al., 2014; Lu et al., 2011; Capela et al., 2016). ~~As high production volume chemicals (>4.5x10^5 kg yr^{-1} produced or imported to the U.S.) their environmental fate is an important topic.~~As high production volume chemicals (>1,000 tonne yr^{-1} produced) (OECD Environment Directorate, 2004), their environmental fate is an important topic. The most prevalent cVMS species in personal care products is decamethylcyclopentasiloxane (D_5), although octamethylcyclotetrasiloxane (D_4) and dodecamethylcyclohexasiloxane (D_6) are also emitted (Horii and Kannan, 2008; Dudzina et al., 2014; Wang et al., 2009; Lu et al., 2011). Atmospheric lifetimes (Atkinson, 1991) are approximately 5-10 days at typical OH concentrations; accordingly, long-range transport (Xu and Wania, 2013; Krogseth et al., 2013a; McLachlan et al., 2010; Genualdi et al., 2011; MacLeod et al., 2011) of cVMS occurs. The environmental fate and transport of cVMS has been widely studied due to concerns of ~~bioaccumulation~~potential persistent, bioaccumulative, and ~~persistence~~toxic (PBT) behavior in the environment~~ (Wang et al., 2013; Rucker and Kummerer, 2015). Several~~, however assessing the environmental risk has been a subject of debate due to unique cVMS properties, evolving scientific information on properties and presence in the environment, and different interpretations of risk assessment information. The parent cyclic siloxanes have been the subject of a number of regulatory screenings ~~in~~including those by Canada (Environment Canada and Health Canada, 2008a, b, c), ~~U.K.~~the UK (Brooke et al., ~~2009a, b~~2009b, a, c)~~, Netherlands (Smit et al., 2012), and Nordic countries (Kaj et al., 2005a; Kaj et al., 2005b; Lassen et al., 2005) have studied the environmental impact of parent cVMS, and while cVMS is widespread, it is not expected to pose a risk to the environment at observed concentrations (Siloxane D5 Board of Review, 2011; Fairbrother et al., 2015; Gobas et al., 2015; Fairbrother and Woodburn, 2016). However, some debate still exists as the European Chemicals Agency recently proposed D$_4$ and D$_5$ restrictions in wash-off (e.g. shampoo) personal care products due to concerns on the aquatic environment~~, and the EU (ECHA, 2015)~~. Fate and transport of cVMS~~; comprehensive review articles (Rucker and Kummerer, 2015; Wang et al., 2013) and recent environmental fate studies (Mackay et al., 2015; Gobas et al., 2015a; Gobas et al., 2015b; Fairbrother et al., 2015) are also relevant. The conceptual model of cVMS fate and transport is summarized as emission (mainly to the atmosphere) in population centers as a result of personal care product (PCP) use (Mackay et al., 2015; Montemayor et al., 2013; Gouin et al., 2013), followed by atmospheric transport and reaction by the hydroxyl radical (OH) (Xu and Wania, 2013). Emissions and concentrations are highly dependent on population, with urban locations (Yucuis et al., 2013; Genualdi et al., 2011; Krogseth et al., 2013b; Buser et al., 2013a; Companioni-Damas et al., 2014; Ahrens et al., 2014) and indoor environments (Tang et al., 2015; Yucuis et al., 2013; Companioni-Damas et al., 2014; Pieri et al., 2013; Tri Manh and Kannan, 2015) having much higher concentrations than remote locations. As this work shows, the population-dependent PCP emissions are best validated for D$_5$, and the importance of other emission types, and the variation of this by cVMS compound, is uncertain.

Substantial insights regarding cVMS fate, transport, and expected concentrations have come from atmospheric modeling studies. ~~McLachlan et al. (2010) simulated atmospheric D$_5$ concentrations using a hemispheric scale 3D atmospheric chemistry and transport model (McLachlan et al., 2010; Genualdi et al., 2011; Krogseth et al., 2013a). MacLeod et al. (2011) simulated D$_5$ globally using a multimedia mass balance at 15° horizontal resolution~~ McLachlan et al. (2010) simulated atmospheric D$_5$ concentrations using the Danish Eulerian Hemispheric Model (DEHM), a hemispheric scale 3D atmospheric chemistry and transport model. ~~(Genualdi et al., 2011;~~ MacLeod et al~~.,~~. (2011)~~.~~ simulated D$_5$ globally using the Berkeley-Trent Global Model (BETR Global), a multimedia mass balance model at 15° horizontal resolution. Global zonally averaged modeling using the multimedia GloboPop model has also been performed (Xu and Wania, 2013; Wania, 2003). Emission estimates have been back-calculated from measured atmospheric concentrations using a multimedia model (Buser et al., 2013a; Buser et al., 2014), and compartmental model studies focusing on specific partitioning or loss processes have also been conducted (Navea et al., 2011; Whelan et al., 2004). These modeling studies have permitted extension, both in time and space, beyond the sparse measurement dataset and testing of key model processes (emissions, fate, and transport) versus modeled concentrations. Latitudinal gradients, urban-rural-remote gradients, seasonal patterns, sensitivity to processes and parameterizations, and diel cycles have been explored using these models. ~~For example, typical concentrations of D_5 in well-mixed air in urban locations are thought to be in excess of 50 ng m^{-3}, while remote concentrations may exhibit D_5 concentrations from 0.04 to 9 ng m^{-3} (Navea et al., 2011; Krogseth et al., 2013a)~~ Modeling studies have shown the large scale concentration patterns with OH as a dominant loss process, and quantified the importance of the atmosphere (relative to sediment and surface waters) for fate and transport. Seasonal and latitudinal trends can be explained in part by availability of OH. Models estimate D_5 concentrations of 50 ng m^{-3} and higher in well-mixed urban air (Navea et al., 2011), while 0.04 to 9 ng m^{-3} is reported from models for remote locations (Krogseth et al., 2013a).

Atmospheric measurements of cyclic siloxanes have been performed in ambient air (McLachlan et al., 2010; Genualdi et al., 2011; Yucuis et al., 2013; Ahrens et al., 2014; Kierkegaard and McLachlan, 2013; Krogseth et al., 2013b; Krogseth et al., 2013a; Buser et al., 2013a; Companioni-Damas et al., 2014). Higher concentration microenvironments have also been surveyed through measurement (WWTP, landfills, and indoor air) (Krogseth et al., 2013b; Cheng et al., 2011; Wang et al., 2001; Pieri et al., 2013; Yucuis et al., 2013; Tri Manh and Kannan, 2015; Companioni-Damas et al., 2014; Tang et al., 2015). In several instances, model-measurement comparison has been conducted and to a large extent, confirmed our understanding of emissions, fate and transport. Generally good agreement for rural and remote locations have been observed (McLachlan et al., 2010; Krogseth et al., 2013a; MacLeod et al., 2011; Navea et al., 2011; Xu and Wania, 2013; Genualdi et al., 2011) while urban areas tend to be under predicted (Genualdi et al., 2011; Yucuis et al., 2013; Navea et al., 2011). Measured seasonal concentration variations have been replicated for sites in rural Sweden and the remote Arctic. ~~However, it was noted that the DEHM model tended to have better agreement during summer/fall compared to winter (McLachlan et al., 2010; Krogseth et al., 2013a). The BETR model conversely had better agreement during winter compared to summer~~However, it was noted that the DEHM model tended to have better agreement during late spring (McLachlan et al., 2010) and late summer (Krogseth et al., 2013a) compared to winter. The BETR model conversely had better agreement during winter compared to late spring for the same rural Sweden site (MacLeod et al., 2011).

The majority of modeling and chamber study investigation, and all of the ambient measurements for cVMS, have focused on the emitted or "parent" cVMS compounds (i.e., D_4, D_5, and D_6). The identity and fate of the cVMS oxidation products has received less scrutiny until recently, compared to the parent compounds. ~~Sommerlade et al. (1993)~~Sommerlade et al. (1993) reacted D_4 with OH in an environmental chamber and identified multiple reaction products by GC-MS, with the single OH substituted silanol (D_3TOH) as the most prevalent resolved species, with species identification confirmed by matching retention time and mass spectra compared to synthesized D_3TOH~~ (Sommerlade et al., 1993).~~. Because of the method of collection (the product was collected from rinsing the environmental chamber walls with solvent) confirmation of secondary aerosol production from D_4 oxidation was not possible from Sommerlade et al. (1993). Chandramouli and Kamens (2001) reacted D_5 in a smog chamber, with separate analysis of gas and aerosol products, confirming the presence of D_4TOH in the GS/MS analysis of the condensed aerosol phase.

Wu and Johnston (2016) conducted more exhaustive characterization of aerosols from photooxidation of D_5, using high performance mass spectrometry, revealing both monomeric and dimeric oxidation products, with molar masses up to 870. Oxidation progressed not only by substitution of a methyl group with OH (e.g. leading to D_4TOH), but also by substitution with CH_2OH; linkages between Si-O rings to form dimers were through O, CH_2, and CH_2CH_2 linkage groups.

Aerosols containing Si and likely from photooxidation of gaseous precursors have been recently identified in multiple locations in the U.S. using laser ablation particle mass spectrometry of ultrafine particles (Bzdek et al., 2014). Bzdek et al. (2014) contend that a photooxidation source is most consistent with observations because of the times of day of occurrence, short atmospheric lifetime of the particle size in question (10-30 nm), lack of wind direction dependence that would be expected from primary sources, ubiquity across disparate measurement sites, and similarity in temporal evolution of nanoaerosol Si to other species with known photochemical sources. Except for the reports of the concentrations of ambient oxidized cVMS in Bzdek et al. (2014), there are no ambient measurements or model-based estimates of the potential aerosol concentrations from cVMS oxidation. This work begins to address that gap by simulating the gas phase oxidation product concentrations using the atmospheric chemistry and transport model Community Multiscale Air Quality (CMAQ). As experimental determinations of aerosol yield become available, the simulations can be updated to include secondary organosilicon aerosol concentrations.

This work builds on the limited information available on the oxidation products. Properties relevant to fate and transport (e.g. Henry's law coefficient) have been predicted in this work and in others based on structure activity relationships (Buser et al., 2013b; Whelan et al., 2004). Latimer et al. (1998) measured equilibrium gas particle partitioning of D_5 and D_4TOH on diesel, wood, coal soot, and Arizona fine dust aerosols. Whelan et al. (2004) performed equilibrium air-particle and air-cloud droplet partitioning modeling of multiple substituted OH silanols. More extensive information is available about the gas-particle partitioning (Latimer et al., 1998; Tri Manh and Kannan, 2015; Tri Manh et al., 2015; Kim and Xu, 2016) and aerosol phase reactions (Navea et al., 2011; Navea et al., 2009a; Navea et al., 2009b) of the precursor compounds, but these confirm that the gas-phase oxidation and transport of the parent compounds are substantially more important than the heterogeneous oxidation pathways and thermodynamic partitioning of the parent compounds onto ambient aerosols.

In this work, atmospheric gas phase concentrations of D_4, D_5, D_6, and its oxidization products are modeled comprehensively using the chemical transport CMAQ model. The purpose of the model-based investigation is twofold. First, it enables the highest resolution (36 km) to-date simulation of the parent compound over the U.S.; the model simulates vertical profiles, urban-to-rural transitions, and the dependence of these on factors such as season and mixed layer height. Second, this paper reports, for the first time in detail, concentrations of the cVMS oxidation products. Some fraction of products is likely distributed into the aerosol phase, thus contributing to aerosol Si concentrations on regional and global scales. We expand upon the modeling first presented in Bzdek et al. (2014), but with improved emission estimates, inclusion of wet and dry deposition, and incorporation of season-dependent boundary conditions.

2 Methods

Cyclic siloxanes and oxidized cyclic siloxanes were modeled with the 3D atmospheric chemical transport model CMAQ (Byun and Schere, 2006) modified to include cyclic siloxane species. CMAQ version 4.7.1 was used and the modeling domain covered the contiguous U.S., northern Mexico, and southern Canada. The domain had 14 vertical layers and a horizontal resolution of 36 km. Four, one-month simulations were performed for January, April, July, and October to characterize seasonal variability of cyclic siloxane atmospheric concentrations. A spin up period of 7 days was used to minimize the influence of zero initial conditions for the cyclic siloxanes species. Meteorology was from the Weather Research and Forecasting (WRF) model version 3.1.1 for the meteorological year of 2004. WRF was run with time steps of 120 s, 30 vertical layers, Morrison double-moment microphysics scheme, RRTMG longwave and shortwave physics scheme, Pleim-Xiu surface layer, Pleim-Xiu land surface model with two soil layers, and the ACM2 PBL scheme. Reanalysis nudging using North American Regional Reanalysis (NARR) data was performed every three hours.

The cyclic siloxanes were added to the CMAQ model by adding D_4, D_5, D_6, and the oxidized species, o-D_4, o-D_5, and o-D_6 to the cb05cl_ae5_aq mechanism. Rate constants for the parent cyclic siloxanes reacting with hydroxyl radicals (OH) were used from Atkinson (1991) where D_4 and D_5 were determined experimentally and D_6 estimated from the reported D_5 per methyl rate. The rate constants used were 1.01×10^{-12}, 1.55×10^{-12}, and 1.92×10^{-12} cm^3 molecule^{-1} s^{-1} for D_4, D_5, and D_6, respectively. Reactions of the oxidation products are not included in the model. In part, this is because information is limited on the kinetics of further oxidation and on the changes that this would cause for fate, transport, and properties. Whelan et al. (2004) modeled subsequent oxidation reactions, and chamber-based oxidation studies observe multiple substitution products likely due to multiple substitution reactions or auto-oxidation by internal rearrangement (Wu and Johnston, 2016). In the model, only the first oxidation is computed. The oxidation products are denoted o-D_4, o-D_5, and o-D_6, and for calculation of physical properties relevant to deposition, the single OH substitution is assumed.

Wet and dry deposition of the primary species (e.g. D_4, D_5) were added to the model using Henry's law coefficients (Xu and Kropscott, 2012). For the oxidized cyclic siloxanes, physicochemical parameters were estimated using EPI Suite HENRYWIN v3.20 (EPA, 2012) for the single OH substitution of one methyl group of the parent cyclic siloxane (e.g., D_3TOH, D_4TOH). Deposition related inputs necessary for the CMAQ deposition routine included Henry's law coefficients, mass diffusivities, reactivity, and mesophyll resistance. ~~The mass diffusivity calculations were calculated according to~~CMAQ calculates dry deposition as a deposition velocity (dependent on mixing/turbulence, molecular properties, and land type) multiplied by the lowest model layer concentration (Byun et al., 1999), and wet deposition using Henry's law coefficients and precipitation rates (Roselle and Binkowski, 1999). Dry deposition therefore treats the surface as an infinite sink, which is consistent with other species in the model. The mass diffusivity values were calculated by the Fuller, Schettler, and Giddings (FSG) method (Lyman et al., 1982) where molar volume was estimated based on element contributions. Sulfur molar volume contribution values were substituted for silicon atoms since silicon values were not available. Calculated mass diffusivity values, as estimated by the FSG method were 0.0512 (D_4), 0.0454 (D_5), 0.0411 (D_6), 0.0527 (o-D_4), 0.0464 (o-D_5), and 0.0419 (o-D_6) cm^2 s^{-1}. The reactivity parameter was set at 2.0 in common with methanol and other species of limited reactivity. The mesophyll resistance, which is used to account for uptake by plants, was set to zero (only a few species had mesophyll resistances specified in CMAQ, such as NO_2, NO, CO, and Hg gas). Molecular weight for the oxidized cyclic siloxanes assumed the single substituted OH species. The molecular weight of D_6 and o-D_6 exceeded the limit of the CMAQ dry deposition routine m3dry (390 g mol^{-1}) and values in excess of the limit were coerced to the limit. The impact of this substitution is expected to be minimal, since it is a minor adjustment to a minor pathway; dry deposition of cVMS is relatively small (McLachlan et al., 2010; Xu and Wania, 2013; Whelan et al., 2004).

Emissions of cyclic siloxanes were distributed according to gridded population for the U.S., Canada, and Mexico while Caribbean countries were neglected. ~~Cyclic siloxane emission rates were calculated from an industry derived country specific D_5 emission rate for U.S., Canada, and Mexico (Buser et al., 2014; van Egmond, 2013). The method of estimating the D_5 emission rates has been described previously (McLachlan et al., 2010), but briefly, country specific antiperspirant sales data was combined with 2009 consumption data.~~The U.S., Canadian, and Mexican per capita emission rates of D_5 provided by personal communication (van Egmond, 2013) and previously used and reported in McLachlan et al. (2010) was adopted for this study. Briefly, as reported in McLachlan et al. (2010), D_5 emission rates were derived from country specific market share based on antiperspirant sales data combined with D_5 consumption data from antiperspirant plus 10% to account for other sources. A table of many available cVMS emissions rates from multiple methods are represented in Table S2, and a wide variation exists. To calculate D_4 and D_6 emission rates, ambient measurements from Chicago (Yucuis et al., 2013) were used to estimate emission ratios relative to D_5. ~~Since~~Chicago was chosen since it is a major urban area and atmospheric measurements should be most fresh and therefore the best representation of emission rates. However, since OH reactivity (and other fate and transport properties) vary from compound to compound, ambient measurements of compound ratios will not match emission ratios, except in air parcels that are so fresh as to have seen no oxidation. To check for the influence of air mass aging in the measurements of Yucuis et al. (2013), the ratio NO_x/NO_y was used as a marker of air mass age (Slowik et al., 2011). This ratio is high in fresh emissions, and decreases as the air mass is oxidized. Hourly measurements of NO_x and NO_y from Northbrook, Illinois (EPA) were inspected during the time period of the Chicago sampling in Yucuis et al. (2013). Using the NO_x/NO_y photochemical age estimate, we calculated that emitted ratios vs. ambient ratios likely differed by less than 1% (see Supplemental section). The Chicago cyclic siloxane measurements were therefore used as emission ratios without photochemical age correction. The resulting emission ratios, 0.243 and 0.0451 for D_4/D_5 and D_6/D_5 respectively, were multiplied by the D_5 emission rate to estimate the D_4 and D_6 emission rates. The resulting D_4, D_5, and D_6 country emission rates, which were constant for all simulations, were multiplied by gridded population and merged with Sparse Matrix Operator Kernel Emissions (SMOKE) model version 2.5 generated year 2004 emissions. ~~Cyclic siloxane emissions were constant for all simulations.~~Population data was from census derived population surrogates from EPA 2011 v6.0 Air Emissions Modeling Platform and is based on permanent residency and does not include seasonal tourism. This may cause inaccuracies in emissions near parks and other tourist destinations. SMOKE emissions were calculated from NEI 2002, version 3, with on-road and point sources projected to 2004 using EGAS, the EPA's Point source and Economic Growth Analysis System. Biogenic emissions were from BEIS 3.13.

Boundary conditions were from previous DEHM modeling ~~(Danish Eulerian Hemispheric Model, DEHM)~~ that modeled D_5 concentrations using 2009 ~~D_5~~ emission rates as described above (Hansen et al., 2008; McLachlan et al., 2010). The DEHM model was run for the Northern Hemisphere at 150 km resolution. We extracted the D_5 concentrations from the DEHM model for year 2011 meteorology along our model boundary. Boundary concentrations were horizontally and vertically resolved, varied by month, but were time invariant within each month. Since the DEHM model only included D_5, D_4 and D_6 concentrations were estimated using measurement ratios taken from a background site at Point Reyes, CA (Genualdi et al., 2011). Point Reyes samples had ratios of 0.646 and 0.0877 for D_4/D_5 and D_6/D_5 respectively. The background ratios combined with the "fresh" emission ratios (described previously) were used to calculate a photochemical age. The calculation of a photochemical age was necessary since the siloxanes have different OH reaction rates and therefore the siloxane ratios change with season due to varying OH concentrations. Using this method, we calculated an age of 17.6 days using the D_4/D_5 ratios and this is the age used for further calculations. The calculated photochemical age was ~~then~~ combined with season specific OH concentrations (Spivakovsky et al., 2000) to calculate monthly resolved D_4/D_5 and D_6/D_5 "background" ratios. These monthly resolved D_4/D_5 and D_6/D_5 ratios were then used for the entire model boundary. Additional details are available in the Supplemental section.

3 Results and Discussion

3.1 Spatial Variation in Concentrations

Figures 1 and 2 show the 30 day averaged D_5 and oxidized D_5 (o-D_5) modeled concentrations for January, April, July, and October. The spatial distribution of cVMS and oxidized cVMS compounds show a strong population dependence with major urban areas having elevated D_5 concentrations and peak o-D_5 concentrations occurring hundreds of km downwind of source regions due to the time it takes for the parent compounds to react with OH. Table 1 displays the monthly minimum, maximum, and average concentrations for the entire modeled domain. The 36-km grid cell with the highest 30-day average surface concentration of D_5 was 432, 379, 301, and 265 ng m^{-3} for January (Los Angeles – Long Beach), April (Los Angeles – Long Beach), October (New York City), and July (New York City), respectively. The domain-averaged surface concentrations of D_5 were 6.82, 6.43, 5.09, and 4.04 ng m^{-3} for January, October, April, and July. Simulated o-D_5 was much lower than simulated D_5 concentrations. For example, the 36-km grid cell with the highest 30-day average surface concentration of o-D_5 was 9.04, 5.21, 4.86, and 3.19 ng m^{-3} for July (NE of Los Angeles – Victorville), October (E of Los Angeles – San Bernardino), April (SE of Los Angeles – Mission Viejo), and January (Los Angeles – Long Beach), respectively. The domain average surface concentration for o-D_5 was 0.81, 0.72, 0.63, 0.37 ng m^{-3} for July, April, October, and January, respectively. The peak domain-averaged concentrations occurred during January for D_5 and July for o-D_5 which is expected based on seasonal trends of OH in North America (Spivakovsky et al., 2000).

