

Scope of Work For
Project 14-003
**Update and evaluation of model algorithms needed to predict
particulate matter from isoprene**

Prepared for

Air Quality Research Program (AQRP)
The University of Texas at Austin

by

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1. BACKGROUND

Atmospheric fine particulate matter (PM_{2.5}, aerosol with aerodynamic diameters of 2.5 μm or less) plays a key role in air quality and climate change, and is associated with damaging effects on human health [1]. Globally, the largest mass fraction of PM_{2.5} is organic, and is mostly dominated by secondary organic aerosol (SOA) formed from the atmospheric oxidation of non-methane hydrocarbons [2]. Isoprene (2-methyl-1,3-butadiene, C₅H₈) is the most abundant non-methane hydrocarbon emitted into Earth's atmosphere and is largely emitted in the southeastern United States (U.S.) during summer [3]. Although only recently considered as the single largest source of global SOA, the exact manner in which isoprene-derived SOA is formed remains unclear [4]. Increasing our fundamental understanding of isoprene-derived SOA formation is key to improving the performance of existing air quality models, especially in the southeastern U.S. where models currently underestimate observations [5-7]. Without accurate model predictions of isoprene-derived SOA formation, the true impact of PM_{2.5} on air quality and human health cannot be fully assessed resulting in the delay of effective control (mitigation) strategies.

By combining organic synthesis, computational calculations, mass spectrometry, smog chamber studies, and field measurements, we have recently characterized (Figure 1) reactive epoxides,

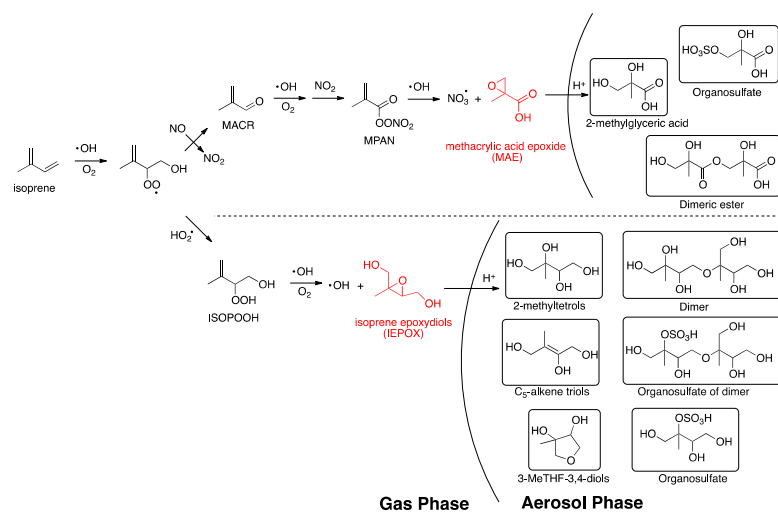


Figure 1. Proposed chemical mechanism leading to isoprene-derived SOA under initially low- and high-NO levels (lower and upper schemes, respectively). All boxed products have been observed in both laboratory-generated and ambient fine aerosol. For simplicity, it is noted that only one of eight possible RO₂ radicals produced from OH-initiated oxidation of isoprene is considered, and only the cis-β-IEPOX isomer is shown here.

conducted at the U.S. EPA indicate that 50% of biogenic (e.g., isoprene)-derived PM is controllable by reducing emissions of anthropogenic pollutants [6].

In the laboratory, we find that the reactive uptake of synthetic IEPOX and MAE standards onto acidified sulfate aerosol yields known isoprene-derived SOA tracers shown in Figure 1 (2-methyltetrols, 2-methylglyceric acid, C₅-alkene triols, 3-methyltetrahydrofuran-3,4-diols, dimers and organosulfates) that we measure in PM_{2.5} samples collected from multiple sites across the southeastern U.S. region using gas chromatography/mass spectrometry (GC/MS) and liquid chromatography coupled to diode array detection and electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (LC/DAD-ESI-QTOFMS) [9-11, 13]. Notably, IEPOX- and MAE-derived SOA tracers shown in Figure 1 account for ~20% of the organic aerosol mass in PM_{2.5} collected from Yorkville, GA [11]. Moreover, recent real-time continuous chemical measurements of PM_{2.5} we made using an Aerodyne Aerosol Chemical Speciation

