

Supplemental Information

Sensitivity of ambient atmospheric formaldehyde and ozone to precursor species and source types across the U.S.

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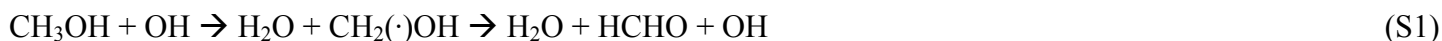
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1.0 Atmospheric formation of formaldehyde from other VOCs

There are multiple routes for secondary photochemical formation of HCHO, with the most important routes include 1.) ozonolysis of alkenes after fragmentation of the biradical Criegee Intermediate¹, and reactions of 2.) alkyl, 3.) alkoxy and 4.) alkylperoxy radicals.

Alkenes react with O₃ through addition of O₃ to the double bond, forming an energy rich primary ozonide, which rapidly fragments.¹ For terminal double bonds, one channel forms HCHO and the other forms the biradical Criegee Intermediate, which can stabilize or decompose, possibly also forming HCHO. Propene, for example, yields 65-78% HCHO through ozonolysis.¹

Rapid unimolecular decomposition of methyl radicals with an alcohol, hydroperoxide, or nitrate group can produce HCHO. These radicals can be formed after photolysis (i.e. from glyoxal), decomposition of an alkoxy radical, or H abstraction by OH. When methanol reacts with OH, it rapidly forms HCHO:



The reaction of nitrate radicals ($\text{NO}_3\cdot$) with alkenes can form a methyl radical after decomposition of the nitrooxy alkoxy radical (most likely following reaction with other peroxy radicals), which rapidly decays to HCHO and NO_2 .¹

Alkoxy radicals are ubiquitous in atmospheric chemistry and can react with oxygen (O_2), decompose by bond fission, or isomerize. The fate depends on number of carbons, number and length of branches, substituents and radical location. Methyl alkoxy radicals react with oxygen to form HCHO:²

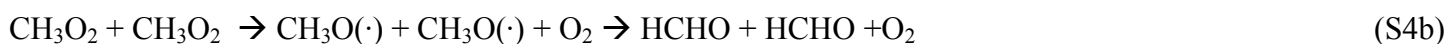


When alkoxy radicals undergo unimolecular decomposition, a carbonyl (which could be HCHO) and alkyl radical are formed. The decomposition rate depends on substituents bonded to the carbons where the structure breaks, and their position relative to the carbon bearing the radical oxygen.³ If either carbon contains a carbonyl, hydroxy, or hydroperoxide functionality, decomposition is likely, i.e. the alkoxy radical formed from acetone can decompose to form HCHO:



Isomerization usually dominates for larger molecules² but radicals formed after multiple isomerizations may favor decomposition.

Methyl peroxy radical reaction with hydroperoxy radical (HO_2) can also form HCHO, as can self and cross-reactions involving methyl peroxy radicals, i.e. methylperoxy radical self reaction produces HCHO through both the reaction channel producing closed-shell products and that producing radicals:²⁰



Every ambient VOC that reacts with OH either rapidly fragments or produces a peroxy radical. In urban environments, these radicals react with NO forming alkoxy radicals.⁴ In areas with lower NO_x concentrations, peroxy radical reactions with other peroxy radicals and HO_2 can be important – one recent estimate quantifies these pathways at 15-58% of total peroxy radical fate.⁵ Thus, almost every VOC can produce formaldehyde, so

our ability to characterize the atmospheric chemistry of formaldehyde is representative of our understanding of overall atmospheric chemistry. Notably, biogenic sources emit VOCs with multiple reactive carbons (such as isoprene with 5 carbons), many with unsaturated bonds that react rapidly with O₃, OH and nitrate radical (NO₃), producing HCHO either in first-generation reactions or through subsequent reactions of products (such as methylvinyl ketone and methacrolein).

