

Isoprene epoxydiol contribution to urban organic aerosol: evidence from modeling and measurements

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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, since 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 factor of 10 less mass 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.

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Introduction

Sub-micron 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 can be absorbed onto the surface of existing particles. This secondary organic aerosol (SOA) is a large fraction of the global burden. Despite this importance, SOA formation is not completely understood¹ and simulations of regional and global SOA underestimate the concentration, fail to capture temporal variability, and incompletely attribute the sources².

Isoprene is thought to play an important role in global SOA formation³. With more than 600 Tg y⁻¹ globally, isoprene is the most abundant non-methane organic compound emitted⁴. 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 phase⁷⁻⁹. One class of aerosol phase compounds, 2-methyltetrols, have been uniquely associated with isoprene^{10,11} and later with IEPOX¹². 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 forms¹¹⁻¹³, a remaining question is to what extent do these compounds contribute to ambient aerosols? Recent ambient measurement approaches employing high-time resolution mass

spectrometry such as the Aerosol Mass Spectrometer (AMS) and Aerosol Chemical Speciation Monitor (ACSM) have attributed a significant fraction of ambient aerosol mass to isoprene¹⁴⁻¹⁶. By applying positive matrix factorization (PMF)¹⁷, 33% of urban organic aerosol in Atlanta, GA was found to have a characteristic mass spectrum that closely resembles 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 to observe the contribution of isoprene emissions to aerosol production.

We employ the Community Multi-scale Air Quality (CMAQv5.0.1) model with isoprene updates to evaluate the link between isoprene, IEPOX, and IEPOX-OA. Recent CMAQ modeling has shown that ambient measurements of 2-methyltetrols can be simulated by reactive uptake of IEPOX to aerosols¹⁸. 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 – September 14, 2011 at 30-minute 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, Georgia, in the southeastern United States¹⁶. This urban setting is in a region known for high levels of biogenic isoprene and anthropogenic emissions. The measurements are fully described in Budisulistiorini *et al.*¹⁶, but briefly, the ACSM provides online, continuous chemical measurements of non-refractory particulate matter with diameter less than 1 μm (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, semi-volatile, 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-hour 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 aerosol²¹. 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 semi-volatile isoprene oxidation products¹⁸. 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 supporting information of Pye *et al.*¹⁸). The epoxide aerosol formation is modeled as a reactive uptake process governed by an uptake coefficient calculated based on the Henry's Law coefficient (solubility of IEPOX in water) and particle-phase composition (including concentration of acids and nucleophiles). Additionally, isoprene SOA production by the absorptive partitioning of semi-volatile isoprene oxidation products remains included for comparison.

To match the measurement period, we simulate from July 27 to September 14, 2011, with the first twelve days discarded as model spin-up. To capture regional influences, the modeling domain includes a large portion of North America covering the contiguous U.S., 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 MOVES²³, which includes year specific estimates of vehicle miles traveled, fleet characteristics, and meteorological conditions. Emissions of biogenic volatile organic compounds, including isoprene, are calculated on-line using BEIS²⁴ using the same meteorological conditions as CMAQ. All other emissions are from the National Emission Inventory²⁵. Meteorological data are from the Weather Research Forecasting (WRF) model, nudged to re-analysis fields to reduce error, and converted to CMAQ inputs²⁶. Hourly chemical boundary conditions are extracted from a GEOS-Chem global simulation for the same time period²⁷.

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 semi-volatile isoprene SOA, to determine if IEPOX is the best explanation for the IEPOX-OA factor. Finally, given that 2-methyltetrols are only one 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 give 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 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, organo-sulfates, and organo-nitrates. Please see supporting information for equations¹⁸ defining $k_{\text{IEPOX}}^{\text{particle}}$. These reactions yield 2-methyltetrols, organosulfates, organonitrates, tetrol dimers, IEPOX organo-sulfate dimers, and

IEPOX organo-nitrate dimers. In CMAQ, concentrations of 2-methyltetrols, organosulfates, 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-II²⁷ and the $k_{\text{IEPOX}}^{\text{particle}}$ rates are calculated using laboratory- and structure-derived third-order rate constants from Eddingsaas *et al.*⁶

Comparing Figures 1d, 1e, and 1f, show that the maximum production of the most abundant CMAQ simulated IEPOX-derived SOA, 2-methyltetrols, occurs coincidentally with the maximum $k_{\text{IEPOX}}^{\text{particle}}$ (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 2-methyltetrols and around noon when maximum production occurs. Predicted 2-methyltetrol concentrations exhibit a diurnal structure very similar to that of the IEPOX-OA measurements ($r = 0.531$) and have higher 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, *Supporting Info*). However, while CMAQ simulates abundant production of gas-phase IEPOX (Figure 1d) CMAQ simulated IEPOX-derived SOA is a factor of 10 less than 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 abundant²⁹. Prior work¹⁸ has shown that where chemically-resolved filter-based measurements are available, CMAQ systematically over predicts 2-methyltetrol measurements by a factor of 2. While acidity can strongly enhance IEPOX-OA production³⁰, CMAQ-simulated aerosol acidity concentrations were not significantly lower than 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 factor of 10 under prediction 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 where 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 maximum $k_{\text{IEPOX}}^{\text{particle}}$, γ_{IEPOX} increases significantly due to the factor of 10 increase and the effect due to decreased $k_{\text{IEPOX}}^{\text{particle}}$ 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 $2.86 \mu\text{g m}^{-3}$ to $2.56 \mu\text{g m}^{-3}$ average), but the amount depleted is very small in comparison to the factor of 5 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^{29} . 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 ($\gamma_{\text{IEPOX}} \times 10$) is shown in green. CMAQ simulated IEPOX derived aerosol in the sensitivity simulation is five 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 contribution of unknown mechanism of gaseous IEPOX leading to higher 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 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, organo-sulfates, and organo-nitrates 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 a factor of 10 times 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 five, 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 *Supporting Info*). 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 about 5 times greater than laboratory-based SOA yields¹² in order to account for the IEPOX-derived aerosol³².

