

Contribution of Isoprene Epoxydiol to Urban Organic Aerosol: Evidence from Modeling and Measurements

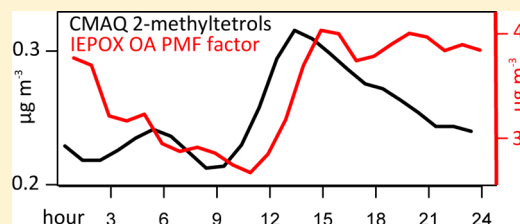
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S Supporting Information

ABSTRACT: In a region heavily influenced by anthropogenic and biogenic atmospheric emissions, recent field measurements have attributed one-third of urban organic aerosol by mass to isoprene epoxydiols (IEPOX). These aerosols arise from the gas-phase oxidation of isoprene, the formation of IEPOX, the reactive uptake of IEPOX by particles, and finally the formation of new compounds in the aerosol phase. Using a continental-scale chemical transport model, we find a strong temporal correspondence between the simulated formation of IEPOX-derived organic aerosol and these measurements. However, because only a subset of isoprene-derived aerosol compounds have been specifically identified in laboratory studies, our simulation of known IEPOX-derived organic aerosol compounds predicts a mass 10-fold lower than the field measurements, despite abundant gas-phase IEPOX. Sensitivity studies suggest that increasing the effective IEPOX uptake coefficient and including aerosol-phase reactions that lead to the addition of functional groups could increase the simulated IEPOX-derived aerosol mass and account for the difference between the field measurements and modeling results.



INTRODUCTION

Submicrometer diameter particles suspended in the atmosphere, known as aerosols, affect human health and climate change. Aerosols are composed of a mixture of inorganic salts and mixed-phase organic compounds. Sources of aerosol emissions include wind-blown dust, ocean spray, wildfires, and combustion of fossil fuels. However, aerosols are also formed from photochemical processes. Gas-phase organic compounds are oxidized and can either nucleate to form new particles or be absorbed onto the surface of existing particles. This secondary organic aerosol (SOA) is a large fraction of the global burden. Despite its importance, SOA formation is not completely understood,¹ and simulations of regional and global SOA underestimate the concentration, fail to capture the temporal variability, and incompletely attribute the sources.²

Isoprene is thought to play an important role in global SOA formation.³ With more than 600 Tg year⁻¹ globally, isoprene is the most abundant non-methane organic compound emitted.⁴ The gas-phase oxidation products of isoprene include epoxydiols (IEPOX),⁵ which either react with hydroxyl radical in the gas phase⁶ or react in particles to form a variety of compounds in the aerosol phase.^{7–9} One class of aerosol-phase compounds, 2-methyltetrols, have been uniquely associated with isoprene^{10,11} and later with IEPOX.¹² However, in these controlled laboratory experiments, these tetrols comprise just a fraction of the total aerosol mass formed, and most of the aerosol products are not known.

While controlled laboratory experiments have clarified the process by which IEPOX SOA forms,^{11–13} a remaining question is the extent to which these compounds contribute to ambient aerosols. Recent ambient measurement approaches employing high-time resolution mass spectrometry such as aerosol mass spectrometry (AMS) and aerosol chemical speciation monitoring (ACSM) have attributed a significant fraction of ambient aerosol mass to isoprene.^{14–16} By applying positive matrix factorization (PMF),¹⁷ we found 33% of urban organic aerosol in Atlanta, GA, to have a characteristic mass spectrum that closely resembles that from laboratory experiments of IEPOX aerosol (IEPOX-OA)¹⁶ and was correlated with known indicators of IEPOX-derived aerosol, including sulfate and 2-methyltetrols. If the IEPOX-OA is indeed uniquely IEPOX-derived aerosol, it provides a high-temporal resolution method for observing the contribution of isoprene emissions to aerosol production.