~~Tables 2 and~~Figure 3 ~~show~~shows the monthly averaged cVMS and oxidized cVMS concentrations versus the model grid cell population for 26 U.S. and Canadian sites. These sites include the most populous ten U.S. metropolitan areas, siloxane measurement sites, and NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) sites~~.~~, see Table S3 for the full list. Modeled concentrations are strongly dependent on population with New York City and Los Angeles having the highest concentrations~~.~~ (Table S4). In addition to the population dependence, concentrations were greatest for D_5 followed by D_4 and D_6. This follows from our assumed emission ratios and agrees with North American measurement data (Yucuis et al., 2013; Genualdi et al., 2011; Ahrens et al., 2014; Krogseth et al., 2013b). The prevalence of D_4 relative to D_6 is of interest because analysis of cVMS composition in consumer products (Horii and Kannan, 2008; Wang et al., 2009; Dudzina et al., 2014; Lu et al., 2011; Capela et al., 2016) suggests that D_6 is more abundant than D_4 – while in our modeling (and atmospheric measurements) D_4 concentrations are higher than D_6 concentrations. Four explanations bear further investigation: (1) ~~D_4 may have~~ non-~~negligible~~ personal care emissions (e.g. cVMS residuals from ~~sources~~ polymer production) may play a more important role for D_4 than other ~~than personal care products (e.g. industrial uses which are not captured in current~~species based on UK emission estimates~~),~~, (Brooke et al., 2009b, a, c), (2) possible siloxane conversion during sample collection (Kierkegaard and McLachlan, 2013; Krogseth et al., 2013a), (3) higher D_4 volatility (Lei et al., 2010) could cause both more difficult detection in personal care products and a larger fraction volatilization from products, and (4) uncertainty and/or spatiotemporal variability in the D_4/D_5 and D_6~~ ratio taken~~/D_5 ratios from ambient measurements in Chicago used to extend the D_5 emissions estimates to D_4 and D_6.

3.2 Seasonal Variation in Concentrations

Since OH concentrations vary seasonally we expect higher cVMS in the winter (low OH) and lower in the summer (high OH). This has been supported by previous measurement studies. For example, McLachlan et al. (2010) measured D_5 at a rural site in Sweden (59°N) and observed reduced D_5 concentrations for the period of May-June compared to January-April. Measurements in a remote Artic location (79°N) observed higher concentrations in the winter compared to ~~the fall~~late summer (Krogseth et al., 2013a). For OH concentrations to influence cVMS concentrations, time for oxidation is required – so the relationship between seasonal OH and cVMS is expected at receptor sites where most cVMS is transported from upwind locations. At source-dominated locations, the influence of OH should be limited. For example, studies from Toronto highlight local meteorological influences as important in determining variation in siloxane (D_3-D_6) concentrations (Ahrens et al., 2014; Krogseth et al., 2013b).

Figure 1 shows similar D_5 spatial distribution between the four months, especially for urban areas. Domain peak and average concentrations (Table 1) have highest concentrations in January and lowest in July which agree with seasonal OH concentrations but specific grid cells (particularly urban locations) often deviate from this. Rural and remote locations are more likely to follow the OH-induced seasonal pattern. Seasonal variation for the 26 sites in Table ~~2~~S3 was examined using the most prevalent month~~,~~ highest concentrations occurred. Sites were classified as either urban or rural based on summer D_5 concentrations. For urban sites, the most prevalent month with highest average D_5 concentration was October (59%), followed by July (23%), and January (18%). Restricting the analysis to the rural sites (summer D_5 concentration below 17 ng m^{-3}), peak D_5 concentrations occurred in January (56%), followed by October (33%), and April (11%). The month of lowest average D_5 concentrations occurred in July for 100% of the rural sites and 24% of the urban sites. Similarly, looking at the breakdown for the monthly averaged oxidized D_5 concentrations, highest concentrations generally occurred in July, which was true for 73% of the 26 sites. Figure 2 shows ~~significant~~ differences in the spatial distribution of o-D_5 between months. The analyzed sites therefore suggest less of a seasonal trend for the parent compounds as compared to the oxidized products, and there are differences in seasonal trends between source and non-source locations. Remote and rural sites are more dependent on lifetime with respect to reaction with OH, while source locations are less sensitive. This agrees with previous modeling which showed reduced seasonal variability of D_5 concentrations for urban areas compared to remote locations (McLachlan et al., 2010; MacLeod et al., 2011; Xu and Wania, 2013).

Statistical relationships between D_5, OH, planetary boundary layer (PBL) height, and wind speed (WS) were explored using least squares multiple linear regression. For the 26 analyzed sites, OH, PBL, and WS values were normalized to their summer values and then used as predictive variables of the ratio of D_5 in each season to its summer value at the same site. In other words, the regression analysis is testing the local season-to-season variability across seasons and sites (e.g. is winter:summer D_5 concentration correlated to winter:summer OH^{-1}). Sites were split between urban and rural as described previously. For urban sites, D_5 concentration was only correlated to OH^{-1} when WS^{-1} was also included, with WS being the dominant variable. The strongest predictive variables were PBL^{-1} and WS^{-1} with an adjusted R^2 fit of 0.50 and a p-value of <0.001. The regression analysis supports the previous conclusion: ventilation of local emissions through PBL height and local winds is the strongest influence on urban siloxane concentrations.

For the rural sites, WS^{-1} was the only variable of significance but had a low adjusted R^2 of 0.10, p-value of 0.056, and a negative coefficient meaning lower wind speed results in lower D_5 concentrations. Repeating the linear regression excluding Canadian sites and Point Reyes (CA), led to similar results. Canadian sites were excluded since non-siloxane Canadian emissions were allocated by population and may cause errors in OH due to misallocation of nitrogen oxides and reactive organic gases from some source sectors (Spak et al., 2012). Point Reyes was excluded due to high grid cell population despite low D_5 concentrations. See the Supplemental section for additional regression results. From this analysis, we conclude that factors other than local OH and local meteorology control rural/remote siloxane concentrations. These factors likely include regional OH and regional transport patterns.

3.3 Model-Measurement Comparison

The model results were compared to measurement values in the Midwest (Yucuis et al., 2013), North American measurements from the Global Atmospheric Passive Sampling (GAPS) network (Genualdi et al., 2011), and several Toronto measurements (Genualdi et al., 2011; Ahrens et al., 2014; Krogseth et al., 2013b).

3.3.1 Midwest Model Comparison

In Yucuis et al. (2013) measurements were taken at three Midwest locations during the summer (June-August) of 2011. The measurements were collected, in duplicate, at sites with varying population density. Measurements from Chicago, IL were collected consecutively as sixteen 12 h samples from August 13 – 21, Cedar Rapids, IA as four 24 h samples non-consecutively from June 29 – July 26, and West Branch, IA as five samples that ranged from 30 – 47 h July 6 and consecutively from July 15 – 22. The measurements were compared to the July 1 – 30 modeled hourly concentrations ~~that were~~ averaged ~~so~~as 12, 24, and 36 h intervals for the ~~periods were of similar duration to the measurement~~Chicago, Cedar Rapids, and West Branch sites respectively. These sampling periods~~. The modeled period does~~ and sample counts are insufficient to establish representativeness of the values as monthly or seasonal averages. The model results were averaged using time-of-day and duration matching the measurements, but do not correspond to the exact measurement days or meteorology~~, but should be representative of typical summer concentrations.~~. Measurements are from 2011 and the model's meteorological fields are from 2004; however, average wind speeds, wind directions, and boundary layer heights are typically similar from year to year.

Figure ~~3~~4 displays the boxplot comparison of the three Midwest sites of Yucuis et al. (2013) and the modeled concentrations. The model does capture the population dependence that the measurements show, with Chicago observing highest concentrations followed by Cedar Rapids and West Branch. Modeled concentrations however are lower for all three locations compared to the measurements with fractional bias (Table ~~S8~~S10) at Chicago of -0.31, -0.31, -0.28 (for D_4, D_5, D_6 respectively), Cedar Rapids -1.25, -0.93, -1.51, and West Branch -1.25, -0.78, -1.23. Comparing the relative percent error of the mean modeled concentrations to the measured values, Chicago sites had relative percent errors of around 25% while the other sites had values ranging from 56% - 86%. For Chicago, error between the species was similar and this is most likely the result that D_4 and D_6 emission rates were calculated based on the Chicago measurements. For Cedar Rapids and West Branch, D_5 had the lowest error while D_4 and D_6 were larger. This may indicate that the siloxane emission ratios vary based on location.

One possible explanation for low model concentrations could be low emission estimates. Current emission estimates (Table S2) vary considerably and the estimates used in this work were 32.8, 135, and 6.10 mg person^{-1} day^{-1} for D_4, D_5, and D_6 respectively for the U.S. and Canada, while the Mexico emissions were 5.92, 24.4, and 1.10 mg person^{-1} day^{-1} for D_4, D_5, and D_6. Previous emission estimates have ranged from 0.001 – 100, 0.002 – 1200, and 0.0009 – 80 mg person^{-1} day^{-1} for D_4, D_5, and D_6 respectively (Tang et al., 2015; Buser et al., 2013a; Buser et al., 2014; Navea et al., 2011; Yucuis et al., 2013; Horii and Kannan, 2008; Dudzina et al., 2014; Wang et al., 2009; Capela et al., 2016). Additionally, ~~there~~ non-personal care product emissions could be ~~other sources of~~ important, as could potential geographical, demographical, or temporal influences on siloxane emissions~~ besides personal care products, or seasonal/regional differences that~~. As datasets of cVMS concentrations, particularly those with simultaneous values for D_4, D_5 and D_6 are ~~not captured~~available in ~~current emission~~more source-oriented locations and seasons, the emissions estimates, particularly for D_4 and D_6, should be refined.

The treatment of deposition as an infinite sink could also cause low gas phase concentrations (deposition overpredicted) if surface concentration are not degraded quickly. Experimental studies show the parent cVMS degradation is slow in soil (Wang et al., 2013), however this is likely minimized due to low deposition potential as predicted by high air-water (K_{AW}) and low octanol-air (K_{OA}) partitioning coefficients (Xu and Wania, 2013). Octanol-air ($\log K_{OA}$) partitioning values, which is an indication of the ability to partition to soil and plants (Shoeib and Harner, 2002), are 4.29 – 5.86 for D_4-D_6 (Xu and Kropscott, 2012), which is similar or higher than other organic species with modeled deposition such as methanol, aldehydes, and carboxylic acids. The oxidized species are likely more sensitive due to greater deposition potential as EPI Suite predicts lower $\log K_{AW}$ and higher $\log K_{OA}$ values, however the surface degradation kinetics of the oxidation products are not known.

3.3.2 GAPS Model Comparison

The model was also compared to measurements of Genualdi et al. (2011). These measurements were collected from passive samplers as part of the GAPS network over three months in 2009, generally from late March to early July. Figure ~~4~~5 shows the CMAQ modeled April month versus measurements for eight locations within our domain. Again as with the Yucuis et al. (2013) comparison, the modeled results do not explicitly represent meteorological conditions of the measurement period. Fractional error (Table ~~S9~~S11) for D_4 varied from 0.02 – 1.93 with Point Reyes having the lowest and Ucluelet the highest. For D_5, fractional error values ranged from 0.02 – 1.24 with Fraserdale the lowest and Bratt's Lake the highest. Similarly, for D_6, the fractional error varied from 0.11 – 1.71 with Bratt's Lake the lowest and Ucluelet the highest. Averaged over the eight sites, the overall fractional biases were -0.41, -0.03, and -0.90 for D_4, D_5, and D_6, respectively. The mean fractional error was 0.95, 0.66, and 0.98 for D_4, D_5, and D_6 species. Therefore, based on the fractional error values, D_5 had the best agreement followed by D_4 and D_6. This is not surprising that D_5 had the best agreement since D_4 and D_6 emission rates are estimated based on Chicago measurements and would have additional uncertainty compared to the D_5 emission uncertainty.

On average, fractional bias for D_5 was close to zero while D_4 and D_6 had greater negative bias due to significant deviations for Fraserdale, Ucluelet, and Whistler. Aside from these three sites, the D_4 predictions generally agreed well with the measurements. These same three sites and Groton were also significantly under predicted for D_6 but other sites were within a factor of 2 of the measurements. Possible explanations for model deviation could be population errors (Ucluelet and Whistler ~~experience seasonal tourism),~~are tourist destinations and the population dataset used did not include visitors), non-personal care product emissions, product transformation of higher molecular weight siloxanes to D_4 on sampling media (Kierkegaard and McLachlan, 2013; Krogseth et al., 2013a), or our boundary conditions could be underestimating Asian cVMS transport. Genualdi et al. (2011) hypothesized the high D_4 concentrations measured at Whistler and Ucluelet could be due to transport from Asia since D_4 concentrations were greatest at west coast locations and especially at high altitude sites.

Model overprediction for D_5 occurred for the Point Reyes and Bratt's Lake sites. Representation error is a likely cause of this, since the actual sampling sites were upwind of large population centers (San Francisco and Regina, SK) in these grid cells; at 36 km resolution, the upwind sampling sites and the downwind emission centers are not resolved. However, Point Reyes and Bratt's Lake D_4 and D_6 concentrations were close to the modeled values.

We also compare the 36 km CMAQ D_5 concentration results to values from the DEHM and BETR models. The BETR model did not report values for Ucluelet or Groton so those sites are not included. The D_5 modeling attempts were ordered from most skilled to least skilled by using the mean of the fractional bias and fractional error (in parenthesis) scores, CMAQ -0.03 (0.66), DEHM -0.53 (0.73), and BETR -0.81 (1.08). The CMAQ and DEHM models had similar performance for Fraserdale, Whistler, Ucluelet, and Point Reyes, while the urban areas (Downsview, Sydney (FL), and Groton) were better predicted in the CMAQ model. Bratt's Lake was overestimated compared to the DEHM model and may have to do with the greater influence of Regina, SK emissions due to improved model resolution. The differences in modeled concentrations are most likely due to higher spatial resolution for CMAQ (36 km) versus 150 km (DEHM), and 15° (BETR) resolutions.

3.3.3 Toronto Model Comparison

Multiple measurement and modeling studies have investigated cVMS concentrations in Toronto, Canada. Table ~~4~~2 shows the mean and hourly range of cVMS concentrations in Toronto for each of the four months as simulated by the CMAQ model. Table ~~4~~2 further includes the March 2010 – April 2011 measured concentrations as collected by both passive and active sampling (Ahrens et al., 2014), active sampling from March 2012 – June 2012 and passive sampling from July 2012 – October 2012 (Krogseth et al., 2013b), and passive sampling (April – June 2009) from the GAPS network (Genualdi et al., 2011). Finally, the BETR and DEHM modeled D_5 concentrations (Apr – Jun 2009) are also tabulated (Genualdi et al., 2011). The CMAQ results compared favorably to the Ahrens et al. (2014) measurements with CMAQ monthly averages that generally fell within the reported measurement concentration ranges. D_4 monthly averages were within a factor of 0.97 – 1.94, D_5 within a factor of 0.59 – 1.39, and D_6 within a factor of 0.33 – 0.78 of the yearly averaged active and passive sampling measurements. Comparing the range of concentrations, CMAQ ~~hourly~~24-hour averaged ranges were ~~1.8 – 110.3~~4.6 – 60.6 (D_4), ~~6.0 – 453~~17.1 – 247.7 (D_5), and 0.~~24 – 20.42~~74 – 11.13 (D_6) ng m^{-3} compared to Ahrens et al. (2014) 24-hour active sampling range of 2.8 – 77 (D_4), 15 – 247 (D_5), and 1.9 – 22 (D_6) ng m^{-3}. ~~The greater modeled range can likely be attributed to hourly concentrations as opposed to 24-hour.~~ Similarly, good agreement was observed for the active and passive sampling measurements from Krogseth et al. (2013b), average April CMAQ D_4, D_5, and D_6 concentrations were a factor of 0.84, 0.88, and 0.67 respectively of the measured average~~. The range of concentrations were similar compared to the April CMAQ month, with the measurements having higher peak concentrations despite a longer sampling time (2-3 days). While~~, the concentration ranges were similar, with higher peak concentrations occurring for the measurements despite sampling for 2-3 days. For the passive samples of Krogseth et al. (2013b), July and October average CMAQ concentrations were 0.69 – 0.76 for D_4 and 0.95 – 1.04 for D_5 compared to the measurements. CMAQ April averages were 1.85, 1.49, and 0.59 times the Genualdi et al. (2011) measurements. Previous Toronto modeling predicted 6.5 ng m^{-3} (BETR) and 28 ng m^{-3} (DEHM) which were significantly lower than the spring CMAQ D_5 concentration of 81.6 ng m^{-3}. Overall, the CMAQ model was able to better predict the higher observed concentrations of Toronto, which again, can most likely be attributed to increased model resolution.

3.4 Compound Ratios

Cyclic siloxane product ratios can be used to gain insight into emission sources and OH photochemical aging (Ahrens et al., 2014; Kierkegaard and McLachlan, 2013; Krogseth et al., 2013b; Krogseth et al., 2013a; Yucuis et al., 2013; Navea et al., 2011). Figures ~~5~~6 and ~~6~~7 show the model-predicted seasonal plots of monthly averaged D_5/D_4 and D_6/D_5 product ratios. It is important to note that the modeling assumes D_4 and D_6 are emitted according to population density, at constant ratios relative to D_5 at all locations and times. Thus, these figures emphasize the influence of differences in chemical aging. Due to differences in OH reactivity rates, cyclic siloxane reactivity increases with Si-O chain length (more methyl groups) so that D_6 is the most reactive and D_4 the least (Atkinson, 1991). Therefore, siloxane ratios depend on emissions, exposure to OH, and relative reactivity rates. ~~Figures 5 and 6 display the mole~~Mole ratios are plotted with the more reactive species as the numerator; as air masses move away from emission sources and are exposed to OH, the ratio decreases due to more rapid depletion of the more reactive species. This is evident in the D_5/D_4 and D_6/D_5 maps which show urban areas have the highest ratios.

Seasonal differences of the product ratios are similar for both D_5/D_4 and D_6/D_5 mole ratios. Urban areas exhibit almost no season-to-season difference (Table ~~S5~~S7), as they reflect the local emission ratios. Seasonal differences are most apparent for rural and remote locations. Domain average ratios are highest in January and lowest in July which is consistent with seasonal OH fluctuations.

Since both SO_2 and cVMS are precursors to secondary aerosol formation, and both compounds have approximately the same OH rate constant, the ratio of gas phase SO_2 to cVMS should predict aerosol-phase ratios of S to Si in photochemically generated particles (Bzdek et al., 2014). Figure ~~7~~8 shows the seasonally modeled, monthly averaged gas phase $SO_2/(D_4 + D_5 + D_6)$ mole ratios. Urban ratios exhibit lowest values which suggest photochemically generated aerosols would have increased Si composition derived from siloxane oxidation. Conversely, rural locations have high SO_2/cVMS ratios and expected low Si aerosol composition. This is consistent with the high nanoparticle Si measured in Pasadena, CA and Lewes, DE by Bzdek et al. (2014). Seasonal variation in the SO_2/cVMS ratio is minor.

3.5 Vertical profile analysis

Modeled monthly averaged D_5 and o-D_5 vertical profiles are shown in Figure ~~8~~9 for three grid cells near Los Angeles. The locations of the analyzed sites include the highest monthly averaged surface July D_5 concentration, the highest averaged surface o-D_5 concentration, and a grid cell over the Pacific Ocean. The grid cell with greatest D_5 concentration, (termed “Peak D_5”) included cities such as Long Beach and Anaheim while the grid cell with highest o-D_5 (“Peak o-D_5”) was approximately 80 km northeast of the peak D_5 grid cell and included Victorville and Hesperia, CA. The third location was over the Pacific Ocean (“Pacific”) approximately 195 km southwest of Los Angeles (Fig. S9).