which include methacrylic acid epoxide (MAE) and isomeric isoprene epoxydiols (IEPOX), produced from the photochemical oxidation of isoprene that are key to SOA formation [8-11]. From recent work it is clear that anthropogenic pollutants, such as of oxides of nitrogen (NO_x = NO + NO₂) and sulfur dioxide (SO₂), significantly enhance isoprene-derived epoxides as a source of PM_{2.5} [8-12]. This is of great public health importance since isoprene is primarily emitted from terrestrial vegetation, and thus, is not controllable, whereas anthropogenic emissions (e.g., NO_x, SO₂, or pre-existing primary aerosol) are controllable. In fact, recent Community Multiscale Air Quality (CMAQ) model simulations

Monitor (ACSM) during summer 2011 in downtown Atlanta, GA, resolved an IEPOX-oxygenated organic aerosol (IEPOX-OOA) factor when applying positive matrix factorization (PMF) to the organic mass spectral time series [14]. In Atlanta, this PMF factor is found to account for ~33% of the PM_{2.5} mass and is correlated with IEPOX-derived SOA tracers ($r^2 = 0.6$) shown in Figure 1, sulfate ($r^2 = 0.5$), and to some extent with aerosol acidity (measured as nmol H⁺ m⁻³, $r^2 = 0.3$), consistent with our recent laboratory work showing that aerosol acidity and sulfate mass loading promote heterogeneous chemistry of IEPOX.

We have recently collaborated with the U.S. EPA to update the CMAQ model to predict isoprene-derived SOA from the heterogeneous (multiphase) chemistry of IEPOX and MAE onto pre-existing aerosols using details from our recent work shown in Figure 1 [15]. The new aqueous aerosol pathways we have added allow for explicit predictions of IEPOX- and MAE-derived SOA tracers (and thus, total SOA mass from isoprene oxidation) that are more consistent with observations than estimates based on semi-volatile partitioning, supporting the role of acid-catalyzed heterogeneous (multiphase) reactions of isoprene-derived epoxides leading to SOA formation. Although a framework exists in CMAQ to predict isoprene SOA, many of the key parameters have yet to be evaluated against smog chamber data. Thus, we first propose to conduct a series of new experiments at UNC to quantitatively measure the reactive uptake of the two predominant isoprene-derived epoxides to particles of different inorganic compositions. By providing these new fundamental measurements, we will be able to more directly evaluate the aerosol-phase processes added to the model. This work addresses the stated priority area of investigating the transformation of gas-phase pollutants to particulate matter that impact Texas air quality.

2. STATEMENT OF WORK

Our goal is to reduce the uncertainty in the reactive uptake coefficients needed to predict both the production/removal of gas-phase epoxide intermediates and SOA formation. We propose four tasks to produce the experimental and modeling data needed to achieve this goal and are detailed below.

Task 1. Integration of Gas-Phase Epoxide Formation and Subsequent SOA Formation into UNC MORPHO Box Model

a. Integration of Gas-Phase Epoxide Chemistry

Through our collaborations with EPA we have access to an expansion of the SAPRC07 mechanism with updated isoprene chemistry (SAPRC07TC) [9, 16]. The expanded SAPRC07TC chemical mechanism includes the explicit formation of IEPOX and MAE as shown in Figure 1. In addition, the model includes the formation of hydroxymethyl- α -lactone (HMML) [17]. The SAPRC07TC mechanism also includes reactions of isoprene with $\cdot\text{OH}$, $\text{NO}_3\cdot$, and O_3 , but epoxides form only through the $\cdot\text{OH}$ reaction. The discrimination between the epoxides depends on the fate of the initial isoprene peroxy radical (RO_2) that is formed after addition of $\cdot\text{OH}$ to isoprene. Under lower- NO_x conditions, when RO_2 reacts with HO_2 , IEPOX is formed relatively promptly. As shown in Figure 1, under high- NO_x conditions, when RO_2 reacts with NO , a series of alternate reactions is simulated, with methacrolein (MACR) as one of the products. Under favorable conditions (high NO_2/NO ratios), methacrolein can form methacryloylperoxynitrate (MPAN) that can further react to produce both MAE and HMML. While the IEPOX in the lower- NO_x pathway can be formed after three reactions, MAE and HMML formation in the high- NO_x route requires a minimum of 5 reactions, with many competing reactions forming other products, thus decreasing the yield of SOA precursors.