We employ the Community Multiscale Air Quality (CMAQ version 5.0.1) model with isoprene updates to evaluate the link among isoprene, IEPOX, and IEPOX-OA. Recent CMAQ modeling has shown that ambient measurements of 2-methyltetrols can be simulated by reactive uptake of IEPOX

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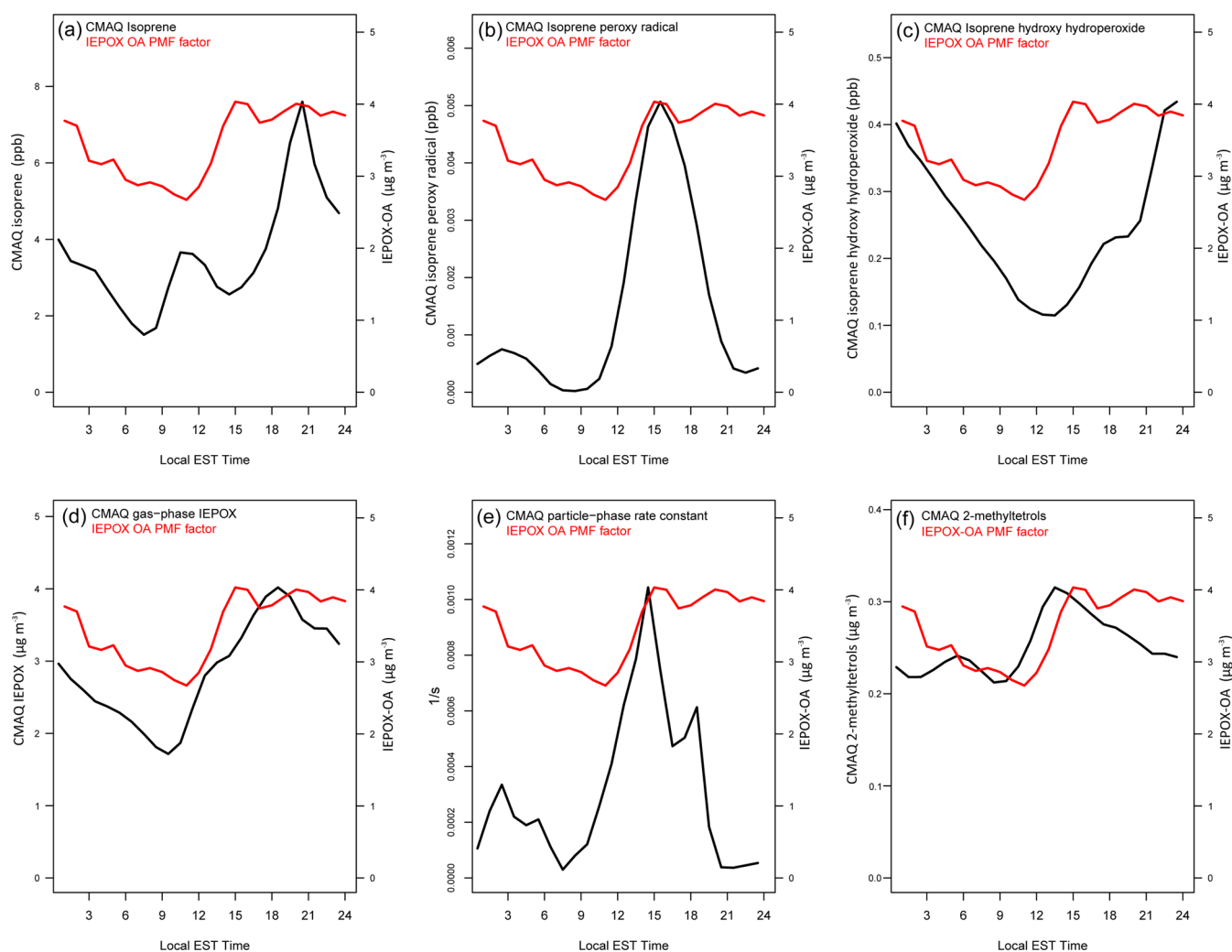


Figure 1. Strong correspondence between CMAQ-simulated 2-methyltetrols (f) and the ACSM IEPOX-OA factor (red) that can be traced to the diurnal variability in the transformation of isoprene (a) to its peroxy radical (b) and peroxide (c), which in turn forms IEPOX (d). The simulated rate of reactive uptake (e) peaks during the time of the maximal increase in the observed IEPOX-OA factor.

to aerosols.¹⁸ We will use this detailed representation of isoprene photochemistry and aerosol formation via reactive uptake to determine if these processes governing IEPOX SOA formation are consistent with the observed variability of IEPOX-OA and assess the contribution of IEPOX to SOA.