2.0 Results: Concentrations, evaluation, and sensitivities of HCHO and O₃ to VOC and NO_x

The monthly averaged concentrations of HCHO are shown in Figure S1 and a summary of the sensitivity of HCHO and O₃ to biogenic versus total VOC, averaged over the month and the country, is presented in Table S1. Scatter plots of model predictions for HCHO compared to observations, based on daily averaged measurements, are shown in Figure S2. Here, the sites located in the Southeastern US, where isoprene concentrations are high, are highlighted, but show no clear difference in the performance of the model. In Figure S3, the performance of the model versus observations is shown for O₃, based on the 8-hr daily maximum value for each day of the month.

Further examination of the sensitivities is shown in Figures S4 and S5. The relative sensitivities of the same group of VOCs is very different between HCHO, O₃ and acetaldehyde. A comparison of regional sensitivities is presented in Figures S6 and S7. While there are small differences between regions, they generally show similar contributions to the same set of VOCs.

Tables and Figures

Table S1. Total VOC and NO_x sensitivities, hourly values in ppb, averaged over the month.

Sensitivity of:	HCHO		O ₃	
	July	January	July	January
Biogenic NMHC	9.00	0.49	8.71	1.90
Total NMHC	9.77	1.67	11.50	16.13
Total NO _x	1.64	-0.24	40.12	-32.63
NMHC/NO _x	5.96	-7.03	0.29	-0.49
biogHC/total NMHC	0.92	0.29	0.76	0.12