In collaboration with the EPA, we have implemented this mechanism into CMAQ and simulated a July-August 2006 modeling episode predicting isoprene and the new SOA precursors of MAE

and IEPOX [15]. As shown in Figure 3 there are significant isoprene concentrations northeast of Houston resulting in predictions of some of the largest concentrations of MAE and IEPOX in the country. These preliminary data suggests that isoprene derived SOA would have an impact on Houston PM.

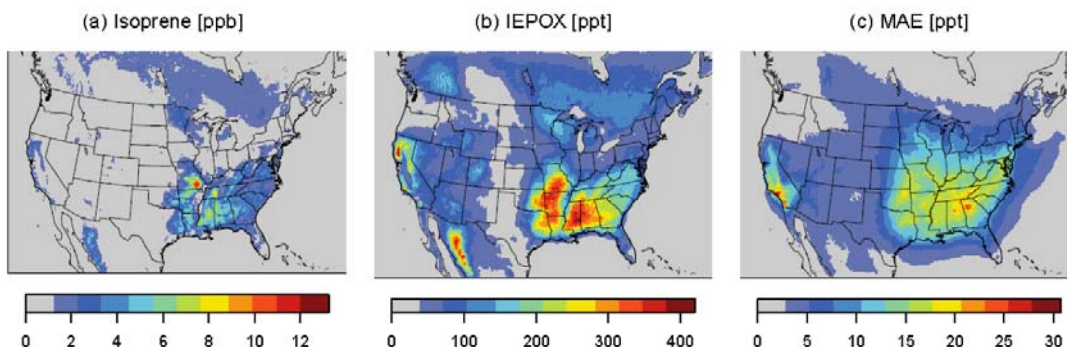


Figure 3. CMAQ model predicted gas phase concentrations of (a) isoprene and aerosol precursors (b) IEPOX and (c) MAE [15].

Deliverable: For this task we will produce a box model framework with the updated SAPRAC07TC gas phase chemical mechanism so that UNC smog chamber experiments can be simulated and the mechanism evaluated [18].

b. Integration of Multiphase Chemistry of Isoprene-derived Epoxides

To predict SOA we will integrate into our Morpho box model the algorithms currently used in air quality models, and a modified version that includes SOA production from IEPOX, MAE, and HMML. As an example of a current algorithm we will describe the version used in CMAQ. In the current version of CMAQ the production of SOA uses the Odum 2-product approach that produces SOA from gas phase species SV_ISO1 and SV_ISO2, as shown in the bottom of Figure 4 [5]. The Odum 2-product values were determined by fitting semivolatile aerosols using low-NO_x chamber experiments [19] followed by an acid enhancement under conditions of strong acidity and oligomerization of the particle phase to nonvolatile form using a fixed rate constant [5, 19]. The Odum 2-product will be integrated into the Morpho modeling system and used as a baseline in this analysis.

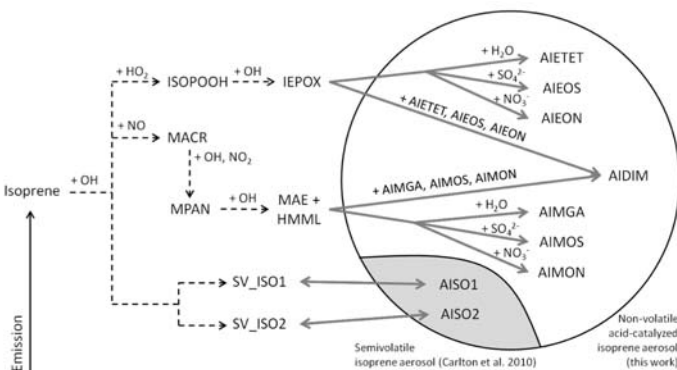


Figure 4. Schematic of Isoprene oxidation by $\cdot\text{OH}$ and subsequent gas and particle phase products. Shown in the bottom branch is the Odum 2-product implementation that produces AISO1 and AISO2. The remaining pathways were implemented by EPA to predict SOA from IEPOX, MAE, and HMML.