METHODS

ACSM Ambient Observations. The Aerosol Chemical Speciation Monitor (ACSM)¹⁹ collected aerosol composition data from August 8 to September 14, 2011, at 30 min time resolution at the Jefferson Street (33.77753°N 84.41666°W) monitoring station, part of the Southeastern Aerosol Research and Characterization (SEARCH) network, in Atlanta, GA, in the southeastern United States.¹⁶ This urban setting is in a region known for high levels of biogenic isoprene and anthropogenic emissions. The measurements were fully described by Budisulistiorini et al.,¹⁶ but briefly, the ACSM provides online, continuous chemical measurements of non-refractory particulate matter with a diameter of $<1 \mu\text{m}$ (PM_{10}). PMF analysis was performed on the organic mass fraction. The best fit was a four-factor solution that included three frequently found factors for low volatility, semivolatile, and hydrocarbon-like organic aerosol (SV-OOA, LV-OOA, and HOA,

respectively). However, a fourth unique factor, IEPOX-OA, was also identified. The time series of IEPOX-OA is correlated with simultaneous measurements of sulfate ($r^2 = 0.48$) and 24 h integrated filter-based measurements of 2-methyltetrols ($r^2 = 0.59$). The mass spectrum is correlated with IEPOX SOA from laboratory experiments ($r^2 = 0.74$).

CMAQ Simulations. CMAQ is a grid-based photochemical model that explicitly simulates the emission, advection, dispersion, gas-phase chemistry, aerosol thermodynamics, and deposition of atmospheric compounds and has been shown to accurately simulate sulfate²⁰ and primary organic aerosol.²¹ In this work, CMAQ simulations include detailed isoprene photochemistry²² as well as formation of isoprene SOA via reactive uptake of epoxides and absorptive partitioning of semivolatile isoprene oxidation products.¹⁸ While the IEPOX SOA particle-phase reaction rates are uncertain, a series of sensitivity tests were conducted by Pye et al.,¹⁸ and parameters that lead to the best agreement with 2-methyltetrol observations were used in this simulation [IEPOX hydrolysis rate constant of $0.011 \text{ M}^{-1} \text{ s}^{-1}$ (see the Supporting Information of ref 18)]. Epoxide aerosol formation is modeled as a reactive uptake process governed by an uptake coefficient calculated on the basis of the Henry's law coefficient (solubility of IEPOX in