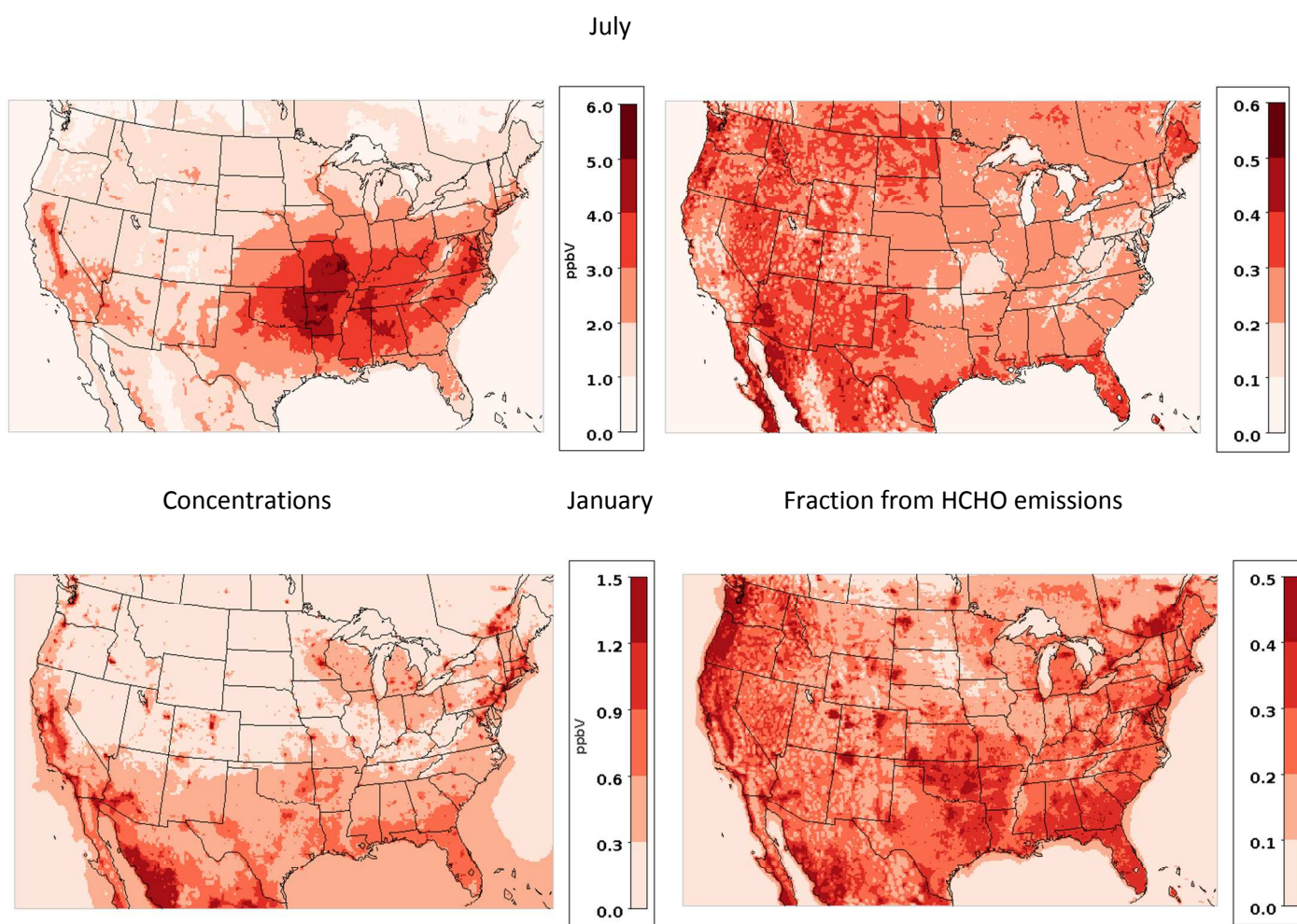


Figure S1. Spatial distribution of HCHO concentrations (left) and fraction of concentration due to primary emissions (right). Plots are monthly averages for July (top) and January (bottom).

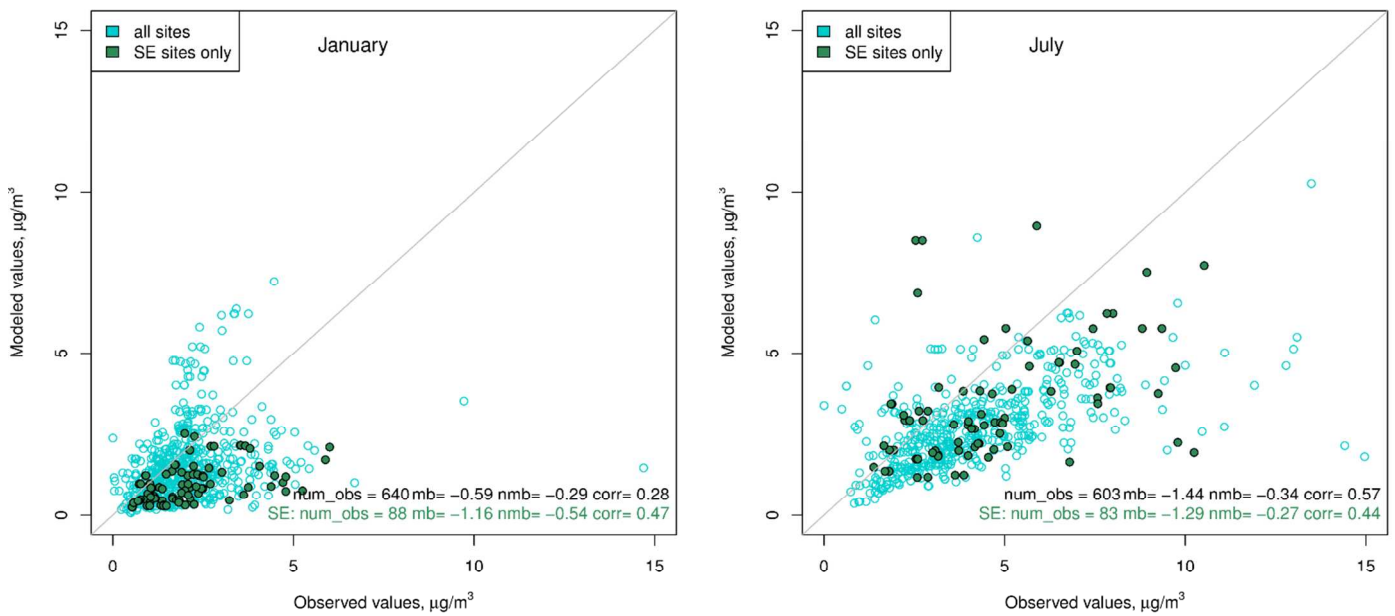


Figure S2. Comparison of daily-averaged observations of formaldehyde with model predictions for January (left) and July (right)