Figure 4 also shows an updated SOA algorithm implemented into a research version of CMAQ to predict SOA from IEPOX, MAE, and HMML [15]. This method will also be implemented in the Morpho modeling framework. In the Morpho implementation, the Odum 2-product model is not used, nor the acid enhancement and oligomerization processes. For modeling purposes, heterogeneous uptake of HMML (57% yield from MPAN + $\cdot\text{OH}$) is treated like MAE (21% yield from MPAN + $\cdot\text{OH}$) providing an upper bound on the amount of SOA from MPAN [20]. The conversion of IEPOX and MAE + HMML to aerosol-phase species is

accomplished via heterogeneous uptake onto pre-existing aerosols. Uptake onto the aerosol

phase can be parameterized using an uptake coefficient, γ , that can be calculated [21]:

$$\gamma = \left(\frac{1}{\alpha} + \frac{\nu}{4HRT\sqrt{D_a k_{particle}}} \frac{1}{f(q)} \right)^{-1} \quad (1)$$

$$f(q) = \coth(q) - \frac{1}{q} \quad (2)$$

$$q = r_p \sqrt{\frac{k_{particle}}{D_a}} \quad (3)$$

where α is the mass accommodation coefficient (0.02) [22], ν is the mean molecular speed, H is the Henry's Law coefficient, R is the gas constant, T is temperature, D_a is diffusivity in the aerosol phase ($1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) [23], $k_{particle}$ is the pseudo-first-order rate constant for reaction of the parent hydrocarbon in the aerosol phase, q is the diffuso-reactive parameter, and r_p is the effective particle radius. The Henry's Law coefficients for IEPOX and MAE are estimated to be 2.7×10^6 and $1.2 \times 10^5 \text{ M atm}^{-1}$ using HenryWin 3.2 (bond contribution method) [24, 25].

The pseudo-first-order particle-phase rate constant, $k_{particle}$, is calculated assuming protonation of the epoxide oxygen and nucleophilic addition. A recent study used information on isotopic effects and NMR analysis that epoxides similar to IEPOX follow an A-2 mechanism in which the rate-determining step in the reaction is concerted nucleophilic addition to the ring [26]. We will assume the A-2 mechanism applies here; thus the particle-phase rate constant for an epoxide during a given model time step (in which the concentrations of nucleophiles and acids are constant) is:

$$k_{particle} = \sum_{i=1}^N \sum_{j=1}^M k_{i,j} [nuc_i] [acid_j] \quad (4)$$

for N nucleophiles and M acids. Concentrations are expressed in molarity (mol L^{-1}). Seven new species will be added to Morpho to represent the results of particle-phase reactions between nucleophiles and H^+ (a specific acid) or bisulfate (a general acid) (Table 1) [26]. IEPOX (and MAE) form 2-methyltetrols (and 2-MG), organosulfates, and organonitrates as a result of addition of water, sulfate, and nitrate. These species can then serve as nucleophiles that add to an epoxide to form oligomers. Only dimers are currently considered (no higher-order oligomers), [27] and all dimers are lumped together. Currently, there is no precedent for including reactions of epoxides with other organic species in the particle phase, and such additional pathways have not been considered. As a result, as described in Task 3 below, no experiments will be conducted with pre-existing organic aerosols. Instead, experiments conducted in Task 3 will only consider ammonium bisulfate or acidified ammonium sulfate aerosols as surfaces for IEPOX and MAE to be removed from the gas phase.

Third-order rate constants for the particle-phase reactions ($k_{i,j}$) are based on the work of [26] and β -IEPOX as shown in [15]. Due to a lack of kinetic data, the MAE rate constants are assumed to be the same as for IEPOX. However, density functional calculations suggest that the barrier for the acid-catalyzed hydrolysis of MAE is higher than for IEPOX; thus, the rate constant may be considerably smaller [28].

Table 1. New isoprene SOA species considered in the CMAQ model with their molecular weight, OM/OC ratio, parent hydrocarbon identity, nucleophile that adds to the parent, and rate constants for H^+ and HSO_4^- catalyzed ring-opening reactions.