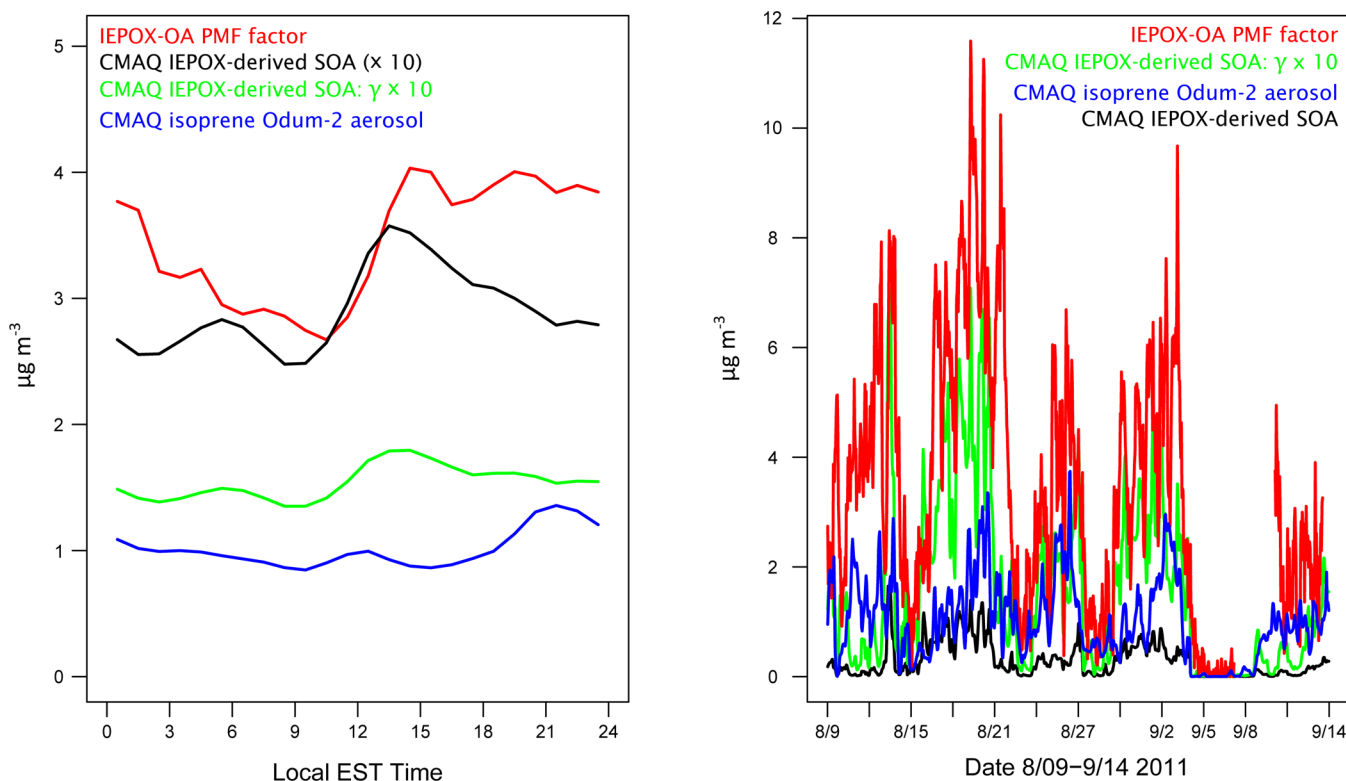


Figure 2. CMAQ-simulated IEPOX-derived SOA and ACSM IEPOX-OA factor, shown as the diurnal average (left) and time series (right). The diurnal average values for the CMAQ-simulated IEPOX SOA have a stronger correlation with the observations than isoprene SOA calculated using an Odum 2-product, semivolatile SOA approach. Assuming a 10-fold increase in γ_{IEPOX} (green line), the CMAQ-simulated IEPOX-derived SOA is within a factor of 2 of the ACSM IEPOX-OA factor. Note that in the left plot, the CMAQ-simulated IEPOX SOA concentration (black line) is multiplied by a factor of 10 to better show the temporal similarities.

water) and particle-phase composition (including the concentration of acids and nucleophiles). Additionally, isoprene SOA production by the absorptive partitioning of semivolatile isoprene oxidation products is still included for comparison.

To match the measurement period, we simulate from July 27 to September 14, 2011, with the first 12 days discarded as model spin-up. To capture regional influences, the modeling domain includes a large portion of North America covering the contiguous United States, southern Canada, and northern Mexico at a 12 km horizontal resolution and 24 vertical layers from the surface to 50 hPa.

Emissions from large power plants are included at hourly time resolution based on facility-level Continuous Emission Monitors. Motor vehicle emissions are simulated using MOVES,²³ which includes year specific estimates of vehicle miles traveled, fleet characteristics, and meteorological conditions. Emissions of biogenic volatile organic compounds, including isoprene, are calculated online using BEIS²⁴ using the same meteorological conditions as CMAQ. All other emissions are from the National Emission Inventory.²⁵ Meteorological data are from the Weather Research Forecasting (WRF) model, nudged to reanalysis fields to reduce error, and converted to CMAQ inputs.²⁶ Hourly chemical boundary conditions are extracted from a GEOS-Chem global simulation for the same time period.²⁷

Specifically, our analysis will examine the correlation between the detailed CMAQ simulation of 2-methyltetrols and the IEPOX-OA factor. We will also look at correlations with other compounds, including semivolatile isoprene SOA, to determine if IEPOX is the best explanation for the IEPOX-OA factor.

Finally, given that 2-methyltetrols are only some of the compounds that contribute to IEPOX-OA, we will examine additional model processes to determine if high concentrations of observed IEPOX-OA can be explained by IEPOX reactive uptake.

RESULTS AND DISCUSSION

Gas-phase oxidation and particle-phase reactions are two key components that drive the diurnal variation of IEPOX-OA production. Pye et al.¹⁸ gave a more detailed description of the reactive uptake pathway mechanism in CMAQ, but a brief overview is included here. Gas-phase IEPOX is a tertiary oxidation product of isoprene and is most abundant during the daytime when the greatest level of isoprene oxidation occurs (Figure 1a). A decline in isoprene concentrations is seen corresponding to an increase in the production of the first isoprene oxidation product, the isoprene peroxy radical (Figure 1b). The peroxy radical then reacts with hydroperoxy radicals to form isoprene hydroxy hydroperoxides (Figure 1c), which almost immediately and completely oxidize to gas-phase IEPOX (Figure 1d).