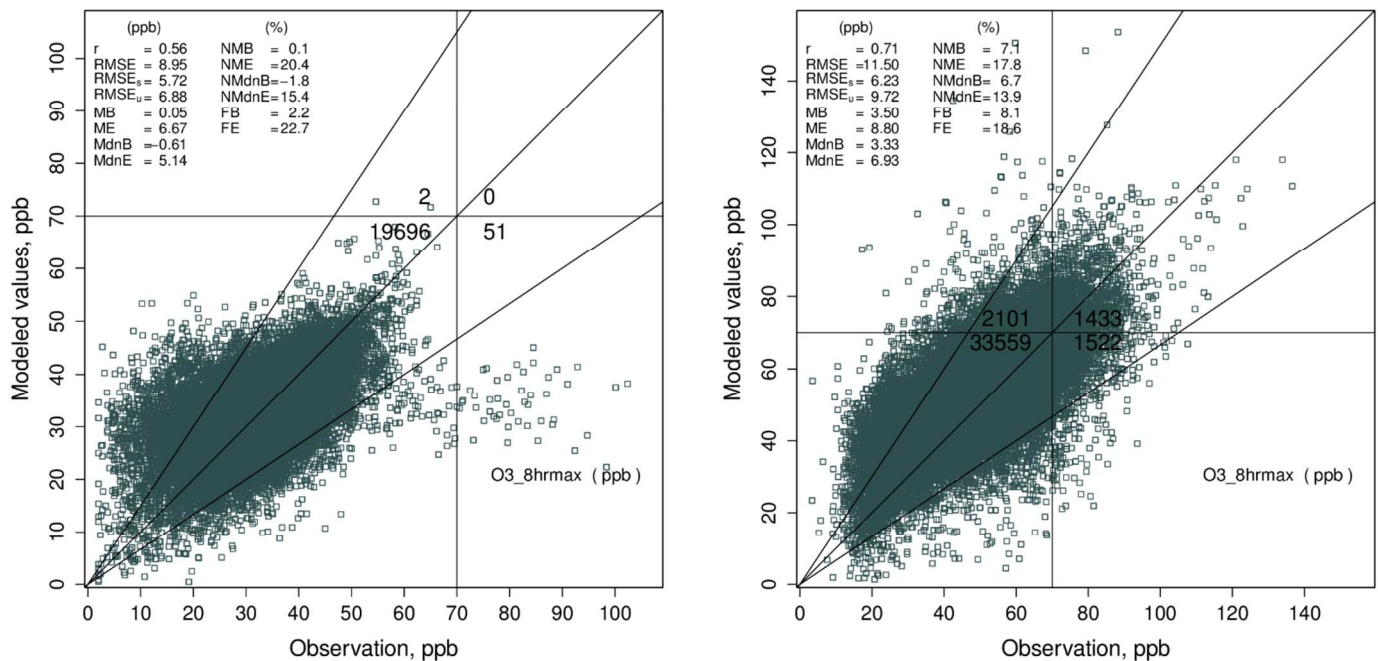


Figure S3. Comparison of modeled and measured O₃ concentrations, 8-hr max average, for January (left) and July (right).