species	MW [g mol ⁻¹]	OM/OC	parent hydrocarbon	nucleophile added	k_{i,H^+} [M ⁻² s ⁻¹]	k_{i,HSO_4^-} [M ⁻² s ⁻¹]
2-methyltetrol	136	2.27	IEPOX	water	9.0×10^{-4a}	1.3×10^{-5}
IEPOX-derived OS	216	3.60	IEPOX	sulfate	2.0×10^{-4b}	2.9×10^{-6}
IEPOX-derived ON	181	3.02	IEPOX	nitrate	2.0×10^{-4}	2.9×10^{-6}
2-MG	120	2.50	MAE, HMML	water	9.0×10^{-4}	1.3×10^{-5}
MPAN-derived OS	200	4.17	MAE, HMML	sulfate	2.0×10^{-4b}	2.9×10^{-6}
MPAN-derived ON	165	3.44	MAE, HMML	nitrate	2.0×10^{-4}	2.9×10^{-6}
			IEPOX	2-methyltetrol	2.0×10^{-4}	2.9×10^{-6}
			IEPOX	IEPOX-derived OS	2.0×10^{-4}	2.9×10^{-6}
			IEPOX	IEPOX-derived ON	2.0×10^{-4}	2.9×10^{-6}
dimers (as tetrol dimer)	248	2.07	MAE, HMML	2-MG	2.0×10^{-4}	2.9×10^{-6}
			MAE, HMML	MPAN-derived OS	2.0×10^{-4}	2.9×10^{-6}
			MAE, HMML	MPAN-derived ON	2.0×10^{-4}	2.9×10^{-6}

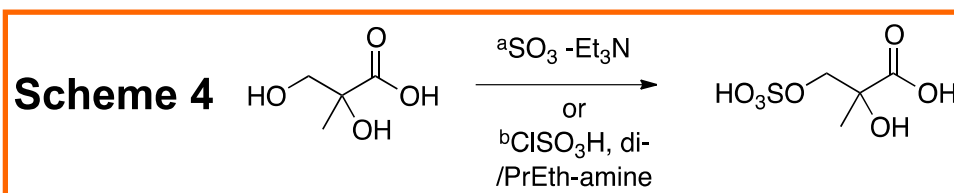
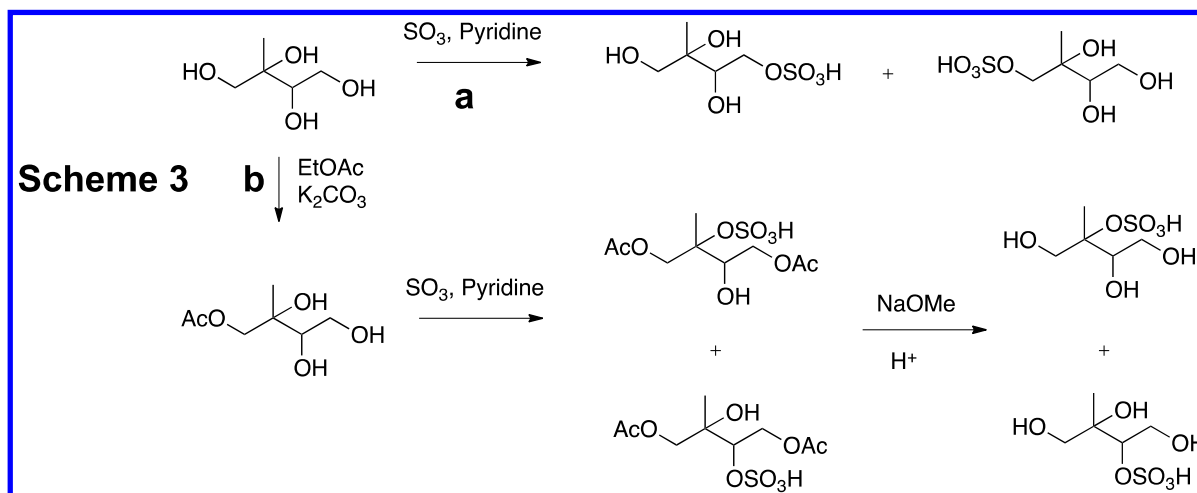
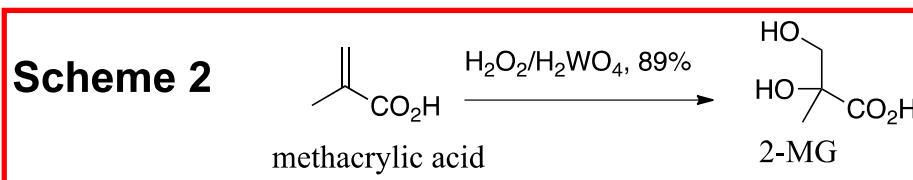
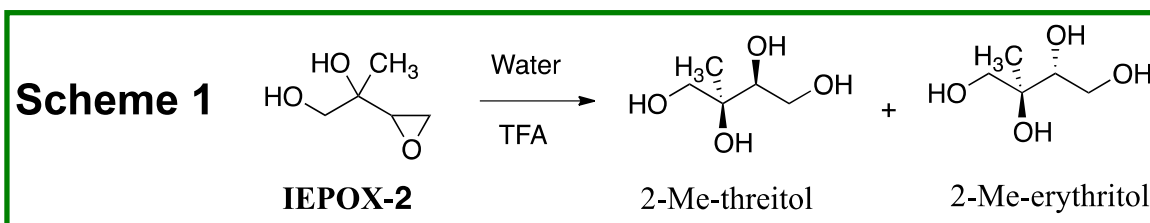
^aSensitivity analysis indicates this value is too high, and a value of $2.0 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ is more consistent with observations of 2-methyltetrols.