The gas-phase IEPOX uptake coefficient, γ_{IEPOX} , governs the transfer of IEPOX to the aerosol phase. It is calculated using $k_{\text{IEPOX}}^{\text{particle}}$, the reaction rate, in the particle, of IEPOX with nucleophiles such as water, sulfate, nitrate, 2-methyltetrols, organosulfates, and organonitrates. Please see the Supporting Information for equations¹⁸ defining $k_{\text{IEPOX}}^{\text{particle}}$. These reactions yield 2-methyltetrols, organosulfates, organonitrates, tetrol dimers, IEPOX organosulfate dimers, and IEPOX organonitrate dimers. In CMAQ, concentrations of 2-methyltetrols, organo-

sulfates, organonitrates, and a lumped dimer species are calculated individually. Here, we refer to these compounds as CMAQ-simulated IEPOX-derived SOA. The concentrations of aerosol accumulation mode water, H^+ , sulfate, and nitrate are calculated by CMAQ using ISORROPIA-II,²⁷ and the $k_{IEPOX}^{particle}$ rates are calculated using laboratory- and structure-derived third-order rate constants from ref 6.

Comparing panels d–f of Figure 1 shows that the maximal production of the most abundant CMAQ-simulated IEPOX-derived SOA, 2-methyltetrols, occurs coincidentally with the maximal $k_{IEPOX}^{particle}$ (Figure 1e) and a slight reduction in IEPOX indicating gas-to-particle conversion (Figure 1d). This is evident both in the early morning when CMAQ predicts a slight increase in the level of 2-methyltetrols and around noon when maximal production occurs. Predicted 2-methyltetrol concentrations exhibit a diurnal structure very similar to that of the IEPOX-OA measurements ($r = 0.531$) and have a stronger correlation with IEPOX-OA than simulated isoprene-derived absorptive-partitioning OA ($r = 0.488$) (Figure 2, blue line), as well as other contributors to organic aerosol (table of the Supporting Information). However, while CMAQ simulates abundant production of gas-phase IEPOX (Figure 1d), the level of CMAQ-simulated IEPOX-derived SOA is 10-fold lower than that of ACSM IEPOX-OA (Figure 2, black line), possibly indicating insufficient aerosol uptake in the model. Removal processes of IEPOX SOA include deposition and oligomerization, but these do not account for the large underprediction between model and measured concentrations.

The possible explanations for the underestimate of IEPOX-OA by CMAQ simulations are (i) insufficient production of known IEPOX-OA constituents and (ii) missing production of unidentified IEPOX-OA compounds. For known IEPOX-OA compounds, 2-methyltetrols are thought to be the most abundant.²⁸ Prior work¹⁸ has shown that in cases in which chemically resolved filter-based measurements are available, CMAQ systematically overpredicts 2-methyltetrol measurements by a factor of 2. While acidity can strongly enhance IEPOX-OA production,^{29,30} CMAQ-simulated aerosol acidity concentrations were not significantly lower than the acidity calculated from the ACSM ion measurements. Additionally, aerosol water, a key ingredient in IEPOX uptake, is abundant and is not considered to be a limiting factor in converting IEPOX to 2-methyltetrol. Therefore, insufficient production of known IEPOX-OA compounds is not a likely explanation for the 10-fold underprediction of IEPOX-OA.

The second explanation is IEPOX reactive uptake processes that yield compounds whose structures are not known. To examine this explanation, we conducted a sensitivity simulation in which γ_{IEPOX} representing particle-phase IEPOX reaction with water, sulfate, and nitrate, was increased by a factor of 10 to account for an unknown IEPOX aerosol species. Simulated IEPOX SOA in the sensitivity simulation is the lump sum of 2-methyltetrols, organosulfates, and organonitrates. Dimer processes were removed in the sensitivity experiment, and although this causes a slight decrease in the maximal $k_{IEPOX}^{particle}$, γ_{IEPOX} increases significantly because of the 10-fold increase and the effect due to the decreased $k_{IEPOX}^{particle}$ is negligible. Ultimately, increasing the uptake coefficient significantly increases the amount of IEPOX aerosol predicted in CMAQ (Figure 2). As a consequence, gaseous IEPOX decreases slightly (from 2.86 to 2.56 $\mu g m^{-3}$ on average), but the amount depleted is very small in comparison to the 5-fold increase in CMAQ-simulated IEPOX derived SOA, because (i) much of the additional