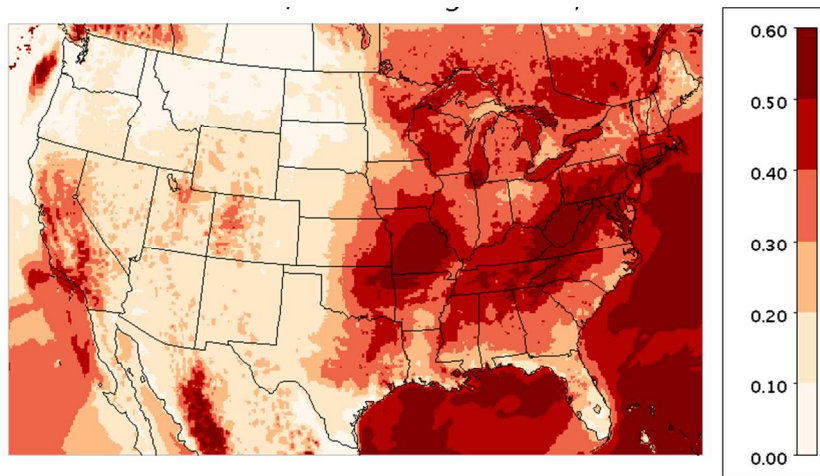


Figure S4. Spatial distribution of the HCHO sensitivity to isoprene relative to the total biogenic VOC sensitivity, average over July.