The CMAQ model was run with 14 vertical layers; plotted is the layer top height versus the monthly averaged July D_5 and o-D_5 concentration. For D_5 concentrations, both the “Peak D_5” and “Peak o-D_5” sites had highest concentrations at the surface. Over the Pacific, concentrations peaked above the surface at approximately 700-1,700 m. Surface D_5 concentrations were 251, 103, and 0.3 ng m^{-3} for the "Peak D_5", "Peak o-D_5", and "Pacific" locations respectively. From heights 475-3,000 m, the "Peak o-D_5" site had higher D_5 concentrations than the "Peak D_5" site and this is most likely due to the plume dilution from the upwind LA source. For o-D_5 concentrations, surface concentrations were highest for the "Peak o-D_5" site (9 ng m^{-3}), followed by the "Peak D_5" site (2 ng m^{-3}), and the "Pacific" site (0.2 ng m^{-3}). From the surface to 3,000 m the "Peak o-D_5" grid cell had highest o-D_5 concentrations as a result of being downwind of a major emission source and the oxidation reaction takes times to occur. Both the "Peak D_5" and "Pacific" sites have peak o-D_5 concentrations not at the surface (475 and 2,300 meters respectively) while the "o-D_5" site is at the surface. The low surface o-D_5 at the peak D_5 site could be due to low OH concentrations caused by urban OH sinks and is consistent with low modeled surface OH (Fig. S10). Vertical concentrations appear to be dependent on transport, reaction time, and OH concentrations.

4 Conclusions

The CMAQ model was modified to include D_4, D_5, D_6, and the oxidation products to investigate urban-rural concentration gradients, seasonal variability, product and SO_2 mole ratios, and vertical profiles. Improved model performance was observed when compared to previous modeling especially for urban areas. Concentrations are heavily dependent on population with strong urban/rural concentration gradients observed. Urban areas have highest cVMS concentrations but are not significantly influenced by seasonal variability of OH, while rural cVMS is influenced by transport and regional OH concentrations. The oxidized product concentrations are significantly lower than the parent compounds with average D_5 concentrations up to 432 ng m^{-3} and average o-D_5 up to 9 ng m^{-3}. Highest oxidized siloxane concentrations occur downwind of major urban centers. Increased error for modeled D_4 and D_6 relative to D_5 is hypothesized to be due to increased uncertainty in emission estimates. Future work should address these emission uncertainties by exploring seasonal, temporal, spatial, and non-personal care product emissions.

While the parent compounds have been extensively studied, the environmental and health impact of the oxidized species have not been addressed. This is especially important since the oxidation products likely form particles. To the best of our knowledge this work provides the first estimated atmospheric loadings and spatial distribution of the oxidized species. Future work should focus on gas and particle phase measurements of the oxidized species to confirm particle formation in the ambient environment and to determine typical loadings in the environment. This is especially important since exposure would be expected to be highest indoors where cyclic siloxane concentrations are greatest.

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Competing Interests

The authors declare that they have no conflict of interest.

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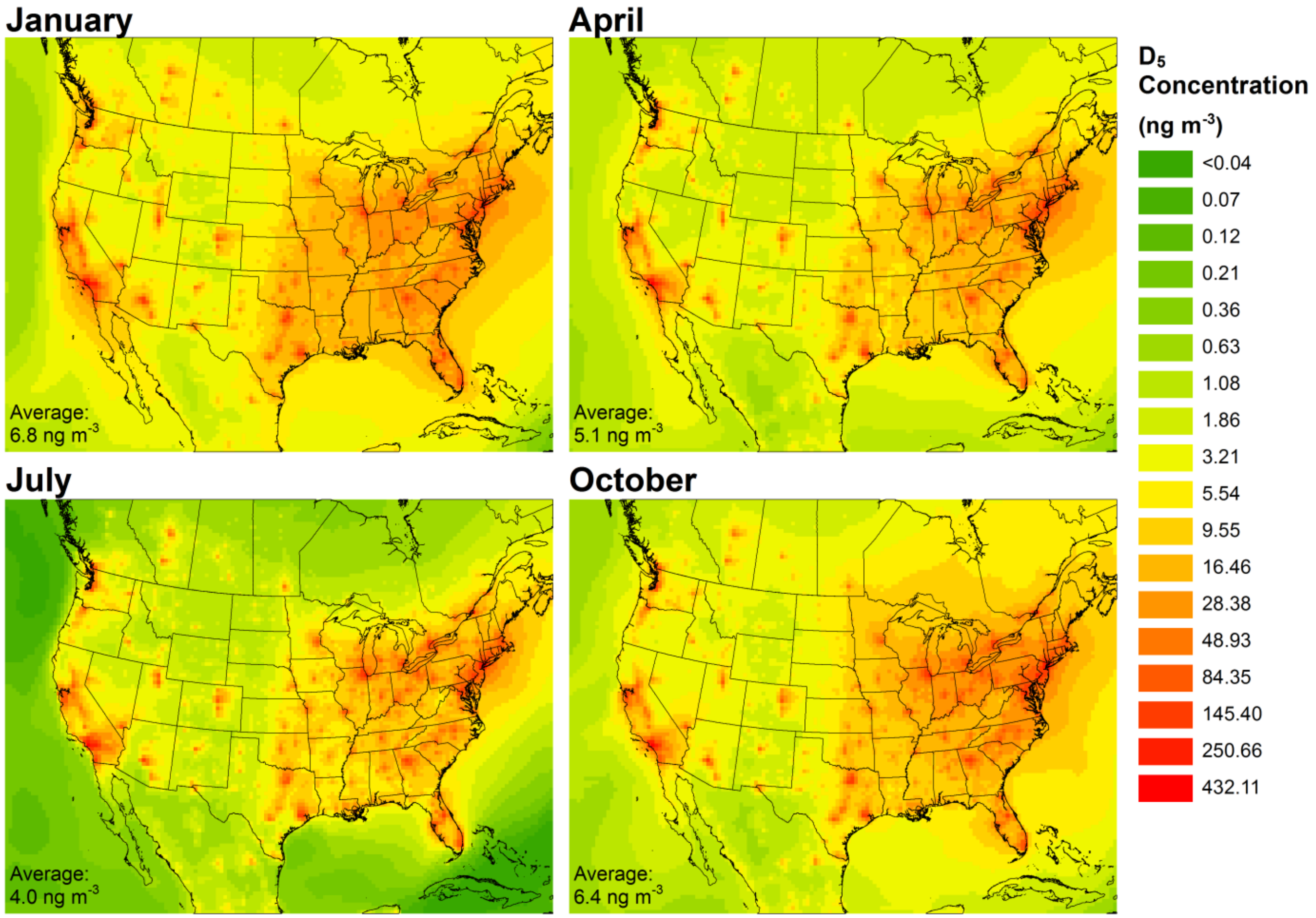

Figure 1: Monthly averaged surface layer D_5 concentrations. The domain average concentration is shown in the lower left for each month.

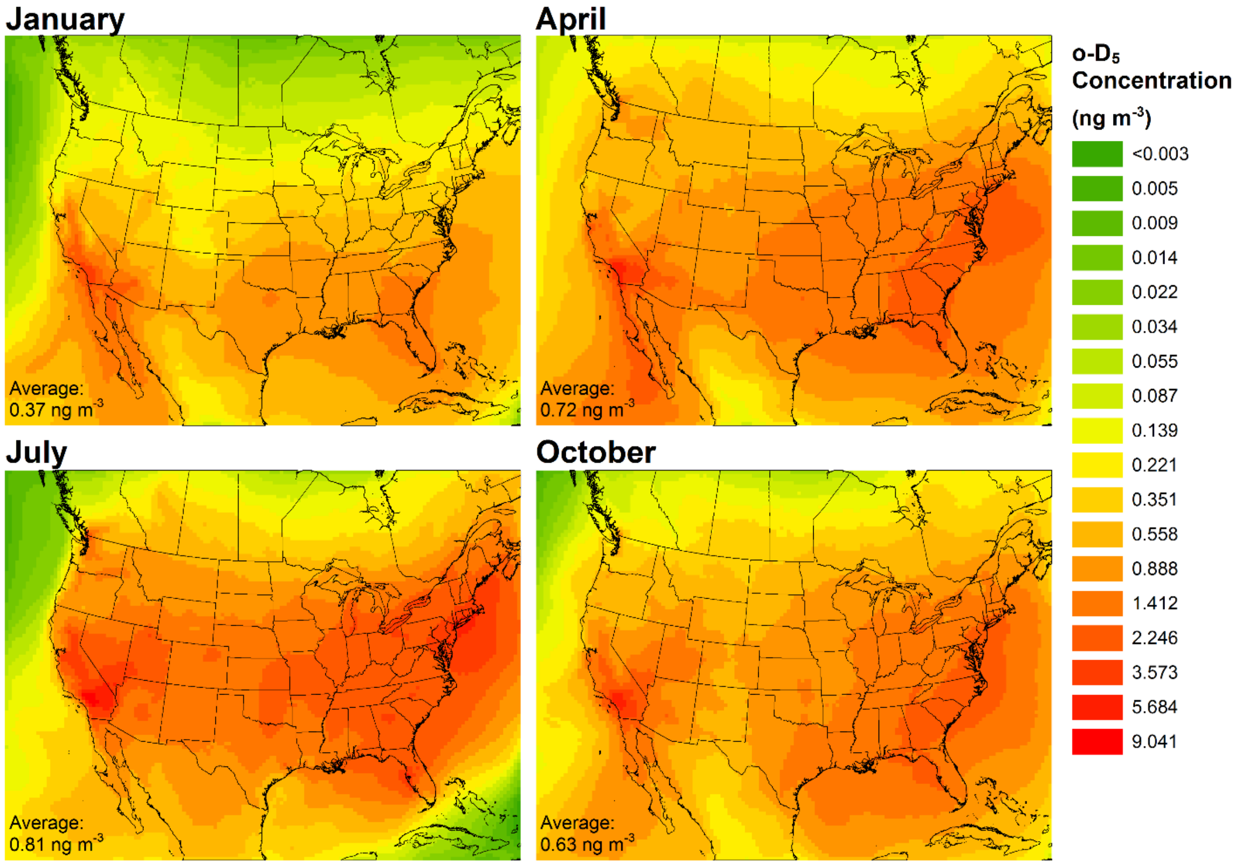

Figure 2: Monthly average surface layer oxidized D_5 (o-D_5) concentrations. The domain average concentration is shown in the lower left for each month.

Table 1: Monthly minimum, maximum, and average D_5 and o-D_5 concentrations in the lowest modeled layer for the domain.

	D_5 Concentrations (ng m^{-3})				o-D_5 Concentrations (ng m^{-3})			
Domain	**January**	**April**	**July**	**October**	**January**	**April**	**July**	**October**
Minimum	0.14	0.27	0.024	0.27	0.0031	0.037	0.0021	0.0033
Maximum	432	379	265	301	3.19	4.86	9.04	5.21
Average	6.82	5.09	4.04	6.43	0.37	0.72	0.81	0.63

~~**Table 2: Average monthly CMAQ modeled surface cVMS concentrations (ng m^{-3}) sorted by population (highest at top of table) in analyzed grid cell. Minimum and maximum values in each column in boldface and italicized.**~~

~~-~~	~~**D_4**~~				~~**D_5**~~				~~**D_6**~~			
~~**Site**~~	~~**January**~~	~~**April**~~	~~**July**~~	~~**October**~~	~~**January**~~	~~**April**~~	~~**July**~~	~~**October**~~	~~**January**~~	~~**April**~~	~~**July**~~	~~**October**~~
~~New York, NY, USA~~	~~57.3~~	~~55.9~~	~~***64.9***~~	~~***73.6***~~	~~234~~	~~228~~	~~***265***~~	~~***301***~~	~~10.5~~	~~10.2~~	~~***11.9***~~	~~***13.5***~~
~~Los Angeles, CA, USA~~	~~***105***~~	~~***92.6***~~	~~61.3~~	~~65.1~~	~~***432***~~	~~***379***~~	~~251~~	~~266~~	~~***19.4***~~	~~***17.0***~~	~~11.3~~	~~12.0~~
~~Chicago, IL, USA~~	~~34.1~~	~~32.4~~	~~40.9~~	~~40.1~~	~~139~~	~~132~~	~~168~~	~~164~~	~~6.26~~	~~5.92~~	~~7.56~~	~~7.37~~
~~Pasadena, CA, USA~~	~~38.9~~	~~39.0~~	~~48.6~~	~~39.5~~	~~159~~	~~159~~	~~198~~	~~161~~	~~7.15~~	~~7.11~~	~~8.90~~	~~7.21~~
~~Houston, TX, USA~~	~~28.4~~	~~25.8~~	~~30.0~~	~~25.9~~	~~116~~	~~105~~	~~123~~	~~106~~	~~5.23~~	~~4.73~~	~~5.55~~	~~4.76~~
~~Washington, DC, USA~~	~~29.4~~	~~30.0~~	~~35.1~~	~~43.5~~	~~120~~	~~122~~	~~144~~	~~178~~	~~5.38~~	~~5.46~~	~~6.47~~	~~8.01~~
~~Miami, FL, USA~~	~~28.1~~	~~17.0~~	~~20.9~~	~~24.3~~	~~115~~	~~69.1~~	~~85.7~~	~~99.3~~	~~5.17~~	~~3.10~~	~~3.86~~	~~4.47~~
~~Boston, MA, USA~~	~~21.0~~	~~21.3~~	~~25.9~~	~~26.1~~	~~84.9~~	~~85.4~~	~~105~~	~~106~~	~~3.79~~	~~3.81~~	~~4.69~~	~~4.74~~
~~Downsview, ON, CAN~~	~~21.7~~	~~20.2~~	~~28.2~~	~~30.9~~	~~88.0~~	~~81.6~~	~~115~~	~~126~~	~~3.94~~	~~3.65~~	~~5.19~~	~~5.64~~
~~Atlanta, GA, USA~~	~~24.8~~	~~21.2~~	~~23.4~~	~~27.1~~	~~101~~	~~86.0~~	~~95.6~~	~~111~~	~~4.54~~	~~3.86~~	~~4.30~~	~~4.98~~
~~Philadelphia, PA, USA~~	~~21.7~~	~~21.7~~	~~21.3~~	~~30.4~~	~~88.2~~	~~87.3~~	~~86.3~~	~~124~~	~~3.95~~	~~3.90~~	~~3.86~~	~~5.54~~
~~Dallas, TX, USA~~	~~20.5~~	~~15.6~~	~~12.8~~	~~22.9~~	~~83.5~~	~~63.4~~	~~52.1~~	~~93.5~~	~~3.75~~	~~2.84~~	~~2.34~~	~~4.20~~
~~Sydney, FL, USA~~	~~12.5~~	~~10.2~~	~~12.6~~	~~11.0~~	~~50.8~~	~~40.7~~	~~50.6~~	~~44.7~~	~~2.27~~	~~1.81~~	~~2.25~~	~~2.00~~
~~Cedar Rapids, IA, USA~~	~~4.91~~	~~4.06~~	~~4.37~~	~~5.88~~	~~19.4~~	~~15.5~~	~~17.4~~	~~23.3~~	~~0.853~~	~~0.675~~	~~0.777~~	~~1.03~~
~~Point Reyes, CA, USA~~	~~8.04~~	~~4.12~~	~~2.10~~	~~4.63~~	~~32.6~~	~~16.1~~	~~8.38~~	~~18.6~~	~~1.46~~	~~0.707~~	~~0.373~~	~~0.826~~
~~Bratt's Lake, SK, CAN~~	~~2.86~~	~~2.25~~	~~1.88~~	~~2.45~~	~~11.2~~	~~8.15~~	~~7.24~~	~~9.53~~	~~0.492~~	~~0.348~~	~~0.320~~	~~0.416~~
~~Groton, CT, USA~~	~~7.62~~	~~11.2~~	~~11.3~~	~~7.91~~	~~30.0~~	~~43.9~~	~~44.3~~	~~30.8~~	~~1.32~~	~~1.93~~	~~1.95~~	~~1.34~~
~~Lewes, DE, USA~~	~~6.99~~	~~6.67~~	~~5.31~~	~~8.61~~	~~27.6~~	~~25.6~~	~~20.8~~	~~34.0~~	~~1.22~~	~~1.12~~	~~0.915~~	~~1.50~~
~~Harvard Forest, MA, USA~~	~~6.06~~	~~5.55~~	~~5.93~~	~~7.06~~	~~23.5~~	~~20.8~~	~~22.9~~	~~27.5~~	~~1.03~~	~~0.901~~	~~1.01~~	~~1.20~~
~~West Branch, IA, USA~~	~~3.42~~	~~2.46~~	~~2.28~~	~~4.66~~	~~13.2~~	~~8.88~~	~~8.82~~	~~18.3~~	~~0.576~~	~~0.378~~	~~0.389~~	~~0.804~~
~~Whistler, BC, CAN~~	~~1.39~~	~~1.30~~	~~0.728~~	~~1.11~~	~~5.40~~	~~4.47~~	~~2.73~~	~~4.21~~	~~0.235~~	~~0.185~~	~~0.118~~	~~0.181~~
~~Trinidad Head, CA, USA~~	~~1.55~~	~~0.900~~	~~0.626~~	~~0.852~~	~~6.03~~	~~2.88~~	~~2.35~~	~~3.11~~	~~0.263~~	~~0.115~~	~~0.102~~	~~0.131~~
~~Park Falls, WI, USA~~	~~1.67~~	~~1.19~~	~~0.911~~	~~2.23~~	~~5.91~~	~~3.59~~	~~3.12~~	~~8.31~~	~~0.242~~	~~0.138~~	~~0.131~~	~~0.354~~
~~Niwot Ridge, CO, USA~~	~~***0.478***~~	~~0.829~~	~~0.468~~	~~***0.649***~~	~~***1.77***~~	~~2.82~~	~~1.54~~	~~***2.35***~~	~~***0.0749***~~	~~0.116~~	~~0.0623~~	~~***0.0985***~~
~~Ucluelet, BC, CAN~~	~~1.66~~	~~***0.827***~~	~~***0.142***~~	~~0.687~~	~~6.46~~	~~2.46~~	~~***0.423***~~	~~2.42~~	~~0.282~~	~~0.0932~~	~~***0.0170***~~	~~0.0992~~
~~Fraserdale, ON, CAN~~	~~1.06~~	~~0.869~~	~~0.350~~	~~1.71~~	~~2.88~~	~~***1.93***~~	~~0.756~~	~~5.88~~	~~0.0929~~	~~***0.0559***~~	~~0.0250~~	~~0.237~~

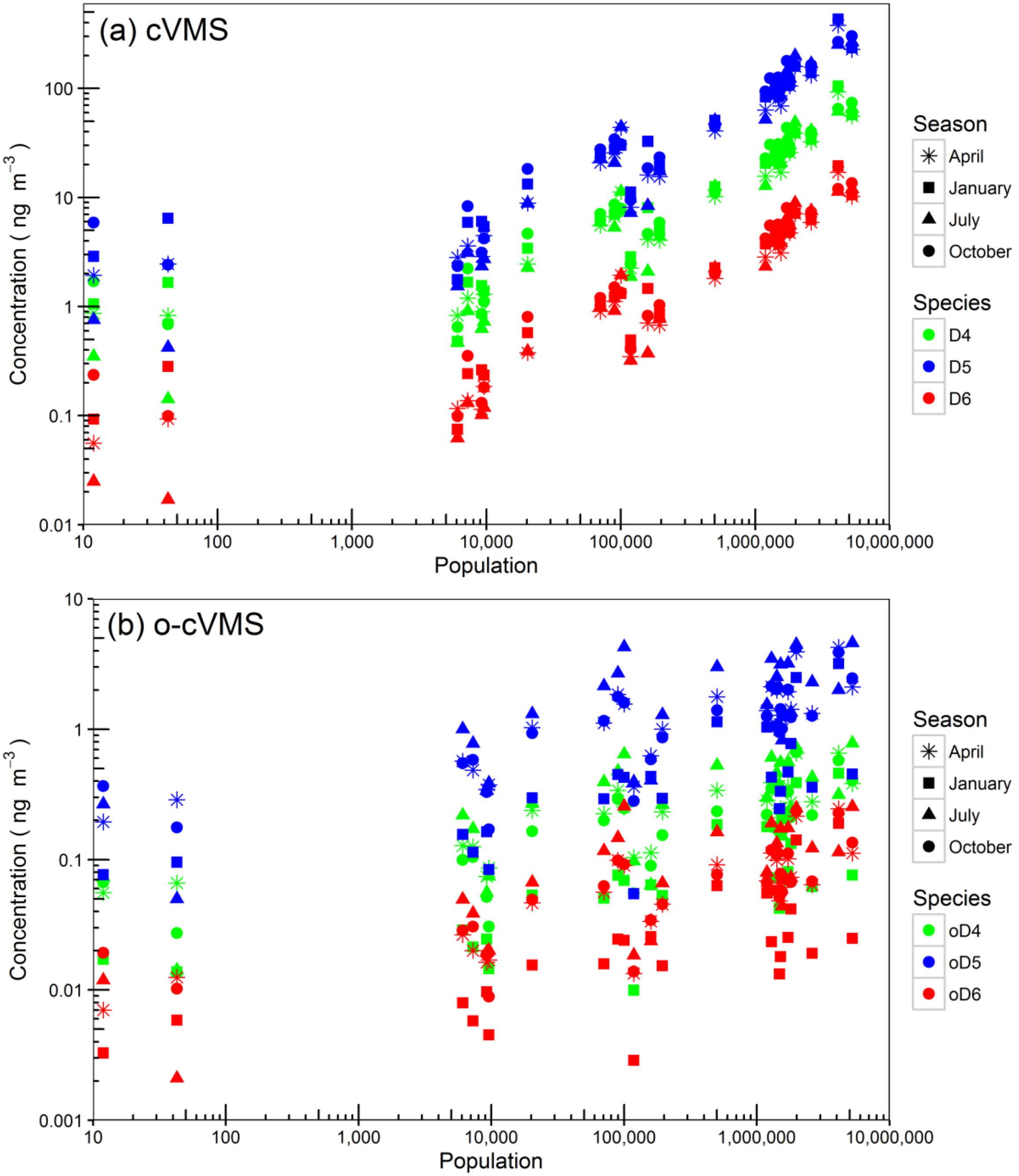

Figure 3: Average monthly CMAQ modeled surface (a) cVMS and (b) oxidized cVMS concentrations are plotted versus 36-km grid cell population for 26 U.S. and Canadian sites. These sites include the ten most populous U.S. metropolitan areas, previous siloxane measurement sites, and NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) sites. See Table S3 for the listing of these sites.