aerosol mass can be attributed to the addition of a functional group on the IEPOX-derived aerosol compounds and (ii) the IEPOX in the aerosol phase is protected from gas-phase loss processes such as reaction with OH.²⁸ In Figure 2, base case concentrations of the sum of CMAQ-simulated IEPOX-derived SOA are shown multiplied by a factor of 10 (black line). The sum of CMAQ-simulated IEPOX-derived SOA in the sensitivity case ($\gamma_{IEPOX} \times 10$) is colored green. CMAQ-simulated IEPOX-derived aerosol in the sensitivity simulation is 5 times greater than the base case and is within a factor of 2 of the ACSM IEPOX-OA measurements. Similar temporal features are exhibited in both the base (black) and γ_{IEPOX} sensitivity (green) cases. Early morning concentrations are still not on trend with the ACSM measurements (red), which might indicate a contribution of an unknown mechanism of gaseous IEPOX leading to a higher level of IEPOX-OA formation. Overall, the diurnal shape in the sensitivity case remains mostly unchanged compared to the base case, and the magnitude of aerosol in the sensitivity case is substantially improved.

We find a temporal correlation between CMAQ-simulated organic aerosol from the reactive uptake of IEPOX and ACSM measurements of the IEPOX-OA factor. For urban areas influenced by substantial regional isoprene emissions, this suggests that a considerable fraction of aerosol may be governed by reactive uptake processes. However, known IEPOX reactive uptake processes that lead to the formation of 2-methyltetrols, organosulfates, and organonitrates are not sufficient to explain the magnitude of ACSM mass concentration measurements.

Concentrations of IEPOX SOA from a base case simulation indicated that the current reactive uptake pathway mechanism in CMAQ predicts IEPOX SOA that is 10-fold smaller than measurements indicate. The production of IEPOX SOA is dependent on the availability of gas-phase IEPOX, aerosol acidity in the form of a specific (H^+) or general (HSO_4^-) acid, and aerosol water. In our simulation, the availability of all three was robust and therefore did not inhibit the formation of IEPOX SOA. Therefore, the formation of IEPOX SOA was hindered by a different factor.

To examine the potential for IEPOX-derived aerosol due to acid-enhanced reactive uptake, we conducted a simulation with an effective reactive uptake coefficient, γ_{IEPOX} , that is 10 times larger than the base simulation. Resulting concentrations of IEPOX-derived SOA increased by a factor of 5, substantially decreasing the discrepancy between the simulated IEPOX-derived SOA and the ACSM factor while retaining the same temporal correlation with observations as in the base case. The increase in IEPOX-derived SOA is not linear because other variables, such as the gas-phase diffusion rate, are also limiting factors (see the Supporting Information). Prior work has also suggested that laboratory measurements of isoprene SOA yield cannot explain high levels of field measurements of SOA from isoprene. A recent modeling analysis of the 82fac aerosol component found in Borneo¹⁵ concluded that IEPOX SOA yields should be ~ 5 times greater than laboratory-based SOA yields¹² to account for the IEPOX-derived aerosol.³¹

Another contributing factor is the fact that the most abundant simulated compounds, 2-methyltetrols, have an organic matter:organic carbon (OM:OC) ratio of 2.26 while the ACSM measurements³² have an OM:OC ratio of 4. This suggests the IEPOX-derived SOA may undergo additional aerosol-phase reactions that lead to the addition of functional groups³³ and the formation of larger oligomers, which are not

included in these CMAQ simulations. This missing organic matter may account for the remaining model–measurement discrepancy.

While complete chemical characterization of all IEPOX-derived aerosol compounds is a worthwhile goal, our sensitivity simulation suggests that measurements to better constrain γ_{IEPOX} and the OM:OC ratio of IEPOX-derived SOA could help reconcile laboratory and field-based measurements of OA formation.

■ ASSOCIATED CONTENT

■ Supporting Information

A description of the modeling system and a table listing the correlation between CMAQ-simulated compounds and the ACSM-measured IEPOX-OA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. Organic aerosol and global climate modelling: A review. *Atmos. Chem. Phys.* **2005**, *5*, 1053–1123.

(2) de Gouw, J.; Jimenez, J. L. Organic Aerosols in the Earth's Atmosphere. *Environ. Sci. Technol.* **2009**, *43*, 7614–7618.

(3) Carlton, A. G.; Wiedinmyer, C.; Kroll, J. H. A review of Secondary Organic Aerosol (SOA) formation from isoprene. *Atmos. Chem. Phys.* **2009**, *9*, 4987–5005.

(4) Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P. I.; Geron, C. Estimates of global terrestrial isoprene emissions using MEGAN (model of emissions of gases and aerosols from nature). *Atmos. Chem. Phys.* **2006**, *6*, 3181.