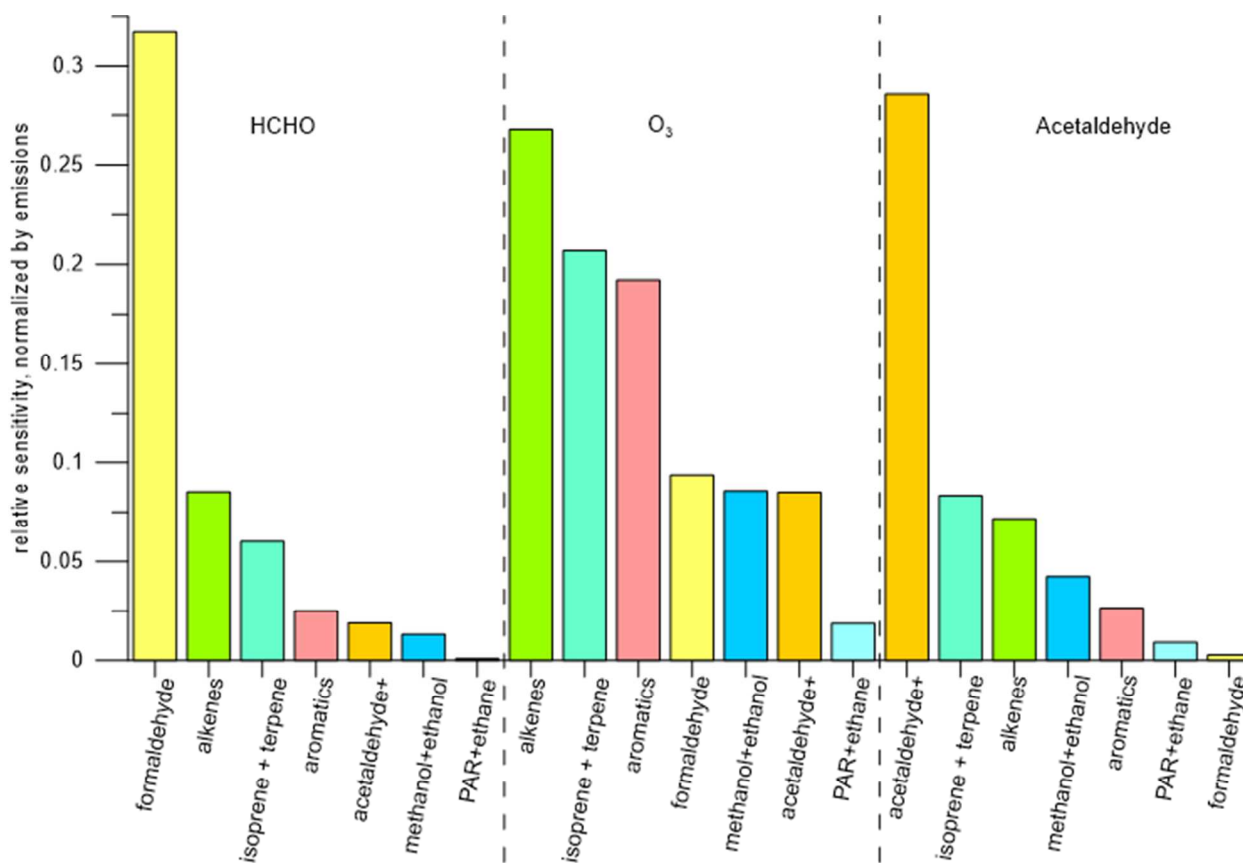


Figure S5. Sensitivity of HCHO, O₃ and acetaldehyde to VOC model species relative to the total anthropogenic emissions. The sensitivities presented earlier are normalized by dividing by national emission rates in moles/month, multiplied by 1.e9.

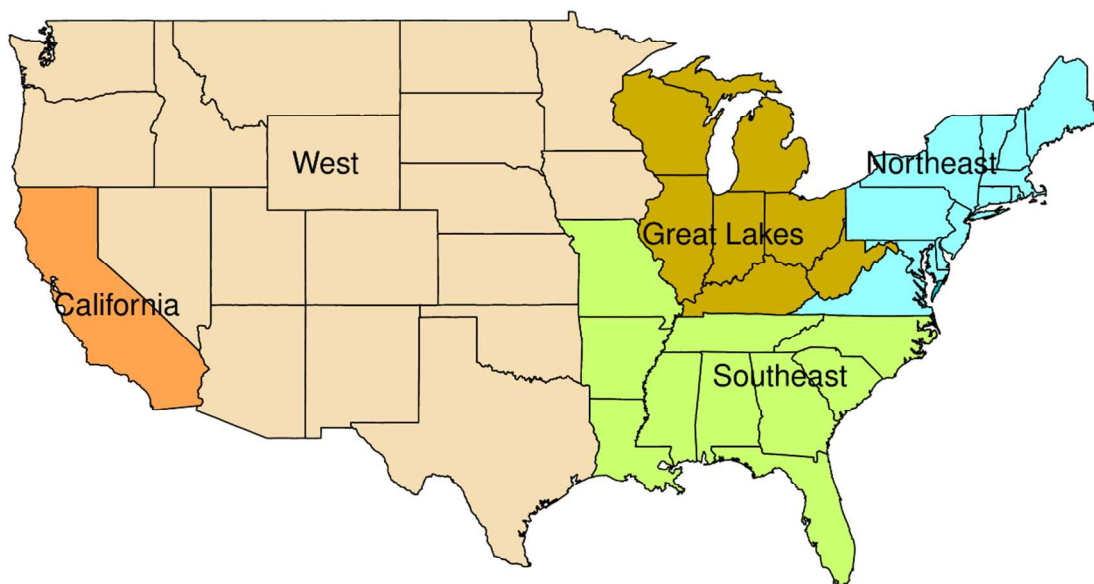


Figure S6. Identification of regions of the US with similar HCHO concentrations and sensitivity for extended regional analysis of sensitivity differences.