~~**Table 3: Average monthly CMAQ modeled surface oxidized cVMS concentrations (ng m^{-3}) sorted by population (highest at top of table) in analyzed grid cell. Minimum and maximum values in each column in boldface and italicized.**~~

~~-~~		~~o-D$_4$~~				~~o-D$_5$~~				~~o-D$_6$~~		
~~Site~~	**~~January~~**	**~~April~~**	**~~July~~**	**~~October~~**	**~~January~~**	**~~April~~**	**~~July~~**	**~~October~~**	**~~January~~**	**~~April~~**	**~~July~~**	**~~October~~**
~~New York, NY, USA~~	~~0.0760~~	~~0.383~~	***~~0.782~~***	~~0.404~~	~~0.454~~	~~2.11~~	***~~4.60~~***	~~2.46~~	~~0.0249~~	~~0.112~~	~~0.254~~	~~0.135~~
~~Los Angeles, CA, USA~~	***~~0.460~~***	***~~0.656~~***	~~0.315~~	~~0.576~~	***~~3.19~~***	***~~4.26~~***	~~2.01~~	~~3.89~~	***~~0.190~~***	***~~0.246~~***	~~0.114~~	~~0.228~~
~~Chicago, IL, USA~~	~~0.0622~~	~~0.278~~	~~0.427~~	~~0.219~~	~~0.359~~	~~1.32~~	~~2.30~~	~~1.27~~	~~0.0191~~	~~0.0642~~	~~0.122~~	~~0.0681~~
~~Pasadena, CA, USA~~	~~0.389~~	~~0.655~~	~~0.720~~	***~~0.666~~***	~~2.49~~	~~3.92~~	~~4.46~~	***~~4.21~~***	~~0.142~~	~~0.215~~	~~0.248~~	***~~0.237~~***
~~Houston, TX, USA~~	~~0.133~~	~~0.274~~	~~0.244~~	~~0.212~~	~~0.776~~	~~1.42~~	~~1.35~~	~~1.24~~	~~0.0417~~	~~0.0731~~	~~0.0726~~	~~0.0673~~
~~Washington, DC, USA~~	~~0.0807~~	~~0.363~~	~~0.560~~	~~0.330~~	~~0.470~~	~~1.94~~	~~3.20~~	~~2.01~~	~~0.0253~~	~~0.101~~	~~0.175~~	~~0.112~~
~~Miami, FL, USA~~	~~0.206~~	~~0.233~~	~~0.151~~	~~0.166~~	~~1.28~~	~~1.20~~	~~0.824~~	~~1.01~~	~~0.0711~~	~~0.0612~~	~~0.0439~~	~~0.0564~~
~~Boston, MA, USA~~	~~0.0579~~	~~0.246~~	~~0.555~~	~~0.239~~	~~0.334~~	~~1.28~~	~~3.14~~	~~1.43~~	~~0.0180~~	~~0.0661~~	~~0.173~~	~~0.0779~~
~~Downsview, ON, CAN~~	~~0.0424~~	~~0.210~~	~~0.373~~	~~0.162~~	~~0.246~~	~~0.994~~	~~2.08~~	~~0.948~~	~~0.0132~~	~~0.0483~~	~~0.113~~	~~0.0514~~
~~Atlanta, GA, USA~~	~~0.176~~	~~0.402~~	~~0.464~~	~~0.344~~	~~1.06~~	~~1.99~~	~~2.52~~	~~2.03~~	~~0.0582~~	~~0.0989~~	~~0.134~~	~~0.110~~
~~Philadelphia, PA, USA~~	~~0.0724~~	~~0.389~~	~~0.607~~	~~0.353~~	~~0.429~~	~~2.12~~	~~3.48~~	~~2.14~~	~~0.0234~~	~~0.112~~	~~0.191~~	~~0.118~~
~~Dallas, TX, USA~~	~~0.179~~	~~0.286~~	~~0.299~~	~~0.221~~	~~1.04~~	~~1.39~~	~~1.54~~	~~1.26~~	~~0.0554~~	~~0.0687~~	~~0.0797~~	~~0.0666~~
~~Sydney, FL, USA~~	~~0.186~~	~~0.340~~	~~0.528~~	~~0.234~~	~~1.14~~	~~1.78~~	~~3.01~~	~~1.40~~	~~0.0630~~	~~0.0914~~	~~0.163~~	~~0.0767~~
~~Cedar Rapids, IA, USA~~	~~0.0531~~	~~0.233~~	~~0.264~~	~~0.154~~	~~0.295~~	~~1.00~~	~~1.29~~	~~0.864~~	~~0.0153~~	~~0.0454~~	~~0.0659~~	~~0.0455~~
~~Point Reyes, CA, USA~~	~~0.0639~~	~~0.113~~	~~0.0639~~	~~0.0898~~	~~0.434~~	~~0.627~~	~~0.405~~	~~0.588~~	~~0.0256~~	~~0.0336~~	~~0.0237~~	~~0.0343~~
~~Bratt's Lake, SK, CAN~~	***~~0.00994~~***	~~0.104~~	~~0.0971~~	~~0.0550~~	***~~0.0547~~***	~~0.362~~	~~0.394~~	~~0.282~~	***~~0.00288~~***	~~0.0134~~	~~0.0185~~	~~0.0138~~
~~Groton, CT, USA~~	~~0.0691~~	~~0.254~~	~~0.644~~	~~0.247~~	~~0.427~~	~~1.56~~	~~4.27~~	~~1.60~~	~~0.0240~~	~~0.0900~~	***~~0.257~~***	~~0.0922~~
~~Lewes, DE, USA~~	~~0.0759~~	~~0.340~~	~~0.478~~	~~0.291~~	~~0.449~~	~~1.85~~	~~2.69~~	~~1.78~~	~~0.0245~~	~~0.0989~~	~~0.147~~	~~0.0986~~
~~Harvard Forest, MA, USA~~	~~0.0506~~	~~0.224~~	~~0.394~~	~~0.199~~	~~0.292~~	~~1.12~~	~~2.15~~	~~1.16~~	~~0.0159~~	~~0.0562~~	~~0.117~~	~~0.0626~~
~~West Branch, IA, USA~~	~~0.0535~~	~~0.238~~	~~0.269~~	~~0.165~~	~~0.298~~	~~1.03~~	~~1.31~~	~~0.933~~	~~0.0155~~	~~0.0465~~	~~0.0669~~	~~0.0494~~
~~Whistler, BC, CAN~~	~~0.0146~~	~~0.0863~~	~~0.0745~~	~~0.0306~~	~~0.0838~~	~~0.375~~	~~0.386~~	***~~0.170~~***	~~0.00453~~	~~0.0170~~	~~0.0201~~	***~~0.00889~~***
~~Trinidad Head, CA, USA~~	~~0.0246~~	~~0.0742~~	~~0.0559~~	~~0.0516~~	~~0.164~~	~~0.345~~	~~0.340~~	~~0.329~~	~~0.00966~~	~~0.0163~~	~~0.0195~~	~~0.0189~~
~~Park Falls, WI, USA~~	~~0.0213~~	~~0.125~~	~~0.172~~	~~0.104~~	~~0.114~~	~~0.486~~	~~0.778~~	~~0.582~~	~~0.00578~~	~~0.0200~~	~~0.0387~~	~~0.0306~~
~~Niwot Ridge, CO, USA~~	~~0.0288~~	~~0.128~~	~~0.219~~	~~0.0994~~	~~0.156~~	~~0.569~~	~~1.00~~	~~0.549~~	~~0.00796~~	~~0.0265~~	~~0.0494~~	~~0.0285~~
~~Ucluelet, BC, CAN~~	~~0.0138~~	~~0.0662~~	***~~0.0142~~***	***~~0.0273~~***	~~0.0955~~	~~0.288~~	***~~0.0499~~***	~~0.177~~	~~0.00587~~	~~0.0125~~	***~~0.00210~~***	~~0.0102~~
~~Fraserdale, ON, CAN~~	~~0.0172~~	***~~0.0557~~***	~~0.0732~~	~~0.0668~~	~~0.0766~~	***~~0.195~~***	~~0.266~~	~~0.367~~	~~0.00328~~	***~~0.00700~~***	~~0.0119~~	~~0.0193~~

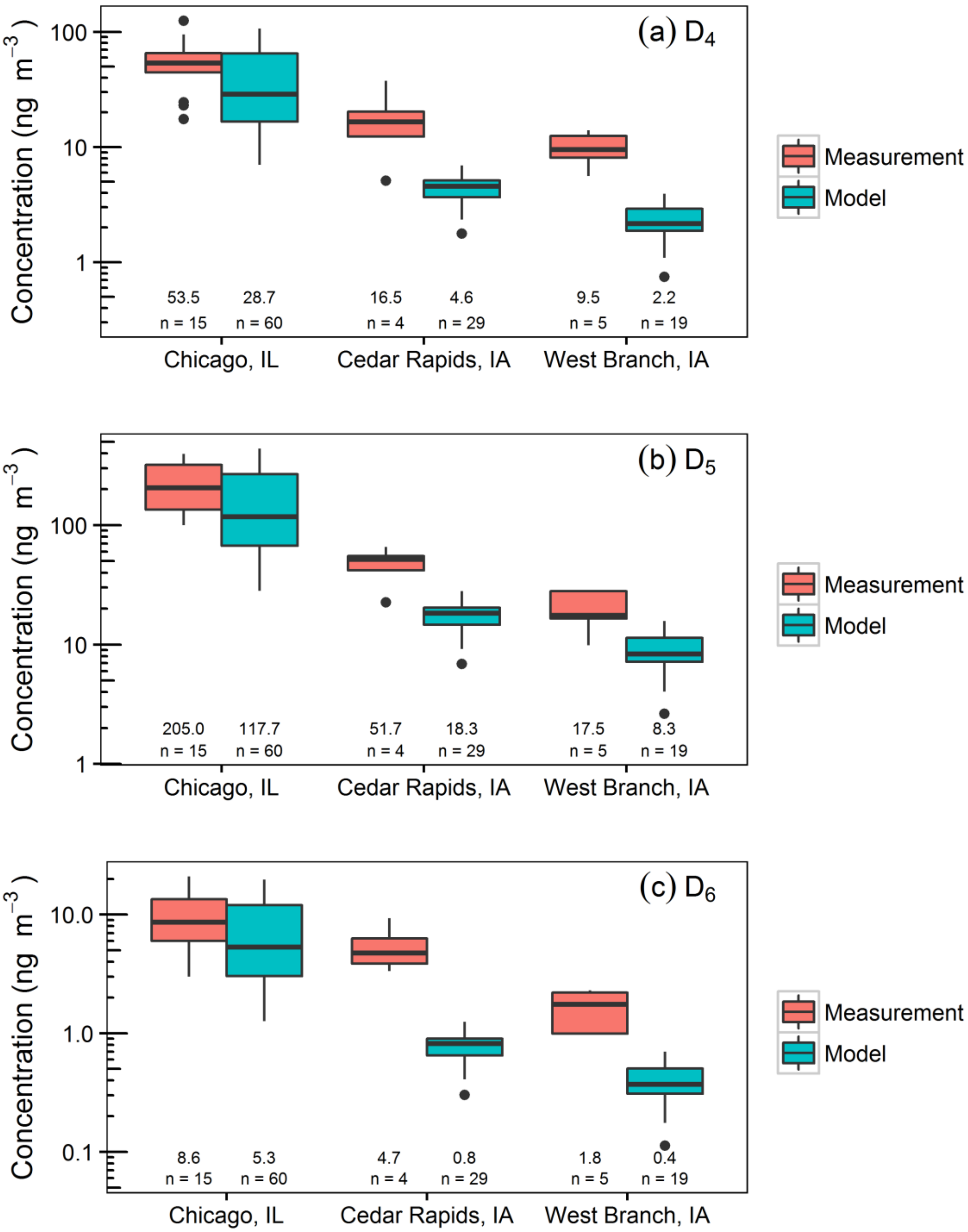

Figure ~~4~~3: Model comparison to Yucuis et al. (2013)~~ Midwest measurements~~. Model results ~~are~~ from CMAQ ~~modeled (~~July 1-30 simulation); ~~month (days 1-30) while~~ measurements were conducted in 2011 from Aug 13-21 (Chicago), Jun 29-Jul 26 (Cedar Rapids), and ~~dates were in 2011 from~~ Jul 6-22 (West Branch), respectively. ~~for Chicago, June 29 – July 26 for Cedar Rapids, and July 6 – 22 for West Branch.~~ Hourly model data was averaged to 12, 24, and 36 hour periods, starting at typical measurement start

times. ~~to match sampling times as explained in the text.~~ Median concentrations and number of observations are tabulated under the boxplots.

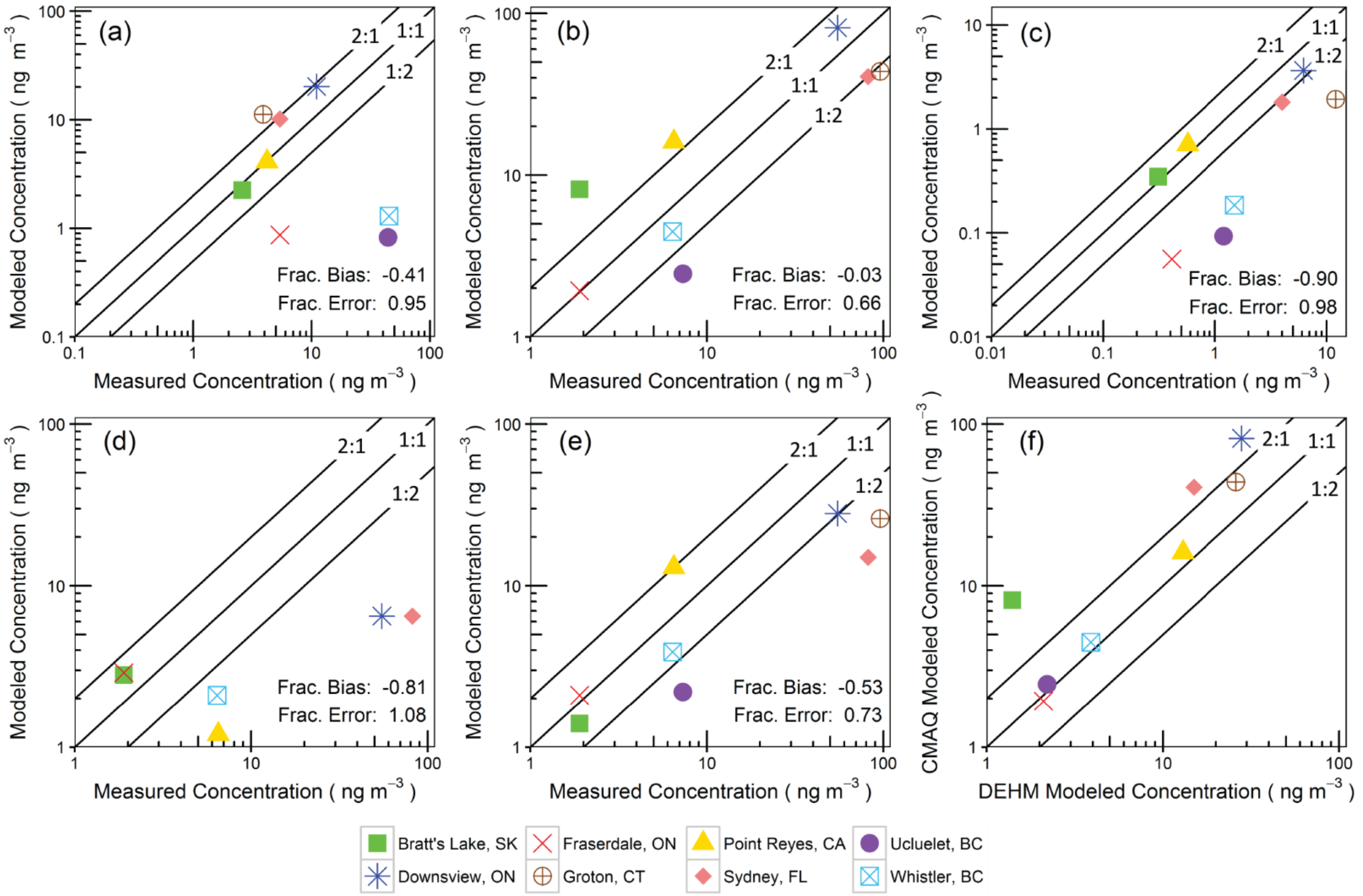

Figure ~~4~~5: ~~Comparison of the April averaged CMAQ model to Genualdi et al. (2011).~~ Plot (a) shows CMAQ D$_4$, (b) CMAQ D$_5$, (c) CMAQ D$_6$, (d) BETR D$_5$, and (e) DEHM D$_5$ modeled concentrations compared to Genualdi et al. (2011) measurements. Plot (f) compares modeled CMAQ D$_5$ versus DEHM D$_5$ concentrations. CMAQ model results are the April averaged concentrations while BETR and DEHM model results are from Genualdi et al. (2011) and represent the same period as the measurements. CMAQ model resolution was 36 km, DEHM 150 km, and BETR 15°.

Table ~~4~~2: Toronto cyclic siloxane comparison between the CMAQ model and previous ~~published measurement and modeling~~ studies. Reported is the mean concentration with the range in parenthesis.