(5) Paulot, F.; Crounse, J. D.; Kjaergaard, H. G.; Krten, A.; St. Clair, J. M.; Seinfeld, J. H.; Wennberg, P. O. Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science* **2009**, *325*, 730.

(6) Bates, K. H.; Crounse, J. D.; St. Clair, J. M.; Bennett, N. B.; Nguyen, T. B.; Seinfeld, J. H.; Stoltz, B. M.; Wennberg, P. O. Gas Phase Production and Loss of Isoprene Epoxydiols. *J. Phys. Chem. A* **2014**, *118*, 1237–1246.

(7) Eddingsaas, N. C.; VanderVelde, D. G.; Wennberg, P. O. Kinetics and Products of the Acid-Catalyzed Ring-Opening of Atmospherically Relevant Butyl Epoxy Alcohols. *J. Phys. Chem. A* **2010**, *114*, 8106–8113.

(8) Darer, A. I.; Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J. Formation and Stability of Atmospherically Relevant Isoprene-Derived Organosulfates and Organonitrates. *Environ. Sci. Technol.* **2011**, *45*, 1895–1902.

(9) Piletic, I.; Edney, E.; Bartolotti, L. A Computational Study of Acid Catalyzed Aerosol Reactions of Atmospherically Relevant Epoxides. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18065–18076.

(10) Edney, E.; Kleindienst, T.; Jaoui, M.; Lewandowski, M.; Offenberg, J.; Wang, W.; Claeys, M. Formation of 2-methyltetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States. *Atmos. Environ.* **2005**, *39*, 5281–5289.

(11) Surratt, J. D.; Chan, A. W. H.; Eddingsaas, N. C.; Chan, M.; Loza, C. L.; Kwan, A. J.; Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6640.

(12) Lin, Y.-H.; Zhang, Z.; Docherty, K. S.; Zhang, H.; Budisulistiorini, S. H.; Rubitschun, C. L.; Shaw, S. L.; Knipping, E. M.; Edgerton, E. S.; Kleindienst, T. E.; Gold, A.; Surratt, J. D. Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive Uptake Studies with Authentic Compounds. *Environ. Sci. Technol.* **2012**, *46*, 250–258.

(13) Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; Andreae, M. O.; Artaxo, P.; Maenhaut, W. Formation of secondary organic aerosols through photooxidation of isoprene. *Science* **2004**, *303*, 1173.

(14) Slowik, J. G.; Brook, J.; Chang, R. Y.-W.; Evans, G. J.; Hayden, K.; Jeong, C.-H.; Li, S.-M.; Liggio, J.; Liu, P. S. K.; McGuire, M.; Mihele, C.; Sjostedt, S.; Vlasenko, A.; Abbatt, J. P. D. Photochemical processing of organic aerosol at nearby continental sites: Contrast between urban plumes and regional aerosol. *Atmos. Chem. Phys.* **2011**, *11*, 2991–3006.

(15) Robinson, N. H.; Hamilton, J. F.; Allan, J. D.; Langford, B.; Oram, D. E.; Chen, Q.; Docherty, K.; Farmer, D. K.; Jimenez, J. L.; Ward, M. W.; Hewitt, C. N.; Barley, M. H.; Jenkin, M. E.; Rickard, A. R.; Martin, S. T.; McFiggans, G.; Coe, H. Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest. *Atmos. Chem. Phys.* **2011**, *11*, 1039–1050.

(16) Budisulistiorini, S. H.; Canagaratna, M. R.; Croteau, P. L.; Marth, W. J.; Baumann, K.; Edgerton, E. S.; Shaw, S. L.; Knipping, E. M.; Worsnop, D. R.; Jayne, J. T.; Gold, A.; Surratt, J. D. Real-Time Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor. *Environ. Sci. Technol.* **2013**, *47*, 5686–5694.

(17) Ulbrich, I. M.; Canagaratna, M. R.; Zhang, Q.; Worsnop, D. R.; Jimenez, J. L. Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data. *Atmos. Chem. Phys.* **2009**, *9*, 2891.

(18) Pye, H. O. T.; Pinder, R. W.; Piletic, I. R.; Xie, Y.; Capps, S. L.; Lin, Y.-H.; Surratt, J. D.; Zhang, Z.; Gold, A.; Luecken, D. J.; Hutzell, W. T.; Jaoui, M.; Offenberg, J. H.; Kleindienst, T. E.; Lewandowski, M.; Edney, E. O. Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation. *Environ. Sci. Technol.* **2013**, *47*, 11056–11064.