Another contributing factor is that the most abundant simulated compounds, 2-methyltetrols, have an organic matter to organic carbon ratio (OM:OC) of 2.26, while the ACSM measurements³³ 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 groups³⁴ 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 of IEPOX-derived SOA could help reconcile laboratory and field-based measurements of OA formation.

Supporting Information: The supporting information contains 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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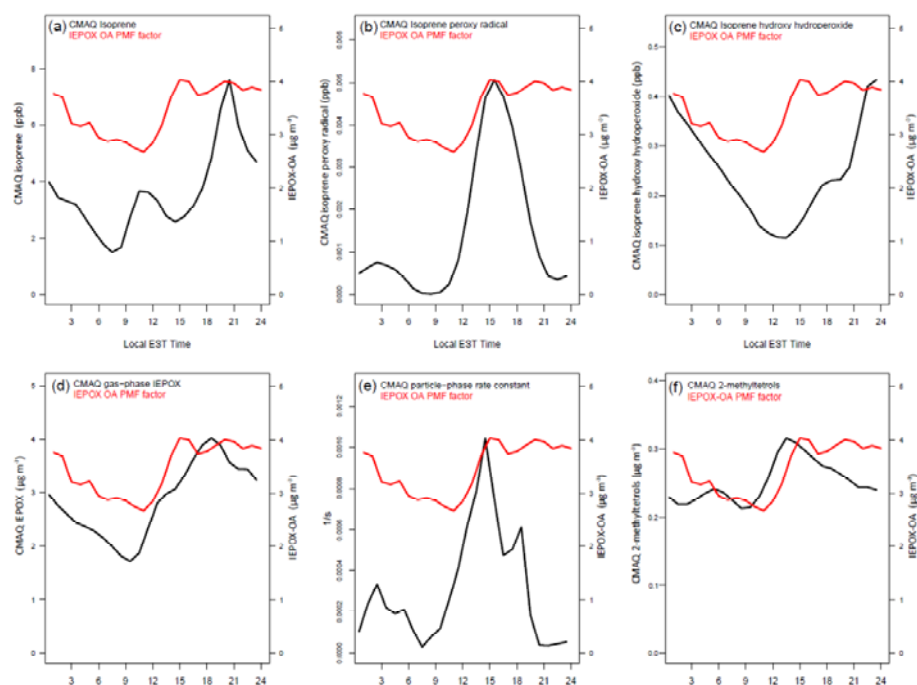


Figure 1: The strong correspondence between CMAQ simulated 2-methyltetrols (f) and the ACSM IEPOX-OA factor (red) can be traced to the diurnal variability in transformation of isoprene (a) to its peroxy radical (b) and peroxide (c), which in turn forms IEPOX (d). The simulated rate of reactive uptake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

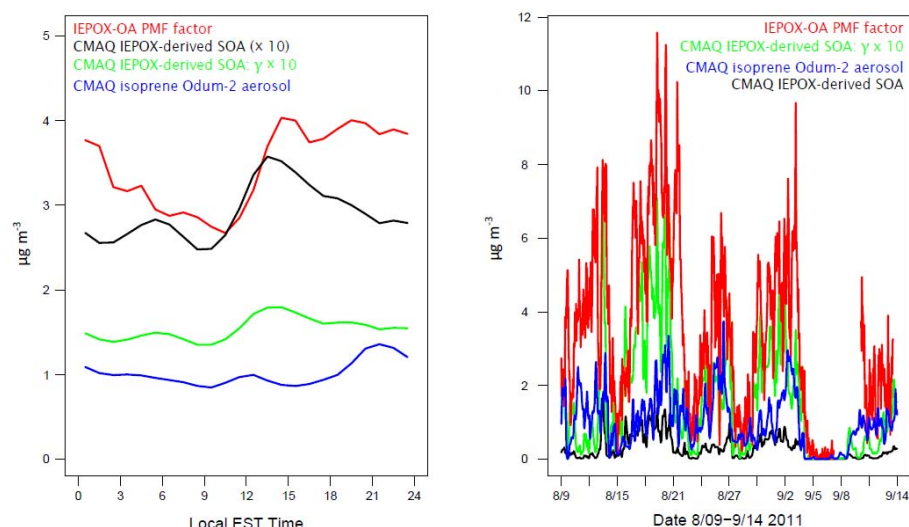


Figure 2: CMAQ simulated IEPOX derived SOA and ACSM IEPOX-OA factor, diurnal average (left) and time series (right). The diurnal averaged values for the CMAQ simulated IEPOX SOA has a higher correlation with the observations than isoprene SOA calculated using an Odum 2-product, semi-volatile SOA approach. Assuming a factor of 10 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.

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