			Atmospheric Concentration, mean (range)			
Period	**Method**	**Averaging Period**	**D_4 (ng m^{-3})**	**D_5 (ng m^{-3})**	**D_6 (ng m^{-3})**	**Reference**
January	CMAQ Model	24 h	21.7 (5.4 - 45.1)	88.1 (21.5 - 184.8)	3.94 (0.95 - 8.31)	*This study*
April	CMAQ Model	24 h	20.4 (4.6 - 43.7)	82.1 (17.1 - 178.2)	3.67 (0.74 - 8.01)	*This study*
July	CMAQ Model	24 h	28.3 (7.5 - 57.0)	115.9 (30.5 - 233.8)	5.22 (1.37 - 10.54)	*This study*
October	CMAQ Model	24 h	31.0 (5.4 - 60.6)	126.3 (20.8 -247.7)	5.67 (0.90 - 11.13)	*This study*
March 2010 - April 2011	Active sampling	24 h (not continuous)	16 (2.8 - 77)	91 (15 - 247)	7.3 (1.9 - 22)	*Ahrens et al. (2014)*
March 2010 - April 2011	Passive sampling	~28 d	21 (9.3 - 35)	140 (89 - 168)	11 (8.0 - 20)	*Ahrens et al. (2014)*
March 2012 - June 2012	Active sampling	2-3 d	24.2 (4.7 - 90.9)	93.5 (22.4 - 355)	5.5 (1.6 - 17.4)	*Krogseth et al. (2013b)*
July 2012 - October 2012	Passive sampling	80-92 d	41	122	-	*Krogseth et al. (2013b)*
April 2009 - June 2009	Passive sampling	89 d	11	55	6.2	*Genualdi et al. (2011)*
April 2009 - June 2009	BETR Model	89 d	-	6.5	-	*Genualdi et al. (2011)*
April 2009 - June 2009	DEHM Model	89 d	-	28	-	*Genualdi et al. (2011)*

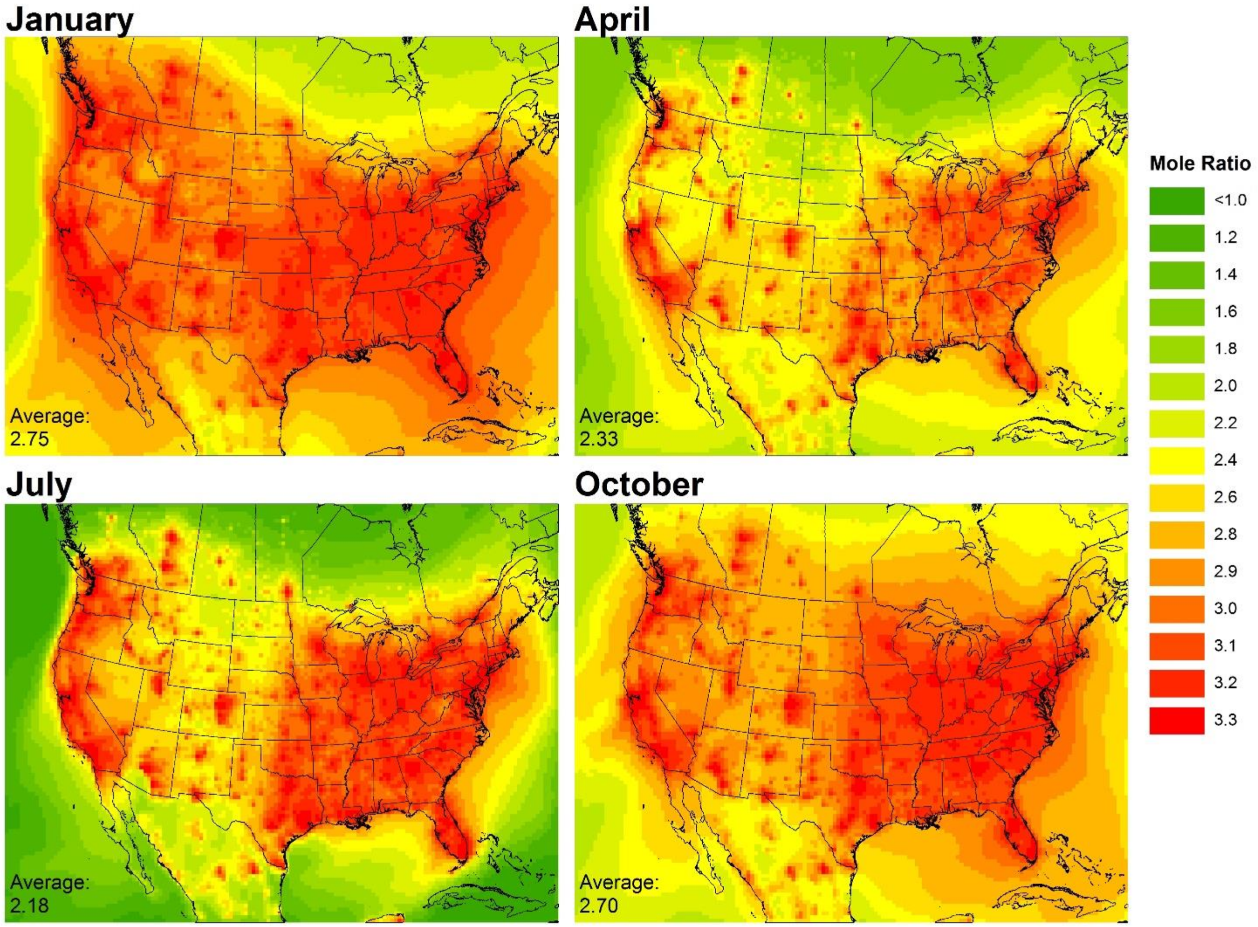

Figure ~~5~~6: Modeled monthly averaged D_5/D_4 mole ratios by season. Larger cVMS species react faster with OH. More reactive species are in the numerator; therefore, ratios decrease with air mass age.

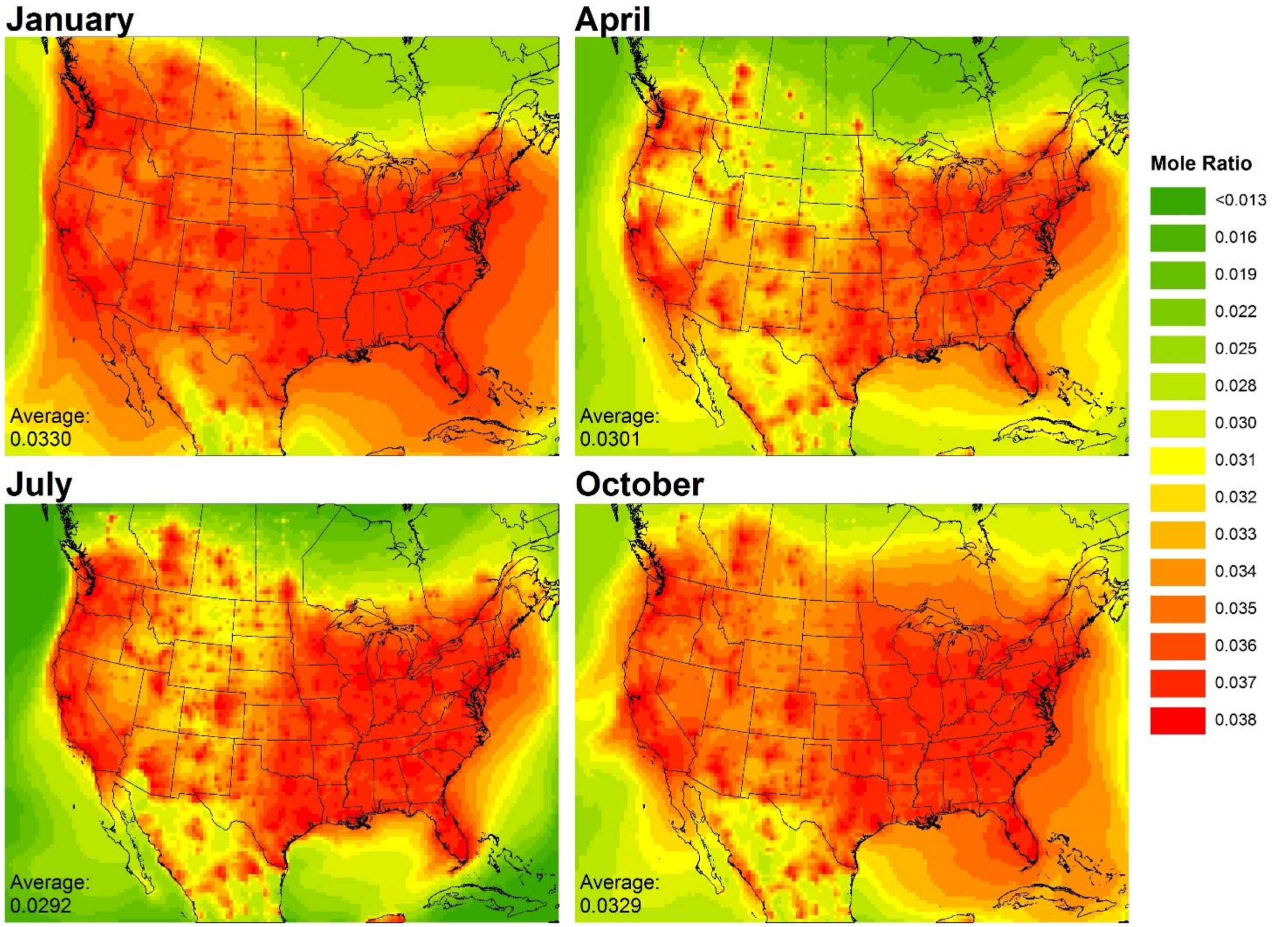

Figure ~~6~~7: Modeled monthly averaged D_6/D_5 mole ratios by season. Larger cVMS species react faster with OH. More reactive species are in the numerator; therefore, ratios decrease with air mass age.

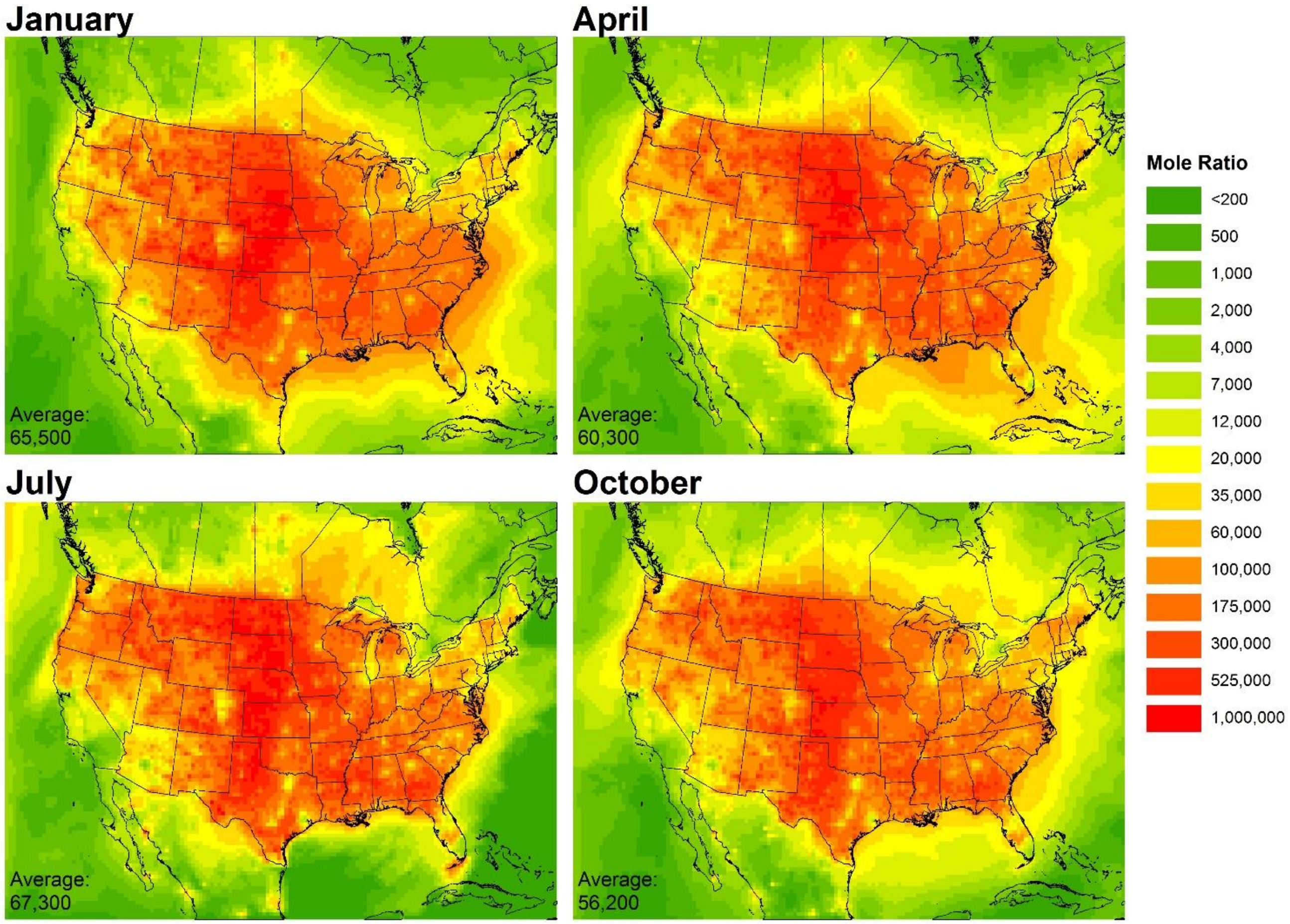

Figure ~~7~~8: Modeled monthly averaged SO_2/ (D_4+D_5+D_6) mole ratio by season.

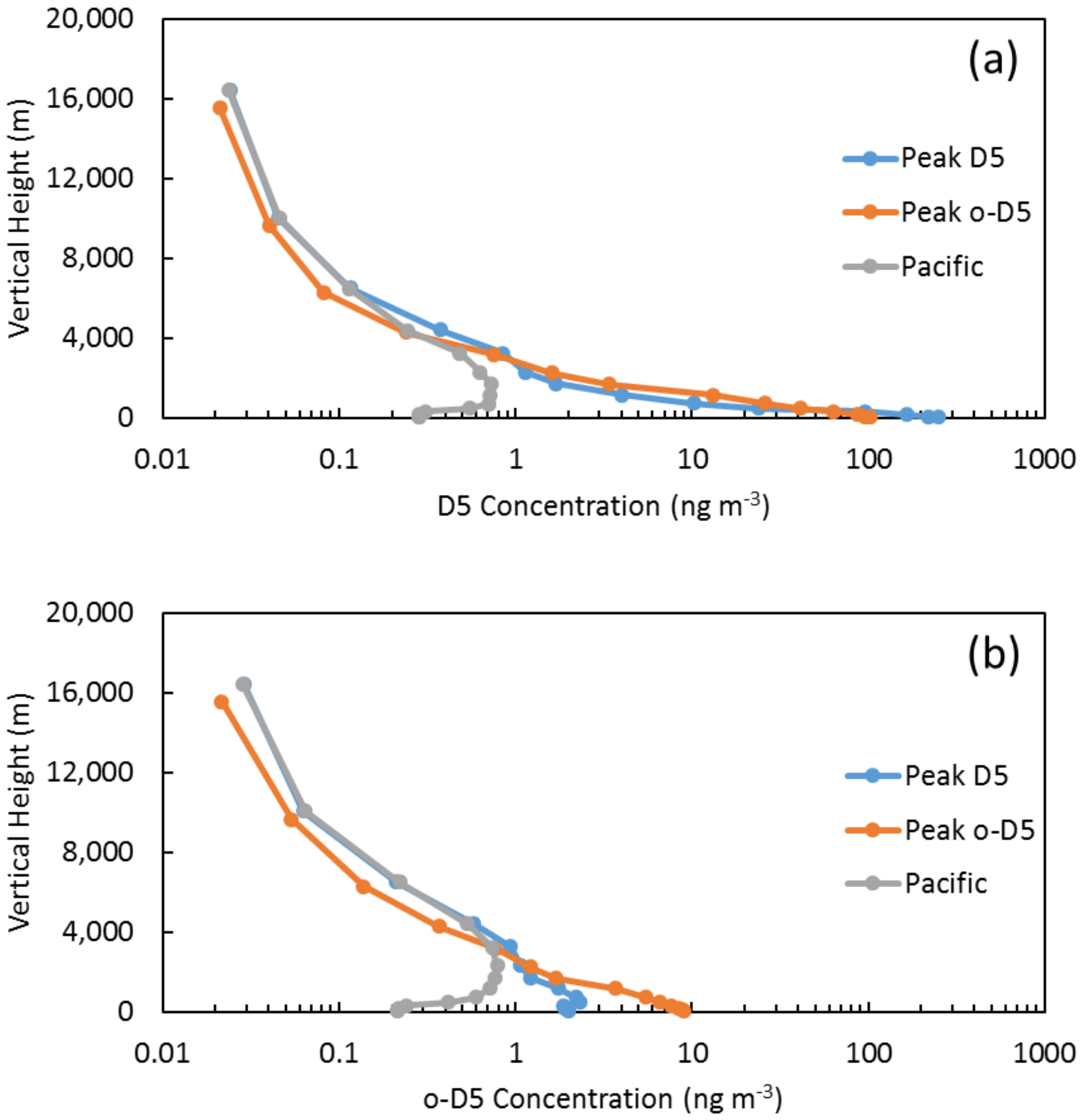

Figure 98: Monthly averaged vertical profiles for grid cells near Los Angeles. Plot (a) shows D_5 and (b) o-D_5 model concentrations. Grid cells refer to the location of maximum July D_5, maximum July o-D_5, and a grid cell over the Pacific Ocean.

Supplemental Material

Comprehensive Atmospheric Modeling of Reactive Cyclic Siloxanes and Their Oxidation Products

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Section S1: Modeled Domain

Figure S1: CMAQ model domain.

Section S2: Deposition Sensitivity

A wet and dry deposition sensitivity test compared gas phase concentrations with and without deposition as a check to verify cVMS deposition parameters. CMAQ includes treatment of dry and wet deposition (Byun et al., 1999; Roselle and Binkowski, 1999) parameterized by Henry's law coefficients, mass diffusivity, reactivity relative to HNO_3, and mesophyll resistance. However, there is considerable uncertainty in these cVMS parameterizations and only the D_4, D_5, and D_6 Henry's law coefficients (Xu and Kropscott, 2012) have been experimentally determined. A 1-week sensitivity analysis for a Chicago grid cell over the period of August 13 – August 20, 2004 was run for three scenarios 1) no deposition, 2) dry deposition only, and 3) dry and wet deposition. The addition of deposition caused gas phase concentrations to decrease, the percent change is displayed in Table S1. Wet deposition for the parent compounds was not observed but the single OH substituted oxidized species did undergo wet deposition, albeit small. Similarly, for dry deposition the parent compounds underwent less deposition than the oxidized species. Modeled wet and dry deposition agree with expected behavior based on the input parameters and the current understanding that as cVMS species are oxidized, deposition increases (Whelan et al., 2004).

Table S1: Deposition sensitivity test. August 13-20, 2004 average mixing ratios for Chicago grid cell.

	No Deposition (ppm)	Dry Deposition (ppm)	Dry and Wet Deposition (ppm)	Percent Change due to Dry Deposition (%)	Percent Change due to Wet Deposition (%)
D_4	6.16E-06	5.86E-06	5.86E-06	4.86	0.000
D_5	1.43E-05	1.36E-05	1.36E-05	4.56	0.000
D_6	1.09E-06	1.04E-06	1.04E-06	4.35	0.000
o-D_4	8.63E-08	5.89E-08	5.89E-08	31.73	0.027
o-D_5	2.85E-07	2.03E-07	2.03E-07	28.71	0.019
o-D_6	2.58E-08	1.90E-08	1.90E-08	26.43	0.014

Section S3: Gridded Population Data

Gridded population was downloaded from EPA 2011 Version 6.0 Air Emissions Modeling Platform data https://www.epa.gov/air-emissions-modeling/2011-version-60-platform. Specifically, we used population spatial surrogates. U.S. gridded population data is based on 2010 census data, Canada on 2001 census data, and Mexico from 1999/2000 census data. U.S. and Mexico population data was already gridded to the 36 km domain but Canada data was regridded from 12 km.

Section S4: Cyclic Siloxane Emission Rates

Table S2: Table of cVMS emission estimates. Numbers with superscripts correspond to [a]mean, [b]range, [c]median, and [d]maximum emission rates. Horii and Kannan (2008), Wang et al. (2009), and Dudzina et al. (2014) report exposure rate instead of air emissions. The values are likely to be similar to air emissions for Wang et al. (2009) since the products analyzed are expected to fully volatilize, the Horii and Kannan (2008) values are likely higher than air emissions since products washed down the drain are not distinguished, and the Dudzina et al. (2014) values are likely lower than air emissions since secondary volatilization from down the drain products is not included.

		Emission Rate (mg person^{-1} day^{-1})			
Location	**Method**	**D_4**	**D_5**	**D_6**	**Reference**
U.S. and Canada	McLachlan et al. (2010) D_5 estimate and Chicago measurements	32.8	135	6.10	*This work*
Mexico	McLachlan et al. (2010) D_5 estimate and Chicago measurements	5.92	24.4	1.10	*This work*
Berkley, CA, USA	Indoor classroom measurements	(0.048 - 30.5)[b]	(4.39 - 235)[b]	(0.46 - 7.27)[b]	*Tang et al. (2015)*
Zurich, Switzerland	Model back-calculated	-	310[a] (170-690)[b]	36[a] (19-81)[b]	*Buser et al. (2013)*
Chicago, IL, USA	Model back-calculated	-	190[a] (100-420)[b]	-	*Buser et al. (2014)*
U.S.	Dow Corning provided emissions	90	137	-	*Navea et al. (2011)*
Iowa City, IA, USA	Indoor lab measurements	(0.0090 - 0.027)[b]	(29 - 590)[b]	-	*Yucuis et al. (2013)*
Canada	Personal care product D_5 usage estimate (3,300 t/yr)	-	260	-	*Buser et al. (2014)*
U.S.	Exposure estimate from personal care products	1.08[a]	233[a]	22.2[a]	*Horii and Kannan (2008)*
Canada	Exposure estimate from lotion and antiperspirant products	98.6[d]	900[d]	-	*Wang et al. (2009)*
Netherlands and Switzerland	Exposure estimate from personal care products	0.08[c] (10.8[d])	260[c] (1,224[d])	-	*Dudzina et al. (2014)*
Portugal	Air emission estimate from personal care products	0.130[a] (0.00131 - 0.519)[b]	0.815[a] (0.00175 - 3.13)[b]	0.500[a] (0.00085 - 2.07)[b]	*Capela et al. (2016)*

Section S5: Calculation of NO_x/NO_y Atmospheric Age

D_4 and D_6 emission rates were estimated using Chicago outdoor concentrations from Yucuis et al. (2013) multiplied by the D_5 emission rate. Chicago was assumed to be representative of fresh concentrations and hence the emission ratios. Due to different OH reactivity rates, product ratios change with photochemical age. NO_x and NO_y measurements from a Chicago EPA measurement site was used to estimate the photochemical age to verify the Chicago measurements represent fresh emissions. NO_x and NO_y has been used previously to estimate photochemical age assuming NO_y is formed by $NO_2 + OH \rightarrow HNO_3$ (Slowik et al., 2011).

Hourly NO_x and NO_y data was extracted from the Northbrook, IL EPA monitoring site. Data was downloaded from Air Quality System Data Mart (http://www.epa.gov/ttn/airs/aqsdatamart). The analyzed period matched the Chicago cVMS measurements (August 13 – 21, 2011). Hourly NO_x/NO_y ratios were calculated for hours that both NO_x and NO_y measurements were available, and then averaged for the measurement period. The cVMS concentrations were calculated by averaging the primary and duplicate Chicago measurements excluding Sample 6 due to being an outlier as discussed in Yucuis et al. (2013). Several D_6 measurements were below the limit of quantification and were treated as LOQ/√2.