^bSensitivity analysis indicates this value might be too low and that additional investigation is needed. ^cOS denotes organosulfate, while ON denotes organonitrate. See Tables S1 and S2 for additional information.

Deliverable: This task will produce the algorithms in the box model needed to predict SOA formation. By completing task 1 we will have created a box model with gas-phase and particle-phase algorithms needed to simulate chamber experiments described in Task 3.

Task 2. Synthesis of Isoprene-derived Epoxides and Known SOA Tracers

Key to the new UNC experiments outlined in Task 3, is the availability of IEPOX, MAE, and SOA marker compounds shown in Figure 1. Since these are either unavailable commercially or too costly to purchase in quantities required, synthesis will be a critical component of this study. Synthetic routes to compounds required on a continuing basis for smog chamber experiments have already been developed by our group. Our group has published routes to the racemic IEPOX geometric isomers and IEPOX-derived SOA tracers, *cis*- and *trans*-3-MeTHF-3,4-diols, as well as for MAE [9, 13]. All reported syntheses yield products in high purity (> 99%).



Synthetic routes to a 1:1 mixture of 2-methyltetrol diastereomers (**Scheme 1**) and 2-methylglyceric acid (**Scheme 2**) have been developed but not yet published. A 1:1 mixture of the diastereomers 2-methylthreitol (2-Me-threitol) and 2-methylerythritol (2-Me-erythritol) is obtained by hydrolysis of **IEPOX-2**, the most easily synthesized IEPOX isomer (**Scheme 1**) [13]. We have also synthesized in high purity (>99%) 2-methylglyceric acid (2-MGA) following [29]. Our remaining synthetic efforts will focus on the organosulfates derived from IEPOX and MAE, since they are among the most abundant SOA constituents observed in laboratory and field samples [11]. All starting compounds are commercially available, and all target synthons will be characterized by ^1H and ^{13}C NMR, and UPLC/DAD-ESI-HR-QTOFMS analytical techniques.

Direct sulfation of the 2-methyltetrols with the sulfur trioxide/pyridine complex (**Scheme 3a**) is expected to yield sulfate esters at the least sterically hindered terminal -OH groups [30]. Protection of the two terminal hydroxyl groups [31], followed by sulfation and subsequent removal of the protecting groups will yield internal sulfates (**Scheme 3b**) [32]. A 1:1 starting mixture of erythritol and threitol diastereomers will yield the four racemic terminal sulfates by **Scheme 3a** and four racemic internal sulfates by **Scheme 3b**, respectively. If characterization of

the product mixtures proves challenging, the starting 2-Me-erythritol and 2-Me-threitol may be separated to simplify the product composition. The 2-MGA sulfate will be obtained by either of the published procedures in **Scheme 4** [33, 34].

Deliverable: The completion of this task will produce the isoprene derived epoxides and known SOA tracers needed for the experiments in Task 3.

Task 3. Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides

There is a critical need to evaluate the updated model's performance against systematically conducted smog chamber experiments that generate SOA formation directly from IEPOX and MAE. As a result, we will conduct dark reactive uptake experiments using synthetic IEPOX and MAE (provided by Task 2) in the UNC indoor 10-m³ flexible Teflon chamber. The details of the chamber operation and type of experiment have been described previously [9, 10]. Measurements needed by the updated modelling framework were not fully provided in prior experiments published by our group. We are now, however, able to measure all required parameters for the modelling of new experiments as outlined in Table 2.