(19) Ng, N. L.; Herndon, S. C.; Trimborn, A.; Canagaratna, M. R.; Croteau, P. L.; Onasch, T. B.; Sueper, D.; Worsnop, D. R.; Zhang, Q.; Sun, Y. L.; Jayne, J. T. An aerosol chemical speciation monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol. *Aerosol Sci. Technol.* **2011**, *45*, 780.

(20) Foley, K. M.; Roselle, S. J.; Appel, K. W.; Bhawe, P. V.; Pleim, J. E.; Otte, T. L.; Mathur, R.; Sarwar, G.; Young, J. O.; Gilliam, R. C.; Nolte, C. G.; Kelly, J. T.; Gilliland, A. B.; Bash, J. O. Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7. *Geosci. Model Dev.* **2010**, *3*, 205–226.

(21) Bhawe, P. V.; Pouliot, G. A.; Zheng, M. Diagnostic Model Evaluation for Carbonaceous PM_{2.5} Using Organic Markers Measured in the Southeastern U.S. *Environ. Sci. Technol.* **2007**, *41*, 1577–1583.

(22) Xie, Y.; Paulot, F.; Carter, W. P. L.; Nolte, C. G.; Luecken, D. J.; Hutzell, W. T.; Wennberg, P. O.; Cohen, R. C.; Pinder, R. W. Understanding the impact of recent advances in isoprene photo-

oxidation on simulations of regional air quality. *Atmos. Chem. Phys.* **2013**, *13*, 8439–8455.

(23) Motor Vehicle Emission Simulator (MOVES) User Guide. Report EPA-420-B-12-001b; U.S. Environmental Protection Agency: Washington, DC, June 2012.

(24) Kinnee, E.; Geron, C.; Pierce, T. United States Land Use Inventory For Estimating Biogenic Ozone Precursor Emissions. *Ecological Applications* **1997**, *7*, 46–58.

(25) Our Nations Air: Status and Trends through 2010. Report EPA-454/R-12-001; U.S. Environmental Protection Agency: Washington, DC, 2012.

(26) Otte, T. L.; Pleim, J. E. The Meteorology-Chemistry Interface Processor (MCIP) for the CMAQ modeling system: Updates through MCIPv3.4.1. *Geosci. Model Dev.* **2010**, *3*, 243–256.

(27) Henderson, B. H.; Akhtar, F.; Pye, H. O. T.; Napelenok, S. L.; Hutzell, W. T. A database and tool for boundary conditions for regional air quality modeling: Description and evaluation. *Geosci. Model Dev.* **2014**, *7*, 339–360.

(28) Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenber, J. H.; Lewis, C. W.; Bhave, P. V.; Edney, E. O. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. *Atmos. Environ.* **2007**, *41*, 8288.

(29) Surratt, J. D.; Lewandowski, M.; Offenber, J. H.; Jaoui, M.; Kleindienst, T. E.; Edney, E. O.; Seinfeld, J. H. Effect of Acidity on Secondary Organic Aerosol Formation from Isoprene. *Environ. Sci. Technol.* **2007**, *41*, 5363–5369.

(30) Jacobs, M. I.; Darer, A. I.; Elrod, M. J. Rate Constants and Products of the OH Reaction with Isoprene-Derived Epoxides. *Environ. Sci. Technol.* **2013**, *47*, 12868–12876.

(31) Janssen, R. H. H.; Vil-Guerau de Arellano, J.; Jimenez, J. L.; Ganzeveld, L. N.; Robinson, N. H.; Allan, J. D.; Coe, H.; Pugh, T. A. M. Influence of boundary layer dynamics and isoprene chemistry on the organic aerosol budget in a tropical forest. *J. Geophys. Res.: Atmos.* **2013**, *118*, 9351–9366.

(32) Budisulistiorini, S.; Canagaratna, M.; Croteau, P.; Baumann, K.; Edgerton, E.; Kollman, M.; Ng, N.; Verma, V.; Shaw, S.; Knipping, E.; Worsnop, D.; Jayne, J.; Weber, R.; Surratt, J. Intercomparison of an Aerosol Chemical Speciation Monitor (ACSM) with ambient fine aerosol measurements in Downtown Atlanta, Georgia. *Atmos. Meas. Tech.* **2013**, *6*, 11181–11213.

(33) Ervens, B.; Turpin, B. J.; Weber, R. J. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): A review of laboratory, field and model studies. *Atmos. Chem. Phys.* **2011**, *11*, 11069–11102.