The photochemical age was calculated using Equation S1. The NO_x/NO_y ratio was 0.864, OH concentration $1.33\text{x}10^6$ molecules cm^{-3} interpolated for Chicago's latitude from Spivakovsky et al. (2000), and the k_{NO2} rate constant $1.08\text{x}10^{-11}$ cm^3 $mole^{-1}$ s^{-1} estimated from the JPL 2011 parameterization for 295 K and surface pressure (Sander et al., 2011). The calculated age was determined to be 2.83 hours. Plugging in this age to Equation S2, the corrected emission ratio was calculated. $[A]_0/[B]_0$ represents the photochemically corrected emission ratio, [A]/[B] the measured Chicago siloxane concentrations, *t* the photochemical age, and k_A and k_B the respective siloxane OH rate constants. Corrected D_4/D_5 and D_6/D_5 emission ratios differed by less than 1% of the measured ratios. We therefore used the measured concentration ratios without photochemical age correction.

$$t = \frac{-\ln\left(\frac{[NO]_x}{[NO]_y}\right)}{[OH]k_{NO_2}} \qquad (\boldsymbol{S1})$$

$$\left(\frac{[A]_0}{[B]_0}\right) = \frac{\left(\frac{[A]}{[B]}\right)}{e^{-[t*[OH]*(k_A-k_B)]}} \qquad (\boldsymbol{S2})$$

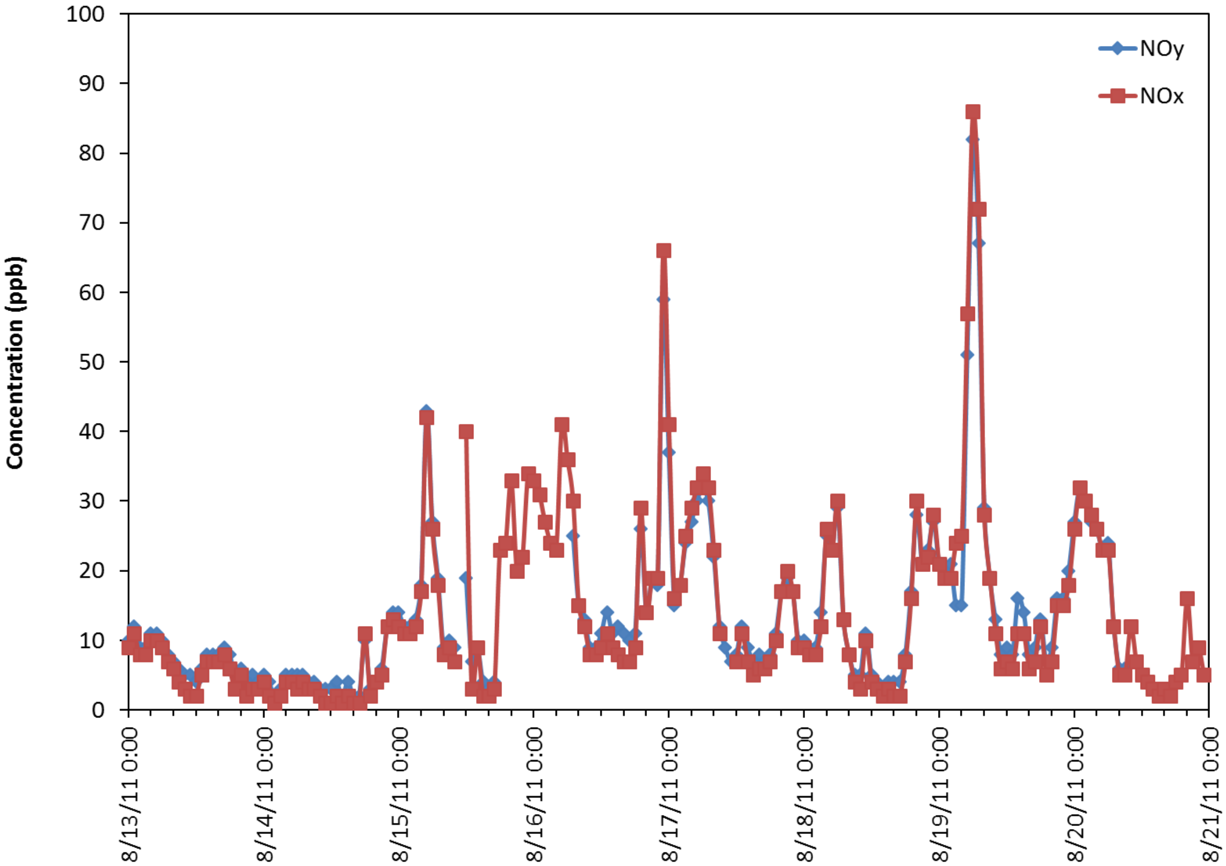

Figure S2: Northbrook hourly NO_x and NO_y measurements.

Section S6: D_4 and D_6 Boundary Concentrations

Cyclic siloxane boundary conditions were generated from the Danish Eulerian Hemispheric Model (DEHM) which simulated D_5 at 150 km resolution for the Northern Hemisphere (Hansen et al., 2008; McLachlan et al., 2010). The DEHM model provided monthly averaged, horizontally and vertically resolved D_5 concentrations. D_4 and D_6 boundary concentrations were estimated using the DEHM D_5 concentrations multiplied by an OH dependent D_4/D_5 and D_6/D_5 ratio.

Since cVMS OH rate constants vary between species, an aged background ratio will differ from a fresh emission ratio and will also be dependent on the seasonally varying OH concentrations. D_4/D_5 and D_6/D_5 boundary ratios were calculated using spring cVMS atmospheric measurements at a rural site in Point Reyes, CA (Genualdi et al., 2011). Using Equation S3, combined with the aged Point Reyes measurements and the Chicago emission measurements, we were able to calculate a photochemical age. Here *t* is the photochemical age, [A]/[B] represents the measured siloxane ratio at Point Reyes, $[A]_0/[B]_0$ the fresh emission siloxane ratio, [OH] the average OH concentration during the 3-month measurement period determined for the latitude of Point Reyes (Spivakovsky et al., 2000), and k the respective cVMS

OH rate constants. Using D_4 and D_5, a photochemical age of 17.6 days was calculated and used for all calculations.

The aged, OH dependent background D_4/D_5 and D_6/D_5 ratios were calculated using Equation S4. Here *t* is 17.6 days, [OH] the monthly dependent OH concentration as fit from Spivakovsky et al. (2000), $[A]_0/[B]_0$ the fresh emission siloxane ratio, and [A]/[B] represents the seasonally corrected boundary siloxane ratio. D_4 and D_6 concentrations were estimated by combining the seasonally specific boundary ratios with the DEHM modeled D_5. The same ratios were used for all four boundaries.

$$t = -\ln\left[\frac{\left(\frac{[A]}{[B]}\right)}{\left(\frac{[A]_0}{[B]_0}\right)}\right] * \frac{1}{[OH] * (k_A - k_B)} \qquad (\boldsymbol{S3})$$

$$\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0} e^{-[OH]*t*(k_A - k_B)} \qquad (\boldsymbol{S4})$$

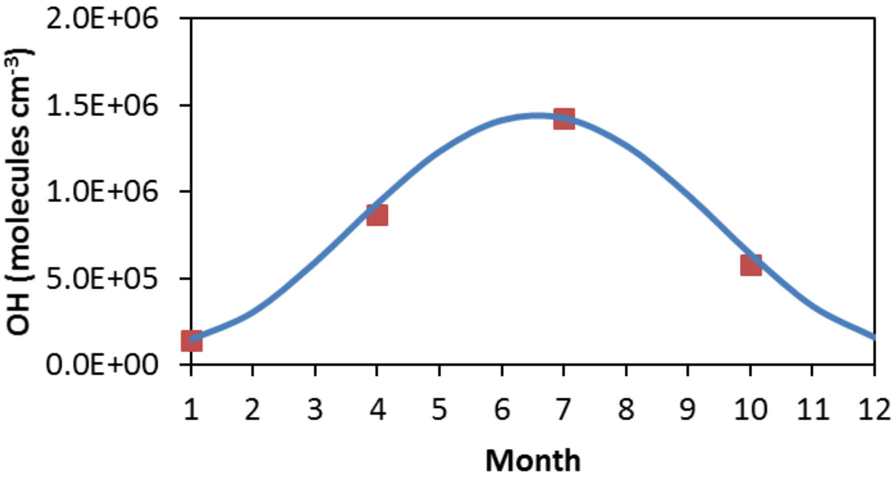

Figure S3: Spivakovsky et al. (2000) OH data for Point Reyes (38° N) latitude.

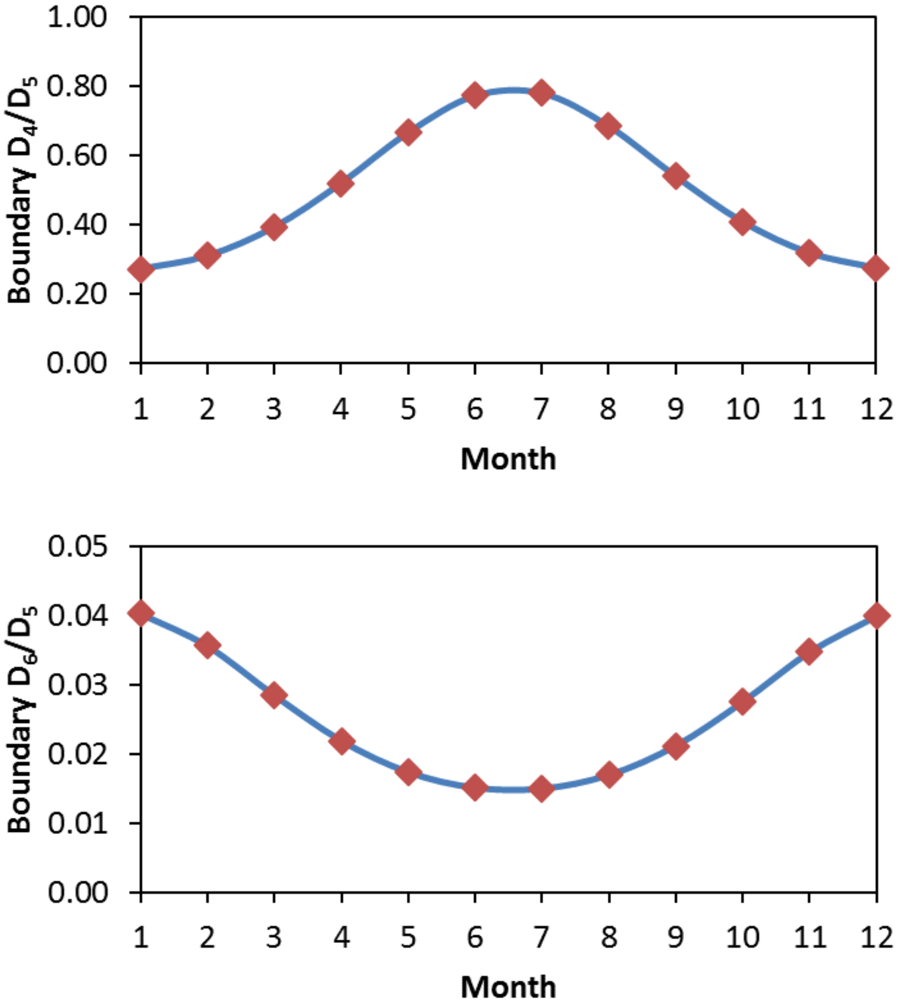

Figure S4: Monthly resolved D_4/D_5 and D_6/D_5 aged ratios.

Section S7: Analyzed Sites

Figure S5: Analyzed 26 sites.

Table S3: Classification of 26 sites. Sites with July D_5 concentrations below 17 ng m^{-3} were classified as rural sites (in bold).

			D_5 (ng m^{-3})			
Location	Grid Cell Population	Classification	January	April	July	October
Fraserdale, ON, CAN	**12**	**Rural**	**2.88**	**1.93**	**0.76**	**5.88**
Ucluelet, BC, CAN	**43**	**Rural**	**6.46**	**2.46**	**0.42**	**2.42**
Niwot Ridge, CO, USA	**6,090**	**Rural**	**1.77**	**2.82**	**1.54**	**2.35**
Park Falls, WI, USA	**7,265**	**Rural**	**5.91**	**3.59**	**3.12**	**8.31**
Trinidad Head, CA, USA	**9,224**	**Rural**	**6.03**	**2.88**	**2.35**	**3.11**
Whistler, BC, CAN	**9,588**	**Rural**	**5.40**	**4.47**	**2.73**	**4.21**
West Branch, IA, USA	**20,291**	**Rural**	**13.24**	**8.88**	**8.82**	**18.30**
Harvard Forest, MA, USA	70,374	Urban	23.54	20.84	22.88	27.48
Lewes, DE, USA	89,714	Urban	27.62	25.59	20.79	34.00
Groton, CT, USA	100,246	Urban	29.99	43.90	44.27	30.80
Bratt's Lake, SK, CAN	**118,400**	**Rural**	**11.22**	**8.15**	**7.24**	**9.53**
Point Reyes, CA, USA	**158,892**	**Rural**	**32.64**	**16.06**	**8.38**	**18.57**
Cedar Rapids, IA, USA	193,991	Urban	19.38	15.48	17.43	23.34
Sydney, FL, USA	500,868	Urban	50.76	40.68	50.57	44.67
Dallas, TX, USA	1,191,994	Urban	83.52	63.43	52.06	93.46
Philadelphia, PA, USA	1,286,968	Urban	88.18	87.35	86.27	123.63
Atlanta, GA, USA	1,413,880	Urban	101.20	86.03	95.64	110.92
Downsview, ON, CAN	1,481,245	Urban	87.97	81.61	115.33	125.74
Boston, MA, USA	1,506,543	Urban	84.87	85.41	104.78	105.89
Miami, FL, USA	1,550,514	Urban	114.90	69.06	85.69	99.31
Washington, DC, USA	1,719,747	Urban	119.77	121.75	143.74	178.12
Houston, TX, USA	1,806,399	Urban	116.29	105.23	123.06	105.84
Pasadena, CA, USA	1,979,007	Urban	159.14	158.60	198.27	160.84
Chicago, IL, USA	2,605,915	Urban	139.34	131.79	167.80	164.02
Los Angeles, CA, USA	4,133,658	Urban	432.11	378.90	251.32	266.15
New York, NY, USA	5,245,179	Urban	234.37	227.78	265.35	301.30

Table S4: Average monthly CMAQ modeled surface cVMS concentrations (ng m^{-3}) sorted by population (highest at top of table) in analyzed grid cell. Minimum and maximum values in each column in boldface and italicized.

Site	D_4				D_5				D_6			
	January	April	July	October	January	April	July	October	January	April	July	October
New York, NY, USA	57.3	55.9	***64.9***	***73.6***	234	228	***265***	***301***	10.5	10.2	***11.9***	***13.5***
Los Angeles, CA, USA	***105***	***92.6***	61.3	65.1	***432***	***379***	251	266	***19.4***	***17.0***	11.3	12.0
Chicago, IL, USA	34.1	32.4	40.9	40.1	139	132	168	164	6.26	5.92	7.56	7.37
Pasadena, CA, USA	38.9	39.0	48.6	39.5	159	159	198	161	7.15	7.11	8.90	7.21
Houston, TX, USA	28.4	25.8	30.0	25.9	116	105	123	106	5.23	4.73	5.55	4.76
Washington, DC, USA	29.4	30.0	35.1	43.5	120	122	144	178	5.38	5.46	6.47	8.01
Miami, FL, USA	28.1	17.0	20.9	24.3	115	69.1	85.7	99.3	5.17	3.10	3.86	4.47
Boston, MA, USA	21.0	21.3	25.9	26.1	84.9	85.4	105	106	3.79	3.81	4.69	4.74
Downsview, ON, CAN	21.7	20.2	28.2	30.9	88.0	81.6	115	126	3.94	3.65	5.19	5.64
Atlanta, GA, USA	24.8	21.2	23.4	27.1	101	86.0	95.6	111	4.54	3.86	4.30	4.98
Philadelphia, PA, USA	21.7	21.7	21.3	30.4	88.2	87.3	86.3	124	3.95	3.90	3.86	5.54
Dallas, TX, USA	20.5	15.6	12.8	22.9	83.5	63.4	52.1	93.5	3.75	2.84	2.34	4.20
Sydney, FL, USA	12.5	10.2	12.6	11.0	50.8	40.7	50.6	44.7	2.27	1.81	2.25	2.00
Cedar Rapids, IA, USA	4.91	4.06	4.37	5.88	19.4	15.5	17.4	23.3	0.853	0.675	0.777	1.03
Point Reyes, CA, USA	8.04	4.12	2.10	4.63	32.6	16.1	8.38	18.6	1.46	0.707	0.373	0.826
Bratt's Lake, SK, CAN	2.86	2.25	1.88	2.45	11.2	8.15	7.24	9.53	0.492	0.348	0.320	0.416
Groton, CT, USA	7.62	11.2	11.3	7.91	30.0	43.9	44.3	30.8	1.32	1.93	1.95	1.34
Lewes, DE, USA	6.99	6.67	5.31	8.61	27.6	25.6	20.8	34.0	1.22	1.12	0.915	1.50
Harvard Forest, MA, USA	6.06	5.55	5.93	7.06	23.5	20.8	22.9	27.5	1.03	0.901	1.01	1.20
West Branch, IA, USA	3.42	2.46	2.28	4.66	13.2	8.88	8.82	18.3	0.576	0.378	0.389	0.804
Whistler, BC, CAN	1.39	1.30	0.728	1.11	5.40	4.47	2.73	4.21	0.235	0.185	0.118	0.181
Trinidad Head, CA, USA	1.55	0.900	0.626	0.852	6.03	2.88	2.35	3.11	0.263	0.115	0.102	0.131
Park Falls, WI, USA	1.67	1.19	0.911	2.23	5.91	3.59	3.12	8.31	0.242	0.138	0.131	0.354
Niwot Ridge, CO, USA	***0.478***	0.829	0.468	***0.649***	***1.77***	2.82	1.54	***2.35***	***0.0749***	0.116	0.0623	***0.0985***
Ucluelet, BC, CAN	1.66	***0.827***	***0.142***	0.687	6.46	2.46	***0.423***	2.42	0.282	0.0932	***0.0170***	0.0992
Fraserdale, ON, CAN	1.06	0.869	0.350	1.71	2.88	***1.93***	0.756	5.88	0.0929	***0.0559***	0.0250	0.237

Table S5: Average monthly CMAQ modeled surface oxidized cVMS concentrations (ng m^{-3}) sorted by population (highest at top of table) in analyzed grid cell. Minimum and maximum values in each column in boldface and italicized.

	o-D$_4$				o-D$_5$				o-D$_6$			
Site	**January**	**April**	**July**	**October**	**January**	**April**	**July**	**October**	**January**	**April**	**July**	**October**
New York, NY, USA	0.0760	0.383	***0.782***	0.404	0.454	2.11	***4.60***	2.46	0.0249	0.112	0.254	0.135
Los Angeles, CA, USA	***0.460***	***0.656***	0.315	0.576	***3.19***	***4.26***	2.01	3.89	***0.190***	***0.246***	0.114	0.228
Chicago, IL, USA	0.0622	0.278	0.427	0.219	0.359	1.32	2.30	1.27	0.0191	0.0642	0.122	0.0681
Pasadena, CA, USA	0.389	0.655	0.720	***0.666***	2.49	3.92	4.46	***4.21***	0.142	0.215	0.248	***0.237***
Houston, TX, USA	0.133	0.274	0.244	0.212	0.776	1.42	1.35	1.24	0.0417	0.0731	0.0726	0.0673
Washington, DC, USA	0.0807	0.363	0.560	0.330	0.470	1.94	3.20	2.01	0.0253	0.101	0.175	0.112
Miami, FL, USA	0.206	0.233	0.151	0.166	1.28	1.20	0.824	1.01	0.0711	0.0612	0.0439	0.0564
Boston, MA, USA	0.0579	0.246	0.555	0.239	0.334	1.28	3.14	1.43	0.0180	0.0661	0.173	0.0779
Downsview, ON, CAN	0.0424	0.210	0.373	0.162	0.246	0.994	2.08	0.948	0.0132	0.0483	0.113	0.0514
Atlanta, GA, USA	0.176	0.402	0.464	0.344	1.06	1.99	2.52	2.03	0.0582	0.0989	0.134	0.110
Philadelphia, PA, USA	0.0724	0.389	0.607	0.353	0.429	2.12	3.48	2.14	0.0234	0.112	0.191	0.118
Dallas, TX, USA	0.179	0.286	0.299	0.221	1.04	1.39	1.54	1.26	0.0554	0.0687	0.0797	0.0666
Sydney, FL, USA	0.186	0.340	0.528	0.234	1.14	1.78	3.01	1.40	0.0630	0.0914	0.163	0.0767
Cedar Rapids, IA, USA	0.0531	0.233	0.264	0.154	0.295	1.00	1.29	0.864	0.0153	0.0454	0.0659	0.0455
Point Reyes, CA, USA	0.0639	0.113	0.0639	0.0898	0.434	0.627	0.405	0.588	0.0256	0.0336	0.0237	0.0343
Bratt's Lake, SK, CAN	***0.00994***	0.104	0.0971	0.0550	***0.0547***	0.362	0.394	0.282	***0.00288***	0.0134	0.0185	0.0138
Groton, CT, USA	0.0691	0.254	0.644	0.247	0.427	1.56	4.27	1.60	0.0240	0.0900	***0.257***	0.0922
Lewes, DE, USA	0.0759	0.340	0.478	0.291	0.449	1.85	2.69	1.78	0.0245	0.0989	0.147	0.0986
Harvard Forest, MA, USA	0.0506	0.224	0.394	0.199	0.292	1.12	2.15	1.16	0.0159	0.0562	0.117	0.0626
West Branch, IA, USA	0.0535	0.238	0.269	0.165	0.298	1.03	1.31	0.933	0.0155	0.0465	0.0669	0.0494
Whistler, BC, CAN	0.0146	0.0863	0.0745	0.0306	0.0838	0.375	0.386	***0.170***	0.00453	0.0170	0.0201	***0.00889***
Trinidad Head, CA, USA	0.0246	0.0742	0.0559	0.0516	0.164	0.345	0.340	0.329	0.00966	0.0163	0.0195	0.0189
Park Falls, WI, USA	0.0213	0.125	0.172	0.104	0.114	0.486	0.778	0.582	0.00578	0.0200	0.0387	0.0306
Niwot Ridge, CO, USA	0.0288	0.128	0.219	0.0994	0.156	0.569	1.00	0.549	0.00796	0.0265	0.0494	0.0285
Ucluelet, BC, CAN	0.0138	0.0662	***0.0142***	***0.0273***	0.0955	0.288	***0.0499***	0.177	0.00587	0.0125	***0.00210***	0.0102
Fraserdale, ON, CAN	0.0172	***0.0557***	0.0732	0.0668	0.0766	***0.195***	0.266	0.367	0.00328	***0.00700***	0.0119	0.0193

Table S6: Monthly averaged modeled OH and meterology.