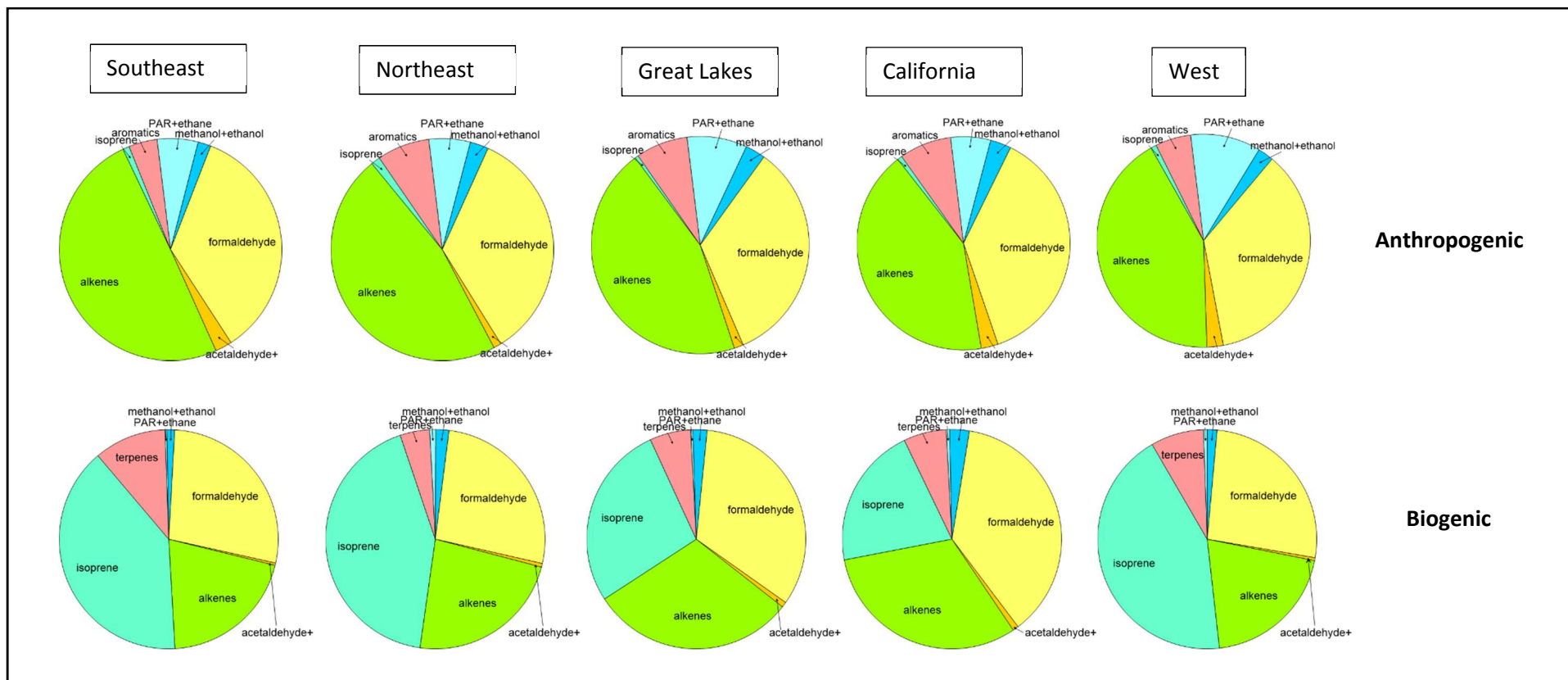


Figure S7. Relative distribution of regional HCHO sensitivity to precursors from different VOCs, for both anthropogenic VOC emissions (top) and biogenic VOC emissions (bottom) for the month of July, 2011. Regions are as shown in Figure S4.

REFERENCES

- (1) Calvert, J.G., Atkinson, R., Kerr, J.A., Madronich, S., Moortgat, G.K., Wallington, T.J., Yarwood, G., 2000. The mechanisms of atmospheric oxidation of the alkenes. Oxford University Press, New York/Oxford.
- (2) Calvert, J.G.; Orlando, J.J.; Stockwell, W.R.; Wallington, T.J. *The Mechanisms of Reactions Influencing Atmospheric Ozone*; Oxford University Press: New York, NY, 2015.
- (3) Vereecken, L., Peeters, J., 2009. Decomposition of substituted alkoxy radicals – part I: A generalized structure-activity relationship for reaction barrier heights. *Phys. Chem. Chem. Phys.*, 11, 9062-9074.
- (4) Orlando, J.J.; Tyndall, G.S. Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance. *Chem. Soc. Rev.* **2012**, 41, 6294-6317.
- (5) Valin, L.C.; Fiore, A.M.; Chance, K.; González Abad, G. The role of OH production in interpreting the variability of CH₂O columns in the southeast U.S. *J. Geophys. Res.: Atmos.* **2016**, 121, 478-493.