	OH (molec cm^{-3})				Surface Temperature (K)				Surface Pressure (Pa)				Planetary Boundary Layer Height (m)				Wind Speed (m s^{-1})			
Site	January	April	July	October	January	April	July	October	January	April	July	October	January	April	July	October	January	April	July	October
New York, NY, USA	2.15E+05	8.93E+05	2.12E+06	5.80E+05	269.3	284.2	296.4	286.5	1.01E+05	1.01E+05	1.01E+05	1.01E+05	743.5	664.6	687.2	522.0	4.18	4.17	3.23	3.20
Los Angeles, CA, USA	2.82E+05	5.38E+05	6.00E+05	4.17E+05	287.0	287.8	289.3	290.8	1.02E+05	1.01E+05	1.01E+05	1.01E+05	199.3	226.7	197.8	415.8	3.81	3.94	3.74	4.18
Chicago, IL, USA	1.81E+05	1.07E+06	2.21E+06	5.13E+05	268.0	284.5	295.3	286.3	9.93E+04	9.90E+04	9.89E+04	9.89E+04	466.3	770.1	645.7	483.3	4.81	5.09	3.54	4.20
Pasadena, CA, USA	5.35E+05	1.46E+06	1.43E+06	8.58E+05	287.1	290.2	292.6	291.1	9.98E+04	9.94E+04	9.93E+04	9.92E+04	417.2	614.6	376.5	494.8	3.14	3.17	2.77	2.91
Houston, TX, USA	4.48E+05	1.61E+06	2.45E+06	1.26E+06	287.5	293.8	300.5	298.2	1.02E+05	1.01E+05	1.01E+05	1.01E+05	466.1	627.3	549.2	561.0	4.13	4.07	3.10	4.00
Washington, DC, USA	2.46E+05	1.02E+06	2.10E+06	6.47E+05	273.1	286.5	297.6	287.6	1.01E+05	1.01E+05	1.01E+05	1.01E+05	646.5	609.1	545.4	376.2	3.48	3.69	2.70	2.53
Miami, FL, USA	1.03E+06	2.26E+06	3.04E+06	1.49E+06	292.4	295.6	300.5	298.4	1.02E+05	1.02E+05	1.01E+05	1.01E+05	473.0	738.9	488.8	495.1	3.02	3.99	2.97	3.25
Boston, MA, USA	2.29E+05	7.48E+05	1.96E+06	5.60E+05	266.4	281.8	294.6	284.7	1.01E+05	1.01E+05	1.01E+05	1.01E+05	718.9	585.0	611.2	507.6	4.34	4.09	3.07	3.46
Downsview, ON, CAN	2.13E+05	1.01E+06	1.95E+06	4.84E+05	264.2	279.9	292.7	283.7	9.81E+04	9.80E+04	9.80E+04	9.82E+04	561.0	648.7	568.3	476.8	4.43	4.58	3.23	3.81
Atlanta, GA, USA	3.75E+05	1.38E+06	2.56E+06	8.82E+05	278.9	289.5	298.9	292.5	9.84E+04	9.82E+04	9.81E+04	9.82E+04	351.3	714.6	618.2	450.2	3.75	3.65	2.96	2.94
Philadelphia, PA, USA	2.31E+05	1.01E+06	2.20E+06	5.96E+05	270.2	285.1	296.8	286.4	1.01E+05	1.01E+05	1.01E+05	1.01E+05	701.2	639.5	646.5	437.0	4.21	3.98	3.15	2.90
Dallas, TX, USA	4.56E+05	1.45E+06	3.46E+06	1.04E+06	284.2	292.4	301.6	296.1	9.96E+04	9.91E+04	9.91E+04	9.90E+04	473.8	696.3	848.3	522.2	4.52	5.17	4.57	4.08
Sydney, FL, USA	6.85E+05	1.99E+06	2.84E+06	1.41E+06	289.6	294.2	300.5	297.7	1.02E+05	1.01E+05	1.01E+05	1.01E+05	431.6	689.1	433.4	529.2	3.28	3.63	2.57	3.13
Cedar Rapids, IA, USA	2.09E+05	1.05E+06	2.22E+06	5.14E+05	267.0	285.4	295.2	285.9	9.88E+04	9.84E+04	9.83E+04	9.83E+04	413.9	720.2	523.9	457.5	5.22	4.98	3.30	4.59
Point Reyes, CA, USA	5.73E+05	1.79E+06	2.72E+06	1.19E+06	284.2	284.9	286.3	287.6	1.02E+05	1.01E+05	1.01E+05	1.01E+05	382.7	201.4	93.7	242.5	6.11	5.65	5.18	5.55
Bratt's Lake, SK, CAN	9.83E+04	1.51E+06	2.27E+06	5.37E+05	257.6	279.6	291.9	278.6	9.44E+04	9.42E+04	9.41E+04	9.39E+04	244.2	849.3	665.2	420.6	4.11	4.99	3.88	4.49
Groton, CT, USA	2.38E+05	6.82E+05	1.64E+06	5.87E+05	270.4	279.9	293.6	287.2	1.01E+05	1.01E+05	1.01E+05	1.01E+05	1023.0	151.3	103.1	686.9	9.86	5.46	4.16	6.62
Lewes, DE, USA	2.40E+05	9.40E+05	1.92E+06	6.48E+05	272.8	285.6	297.7	287.9	1.01E+05	1.01E+05	1.01E+05	1.01E+05	562.0	545.7	560.2	416.1	4.33	4.20	3.08	2.97
Harvard Forest, MA, USA	2.03E+05	7.81E+05	1.86E+06	5.17E+05	264.6	280.9	293.3	283.3	9.80E+04	9.81E+04	9.83E+04	9.85E+04	679.8	635.1	578.9	511.1	4.64	4.14	2.88	3.28
West Branch, IA, USA	2.14E+05	1.07E+06	2.20E+06	5.33E+05	267.8	285.9	295.7	286.4	9.92E+04	9.88E+04	9.87E+04	9.87E+04	420.6	748.2	531.5	455.7	5.21	5.08	3.30	4.64
Whistler, BC, CAN	2.01E+05	8.29E+05	8.97E+05	4.14E+05	270.7	278.3	287.5	278.6	8.84E+04	8.88E+04	8.90E+04	8.84E+04	237.6	590.0	650.2	343.1	3.79	3.20	3.24	3.78
Trinidad Head, CA, USA	3.63E+05	1.31E+06	2.30E+06	6.99E+05	283.9	284.9	288.4	287.8	1.02E+05	1.02E+05	1.01E+05	1.01E+05	404.9	259.7	144.2	285.6	6.21	6.14	6.24	5.25
Park Falls, WI, USA	1.61E+05	7.54E+05	1.97E+06	4.36E+05	260.7	278.3	291.3	281.7	9.61E+04	9.59E+04	9.60E+04	9.58E+04	434.1	509.3	571.7	450.4	4.54	4.08	3.43	4.53
Niwot Ridge, CO, USA	4.90E+05	1.51E+06	3.26E+06	9.85E+05	264.1	273.0	285.2	275.3	7.03E+04	7.04E+04	7.13E+04	7.06E+04	389.3	747.9	999.6	700.4	4.76	5.02	3.58	4.97
Ucluelet, BC, CAN	1.53E+05	9.79E+05	1.15E+06	4.27E+05	280.2	282.7	288.3	285.8	1.01E+05	1.02E+05	1.01E+05	1.01E+05	536.8	275.8	200.3	425.1	8.89	5.08	4.21	5.98
Fraserdale, ON, CAN	1.60E+05	5.28E+05	4.99E+05	2.44E+05	251.7	272.6	290.4	279.6	9.95E+04	9.93E+04	9.90E+04	9.90E+04	365.9	606.4	643.6	438.5	3.05	3.44	3.25	3.51

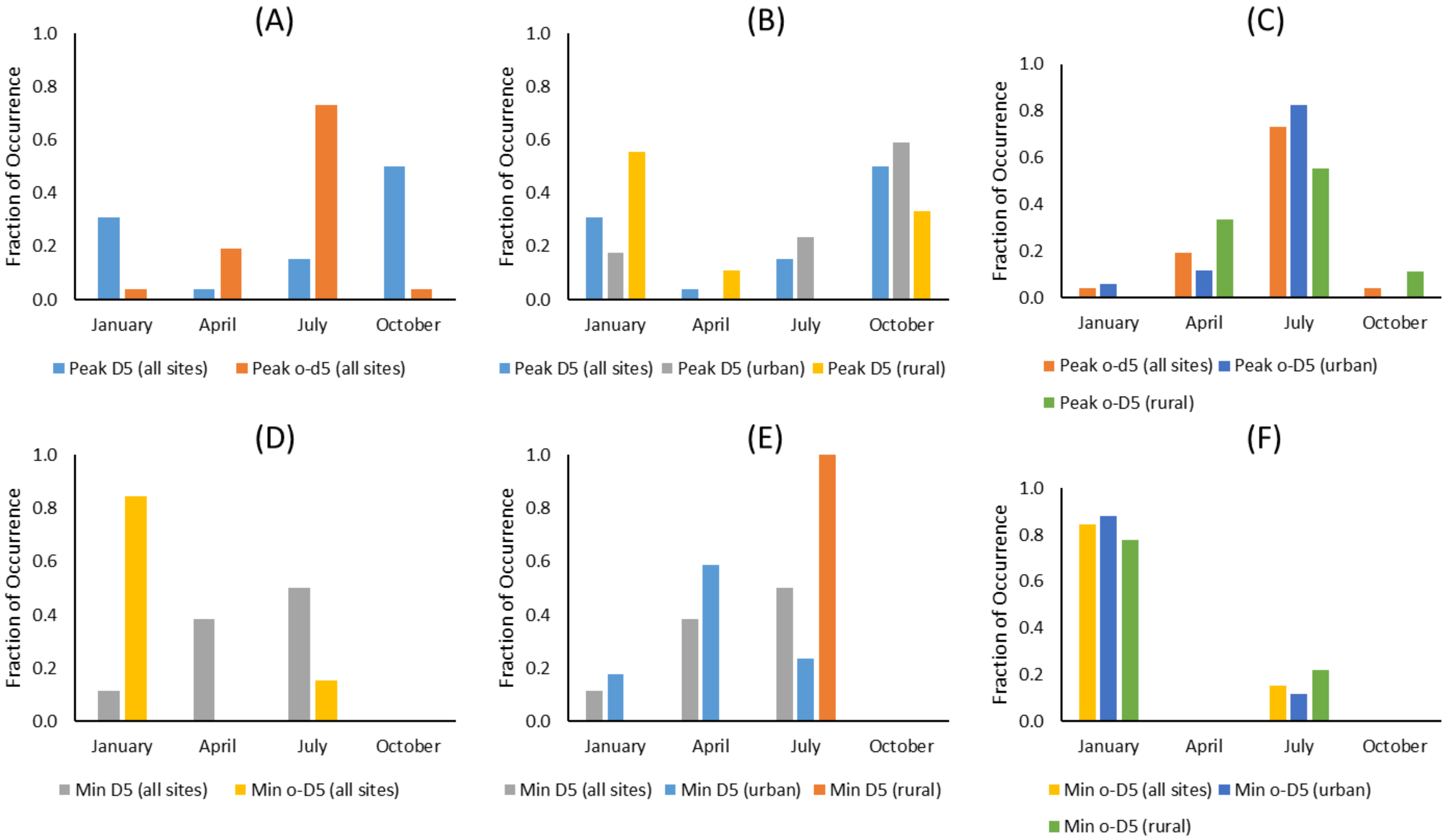

Figure S6: Seasonal trends of D_5 and o-D_5 concentrations for the 26 analyzed sites. Of the four months modeled, the month of highest or lowest average D_5 and o-D_5 concentrations are tabulated. Panel (A) shows monthly occurrence of highest D_5 and o-D_5 concentrations for all sites, (B) occurrence of highest D_5 for urban and rural sites, (C) occurrence of highest o-D_5 for urban and rural sites, (D) occurrence of lowest D_5 and o-D_5 for all sites, (E) occurrence of lowest D_5 for urban and rural sites, and (F) occurrence of lowest o-D_5 for urban and rural sites.

Table S7: Monthly averaged modeled compound ratios.

	D_5/D_4				D_6/D_5				SO_2/cVMS			
Site	**January**	**April**	**July**	**October**	**January**	**April**	**July**	**October**	**January**	**April**	**July**	**October**
New York, NY, USA	3.27	3.26	3.27	3.27	0.0375	0.0374	0.0375	0.0375	9,294	6,937	5,960	8,247
Los Angeles, CA, USA	3.28	3.27	3.28	3.27	0.0375	0.0375	0.0375	0.0374	337	251	185	319
Chicago, IL, USA	3.27	3.26	3.28	3.27	0.0375	0.0374	0.0376	0.0375	11,538	8,616	5,662	9,615
Pasadena, CA, USA	3.27	3.26	3.26	3.26	0.0374	0.0374	0.0374	0.0374	761	283	266	503
Houston, TX, USA	3.27	3.27	3.28	3.27	0.0375	0.0375	0.0376	0.0375	9,611	4,697	4,104	5,211
Washington, DC, USA	3.26	3.25	3.27	3.27	0.0374	0.0374	0.0375	0.0375	33,544	24,260	21,360	24,316
Miami, FL, USA	3.28	3.25	3.28	3.27	0.0375	0.0374	0.0375	0.0375	5,194	4,778	1,945	2,641
Boston, MA, USA	3.24	3.21	3.23	3.24	0.0372	0.0372	0.0373	0.0373	15,531	12,303	9,211	14,497
Downsview, ON, CAN	3.24	3.23	3.27	3.26	0.0373	0.0373	0.0375	0.0374	1,546	2,973	588	2,185
Atlanta, GA, USA	3.26	3.24	3.27	3.27	0.0374	0.0374	0.0375	0.0375	30,866	28,251	18,309	22,427
Philadelphia, PA, USA	3.25	3.22	3.24	3.25	0.0373	0.0372	0.0373	0.0373	20,139	17,350	15,060	17,912
Dallas, TX, USA	3.26	3.24	3.26	3.27	0.0374	0.0374	0.0374	0.0375	23,995	15,536	15,158	11,614
Sydney, FL, USA	3.24	3.20	3.22	3.24	0.0373	0.0371	0.0372	0.0373	21,592	16,777	7,641	12,545
Cedar Rapids, IA, USA	3.16	3.05	3.19	3.18	0.0367	0.0363	0.0372	0.0368	144,645	126,766	97,014	89,098
Point Reyes, CA, USA	3.25	3.12	3.19	3.21	0.0373	0.0367	0.0371	0.0371	2,581	2,732	2,436	5,866
Bratt's Lake, SK, CAN	3.14	2.90	3.09	3.11	0.0366	0.0355	0.0368	0.0364	8,505	6,449	5,263	19,517
Groton, CT, USA	3.15	3.13	3.13	3.11	0.0366	0.0367	0.0367	0.0364	23,025	14,862	18,158	24,402
Lewes, DE, USA	3.16	3.07	3.13	3.16	0.0367	0.0364	0.0367	0.0367	49,557	39,235	40,384	34,715
Harvard Forest, MA, USA	3.11	3.01	3.09	3.12	0.0364	0.0360	0.0366	0.0364	25,561	30,775	20,004	32,611
West Branch, IA, USA	3.10	2.89	3.10	3.14	0.0363	0.0354	0.0367	0.0366	207,140	217,583	194,708	115,970
Whistler, BC, CAN	3.10	2.76	3.00	3.03	0.0363	0.0345	0.0361	0.0359	1,885	3,819	8,098	3,585
Trinidad Head, CA, USA	3.10	2.56	3.00	2.92	0.0363	0.0332	0.0361	0.0351	7,626	22,248	33,099	30,096
Park Falls, WI, USA	2.83	2.40	2.74	2.99	0.0341	0.0320	0.0350	0.0355	121,956	255,080	184,828	128,076
Niwot Ridge, CO, USA	2.96	2.72	2.62	2.90	0.0353	0.0343	0.0338	0.0349	256,457	84,118	161,838	123,540
Ucluelet, BC, CAN	3.11	2.38	2.38	2.82	0.0364	0.0316	0.0336	0.0341	3,929	3,915	2,625	7,795
Fraserdale, ON, CAN	2.18	1.78	1.73	2.75	0.0269	0.0241	0.0275	0.0336	4,935	4,603	21,266	16,309

Section S8: Linear Regression

Table S8: Linear least-squares regression results of normalized D_5 as a function of the inverse of normalized OH, PBL, and wind speed for the 26 sites. All values are dimensionless. Normalization is through division by the July value of the variable at that location.

All 26 Sites		
Sites	Variable (Coefficient); variables with $p<0.1$ bolded	Adjusted R^2
Urban	OH^{-1} (-0.0039)	-0.019
Urban	**PBL^{-1} (0.48)**	0.333
Urban	**WS^{-1} (1.35)**	0.450
Urban	**$PBL^{-1} \cdot WS^{-1}$ (0.52)**	0.492
Urban	OH^{-1} (0.0068), PBL^{-1} (0.20), **WS^{-1} (1.11)**	0.489
Urban	OH^{-1} (0.0046), PBL^{-1} (-0.32), WS^{-1} (0.37), **$PBL^{-1} \cdot WS^{-1}$ (0.68)**	0.509
Urban	OH^{-1} (-0.0083), **$PBL^{-1} \cdot WS^{-1}$ (0.52)**	0.490
Urban	PBL^{-1} (-0.31), WS^{-1} (0.29), **$PBL^{-1} \cdot WS^{-1}$ (0.70)**	0.517
Urban	**PBL^{-1} (0.24)**, **WS^{-1} (1.01)**	0.496
Urban	OH^{-1} (-0.018), **PBL^{-1} (0.52)**	0.356
Urban	**OH^{-1} (0.017), WS^{-1} (1.46)**	0.471
Rural	OH^{-1} (0.0033)	-0.040
Rural	PBL^{-1} (-1.15)	0.039
Rural	**WS^{-1} (-7.27)**	0.104
Rural	$PBL^{-1} \cdot WS^{-1}$ (-1.27)	0.035
Rural	OH^{-1} (0.062), PBL^{-1} (-1.32), **WS^{-1} (-7.00)**	0.119
Rural	OH^{-1} (-0.022), **PBL^{-1} (-18.02)**, **WS^{-1} (-23.79)**, **$PBL^{-1} \cdot WS^{-1}$ (19.69)**	0.425
Rural	OH^{-1} (0.093) $PBL^{-1} \cdot WS^{-1}$ (-1.55)	0.014
Rural	**PBL^{-1} (-17.89)**, **WS^{-1} (-23.52)**, **$PBL^{-1} \cdot WS^{-1}$ (19.47)**	0.449
Rural	PBL^{-1} (-1.14), **WS^{-1} (-7.24)**	0.148
Rural	OH^{-1} (0.10), PBL^{-1} (-1.43)	0.020
Rural	OH^{-1} (-0.028), **WS^{-1} (-7.38)**	0.069

Table S9: Linear least-squares regression results of normalized D_5 as a function of the inverse of normalized OH, PBL, and wind speed excluding Canadian and Point Reyes sites. All values are dimensionless. Normalization is through division by the July value of the variable at that location.

Without Canadian and Point Reyes Sites		
Sites	Variable (Coefficient); variables with $p<0.1$ bolded	Adjusted R^2
Urban	OH^{-1} (-0.0023)	-0.021
Urban	**PBL^{-1} (0.48)**	0.342
Urban	**WS^{-1} (1.31)**	0.438
Urban	**PBL^{-1}·WS^{-1} (0.51)**	0.493
Urban	OH^{-1} (0.0081), PBL^{-1} (0.20), **WS^{-1} (1.07)**	0.484
Urban	OH^{-1} (0.0057), PBL^{-1} (-0.29), WS^{-1} (0.38), PBL^{-1}·WS^{-1} (0.64)	0.501
Urban	OH^{-1} (-0.0070) **PBL^{-1}·WS^{-1} (0.51)**	0.487
Urban	PBL^{-1} (-0.28), WS^{-1} (0.27), PBL^{-1}·WS^{-1} (0.66)	0.510
Urban	**PBL^{-1} (0.25)**, **WS^{-1} (0.96)**	0.491
Urban	OH^{-1} (-0.017), **PBL^{-1} (0.51)**	0.359
Urban	**OH^{-1} (0.019), WS^{-1} (1.44)**	0.465
Rural	OH^{-1} (0.042)	-0.029
Rural	PBL^{-1} (-0.14)	-0.076
Rural	WS^{-1} (-0.0088)	-0.100
Rural	PBL^{-1}·WS^{-1} (-0.25)	-0.064
Rural	OH^{-1} (0.053), PBL^{-1} (-0.28), WS^{-1} (-0.29)	-0.204
Rural	OH^{-1} (0.047), PBL^{-1} (0.94), WS^{-1} (0.67), PBL^{-1}·WS^{-1} (-1.56)	-0.366
Rural	OH^{-1} (0.052) PBL^{-1}·WS^{-1} (-0.35)	-0.068
Rural	PBL^{-1} (2.37), WS^{-1} (1.66), PBL^{-1}·WS^{-1} (-3.34)	-0.282
Rural	PBL^{-1} (-0.21), WS^{-1} (-0.41)	-0.183
Rural	OH^{-1} (0.054), PBL^{-1} (-0.23)	-0.077
Rural	OH^{-1} (0.044), WS^{-1} (0.21)	-0.139

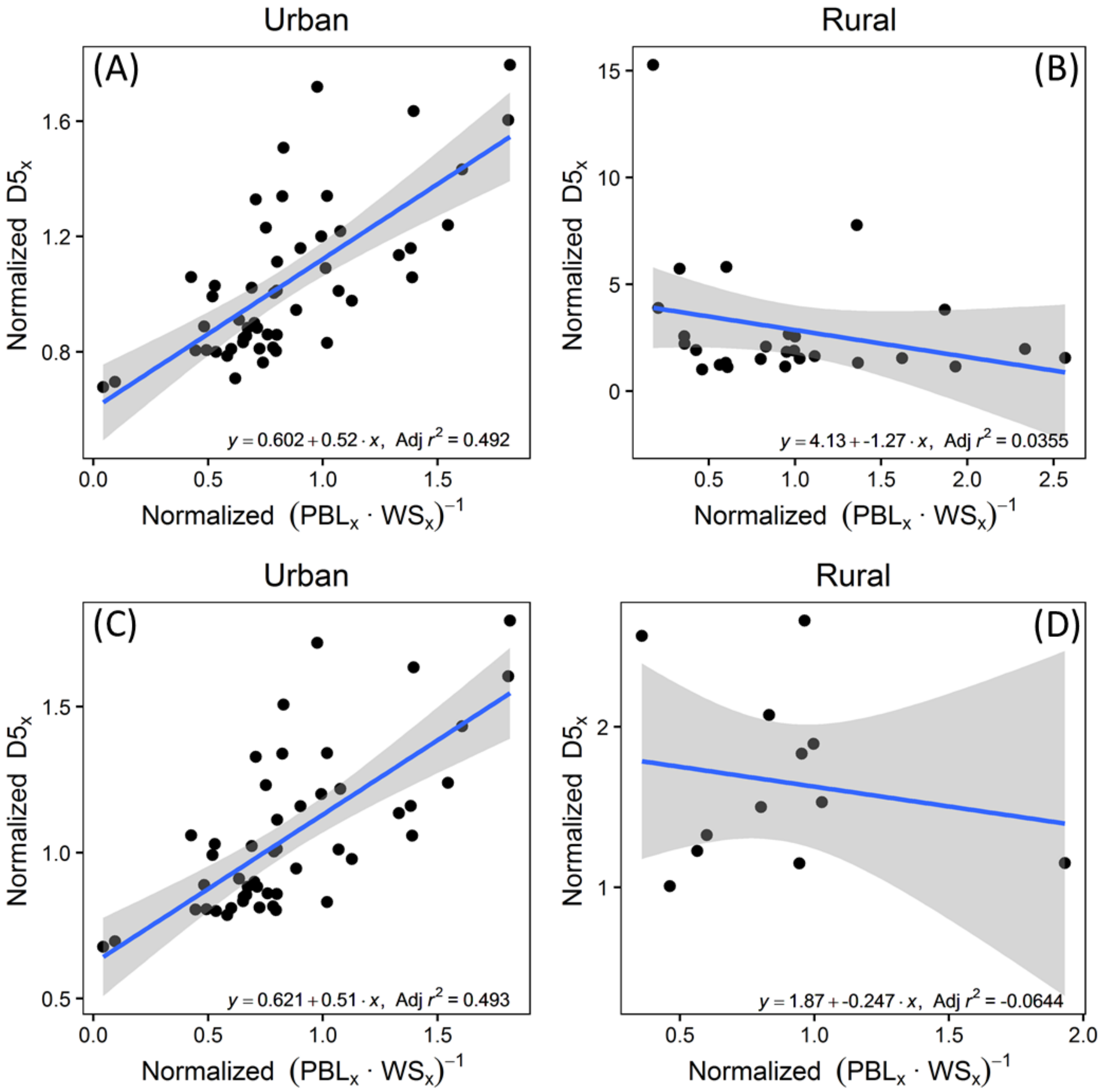

Figure S7: Linear least-squares regression fit of monthly averaged normalized D_5 concentrations versus the inverse of normalized boundary layer height and normalized wind speed for all 26 analyzed sites urban (A) and rural (B) sites. The same sites excluding Canadian and Point Reyes, CA locations are also shown for urban (C) and rural (D) sites. Normalization is through division by the July value of the quantity.

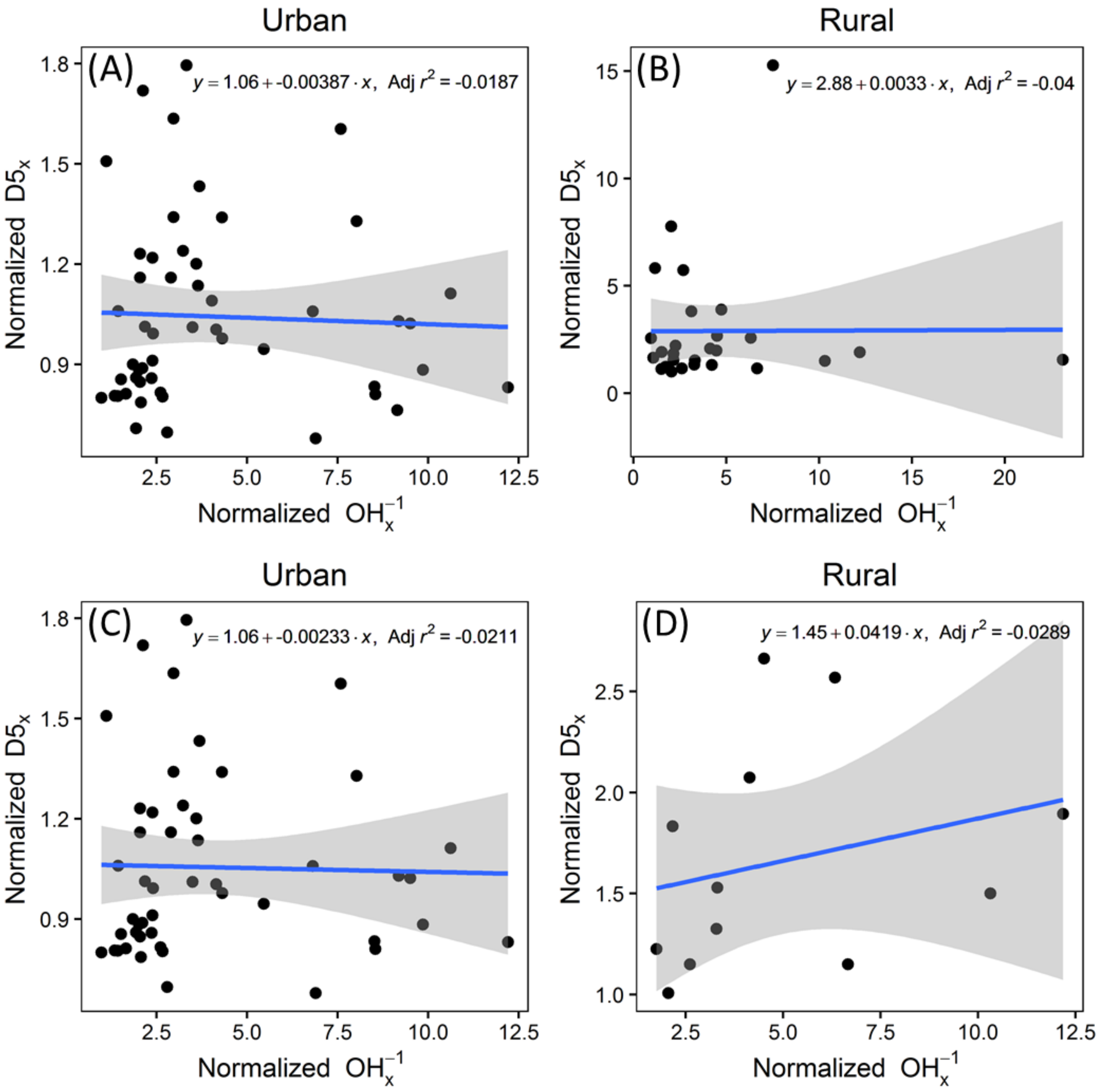

Figure S8: Linear least-squares regression fit of monthly averaged normalized D_5 concentrations versus the inverse of normalized OH concentration for all 26 analyzed sites urban (A) and rural (B) sites. The same sites excluding Canadian and Point Reyes, CA locations are also shown for urban (C) and rural (D) sites. Normalization is through division by the July value of the quantity.

Section S9: Midwest Model Performance

Table S10: Model performance to Yucuis et al. (2013) Midwest sites. Fractional bias can range from -2 to +2 while fractional error ranges from 0 to +2.

	Chicago			**Cedar Rapids**			**West Branch**		
	D_4	D_5	D_6	D_4	D_5	D_6	D_4	D_5	D_6
CMAQ Mean (ng m^{-3})	41.2	169	7.61	4.36	17.4	0.777	2.28	8.83	0.389
Yucuis et al. Mean (ng m^{-3})	56.3	232	10.1	18.9	47.9	5.56	9.94	20.1	1.65
Measured to Model Factor	1.37	1.37	1.33	4.33	2.75	7.16	4.36	2.27	4.23
Frac. Bias	-0.309	-0.313	-0.281	-1.25	-0.933	-1.51	-1.25	-0.777	-1.23
Frac. Error	0.309	0.313	0.281	1.25	0.933	1.51	1.25	0.777	1.23
Error	-15.1	-62.7	-2.49	-14.5	-30.5	-4.79	-7.66	-11.2	-1.26
% Relative Error	-26.8	-27.1	-24.6	-76.9	-63.6	-86.0	-77.1	-56.0	-76.4

$$Frac.Bias = \left(\frac{m-o}{\frac{m+o}{2}}\right)$$

$$Frac.Error = \left(\frac{|m-o|}{\frac{m+o}{2}}\right)$$

$$Error = m - o$$

$$\%\ Relative\ Error = \left(\frac{m-o}{o}\right) \times 100$$

Section S10: GAPS Model Performance

Table S11: Measurement and model fractional bias, fractional error, and absolute error. Measurement concentrations are from Genualdi et al. (2011). Fractional bias can range from -2 to +2 while fractional error can range from 0 to +2.

	CMAQ D_4			**CMAQ D_5**			**CMAQ D_6**			**BETR D_5**			**DEHM D_5**		
Site	**Frac. Bias**	**Frac. Error**	**Error**	**Frac. Bias**	**Frac. Error**	**Error**	**Frac. Bias**	**Frac. Error**	**Error**	**Frac. Bias**	**Frac. Error**	**Error**	**Frac. Bias**	**Frac. Error**	**Error**
Bratt's Lake, SK	-0.145	0.145	0.352	1.24	1.24	6.25	0.114	0.114	0.0376	0.383	0.383	0.900	-0.303	0.303	0.500
Whistler, BC	-1.89	1.89	43.7	-0.354	0.354	1.93	-1.56	1.56	1.31	-1.01	1.01	4.30	-0.485	0.485	2.50
Downsview, ON	0.591	0.591	9.23	0.390	0.390	26.6	-0.518	0.518	2.55	-1.58	1.58	48.5	-0.651	0.651	27.0
Fraserdale, ON	-1.45	1.45	4.53	0.0164	0.0164	0.0313	-1.52	1.52	0.354	0.417	0.417	1.00	0.100	0.100	0.200
Ucluelet, BC	-1.93	1.93	43.2	-0.992	0.992	4.84	-1.71	1.71	1.11	-	-	-	-1.07	1.07	5.10
Point Reyes, CA	-0.0195	0.0195	0.0813	0.848	0.848	9.56	0.215	0.215	0.137	-1.38	1.38	5.30	0.667	0.667	6.50
Sydney, FL	0.613	0.613	4.77	-0.674	0.674	41.3	-0.753	0.753	2.19	-1.71	1.71	75.5	-1.38	1.38	67.0
Groton, CT	0.969	0.969	7.32	-0.745	0.745	52.1	-1.45	1.45	10.1	-	-	-	-1.15	1.15	70.0
Mean	-0.407	0.950	14.1	-0.0334	0.658	17.8	-0.897	0.980	2.22	-0.812	1.08	22.6	-0.534	0.726	22.4
Median	-0.0825	0.791	6.05	-0.169	0.709	7.91	-1.10	1.10	1.21	-1.19	1.19	4.80	-0.568	0.659	5.80

$$Frac.\,Bias = \left(\frac{m-o}{\frac{m+o}{2}}\right)$$

$$Frac.\,Error = \left(\frac{|m-o|}{\frac{m+o}{2}}\right)$$

$$Error = |m-o|$$

Section S11: Vertical Concentrations

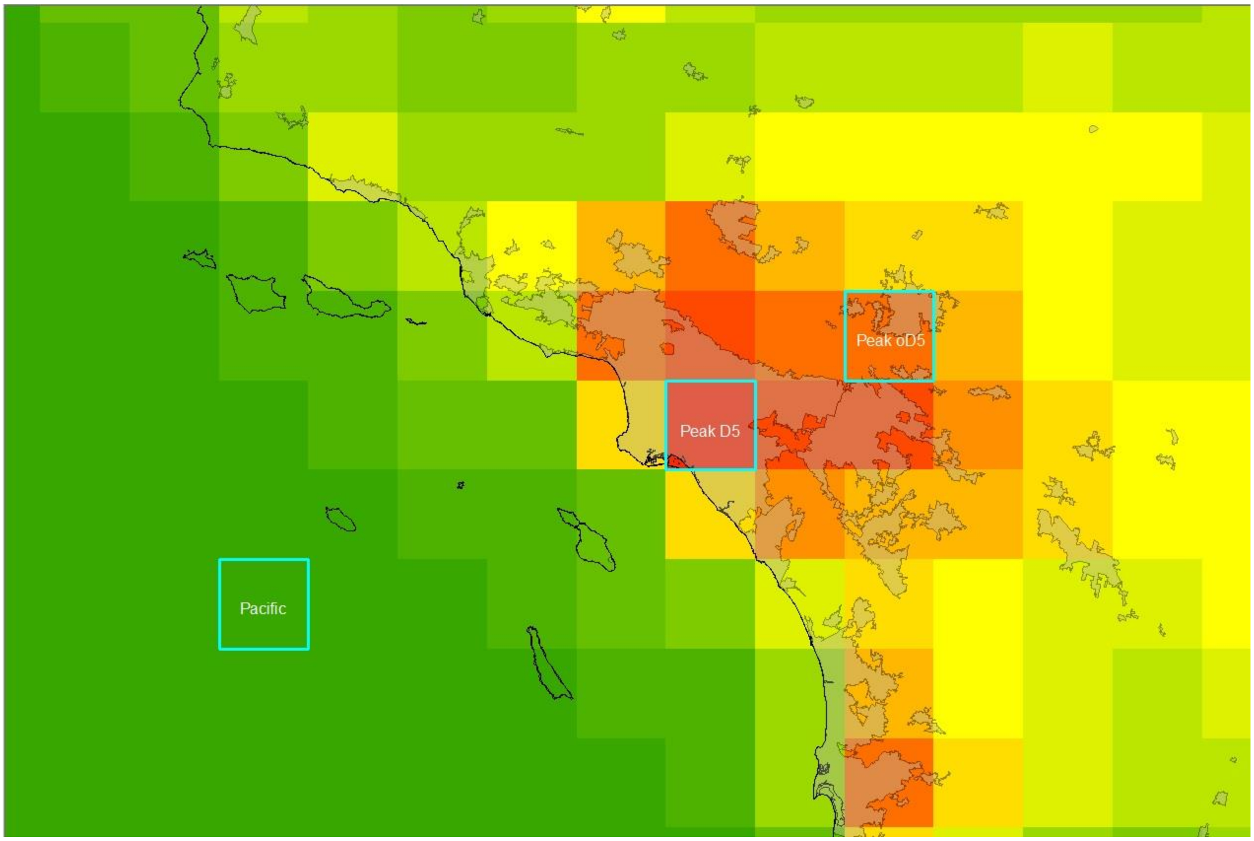

Figure S9: Grid cell locations for vertical analysis in Los Angeles area.

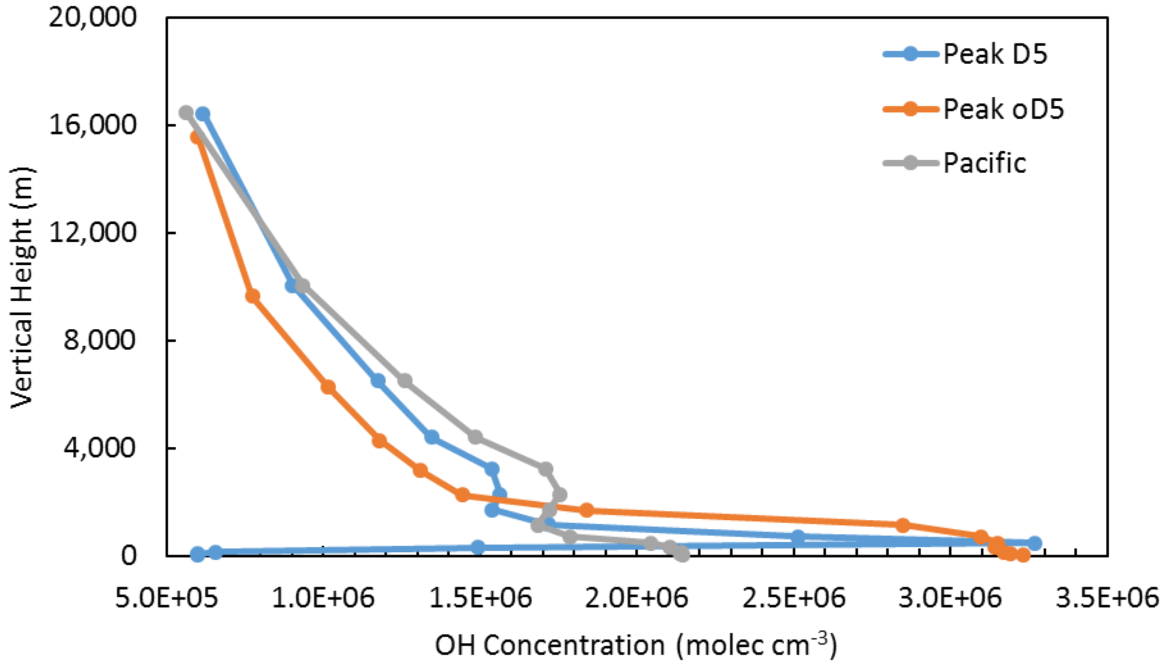

Figure S10: Monthly averaged modeled vertical OH profiles for grid cells near Los Angeles. Grid cells refer to the location of maximum July D_5, maximum July o-D_5, and a grid cell over the Pacific Ocean.

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