Experiments will be conducted with either aqueous ammonium sulfate or acidified ammonium sulfate particles in a humid (RH ~ 50-60%) chamber to create a deliquesced less or more acidic seed aerosol type. Inorganic seed aerosol loadings will be 20-30 $\mu\text{g m}^{-3}$. These loadings are similar to those used previously to study IEPOX and MAE SOA formation, and are similar to atmospheric levels [35]. Epoxide will be injected into the chamber using concentrations ranging between 10 ppb (near atmospheric levels) to 300 ppb. The latter will be used owing to our prior work showing we generate sufficient amounts for off-line quantitative chemical characterization of the resultant SOA. Once the reactive uptake has ceased, as measured by the SMPS and HRTof-CIMS instruments, IEPOX or MAE additions will cease, and the resultant SOA will be allowed to age in the dark chamber for another 6-8 hours. For SOA product analyses, we will collect a Teflon filter after the initial production of "fresh" IEPOX- or MAE-derived SOA (at ~ 2 hours) and another at ~ 6-8 hours into the experiment to examine how the composition of the SOA has changed ("aged") over time. SOA tracers shown in Figure 1 will be characterized by GC/MS and (LC/DAD-ESI-QTOFMS), as previously demonstrated by our group [9, 10]. For statistical purposes, we will conduct all experiments in triplicate.

Deliverable: The completion of this task will produce the experimental data needed for modifying parameters in the algorithms used in the box model. The data will also be used to evaluate the gas and particle phase algorithms by simulating the experimental data as described in Task 4.

Table 2: Model Inputs to be Measured from Indoor Smog Chamber Experiments

Variable	Description	Purpose	Instrumentation at UNC to Measure Variable
r_p	particle radius	Equations for calculating change in [IEPOX _{gas}] or [MAE _{gas}] for each time step	Scanning Mobility Particle Sizer (SMPS) (TSI, Inc.) ^a
A	particle surface area	Equation for heterogeneous uptake rate constant (k_{het}) for IEPOX and MAE	SMPS ^a
T	temperature	Equations for mean molecular speed of epoxides, uptake coefficient (g), and calculating aerosol acidity using ISOROPIA	Vaisala T recorder ^a
RH	relative humidity	Input to ISOROPIA	Viasala RH recorder ^a
total SO ₄ ²⁻	inorganic sulfate in form of sulfate or bisulfate	Input to ISOROPIA	Ion Chromatography (IC) ^b
total NO ₃ ⁻	inorganic nitrate	Input to ISOROPIA	IC ^b
total NH ₄ ⁺	inorganic ammonium	Input to ISOROPIA	IC ^b
Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Cl ⁻	other inorganic ions	Input to ISOROPIA	IC ^b
[Epoxide _{gas}]	concentration of IEPOX or MAE in gas phase	Equations for calculating change in [Epoxide _{gas}] for each time step	Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometry (HRToF-CIMS) ^c
Wall loss	characterization of aerosol and isoprene-derived epoxide wall losses	Used to correct for losses of epoxides and seed aerosol to surfaces of chamber wall	HRToF-CIMS and SMPS ^d

^aDescribed in detail in Zhang et al. (2011, ACP)

^bDescribed in detail in Lund et al. (2013, Inhal. Toxic.)

^cDescribed in detail in Bertram et al. (2011, AMT)

^dDescribed in detail in Lin et al. (2012, ES&T) and Lin et al. (2013, PNAS)

Task 4. Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers

Using the Morpho box model we will simulate the SOA formation of IEPOX and MAE from the indoor experiments described in Task 3. In this Morpho implementation the SOA formation algorithm described in the research version of CMAQ will be used. Evaluations of model predictions will be made against measured data and series of sensitivity studies will be conducted.

Next we will use Morpho and the SAPRC07TC isoprene mechanism to simulate 52 outdoor smog chamber experiments with a range of initial isoprene to NO_x ratios of 0.3-25.9. Also included in this observational data set are experiments where urban VOCs were injected into the chamber along with isoprene and NO_x. All experimental data have been processed and are housed in the UNC chamber database. This database includes real-time measurements of temperature, relative humidity, dilution rates, gas-phase concentrations, and particle concentrations. All experiments were performed at the UNC 274 m³ dual outdoor smog chamber located in Pittsboro, NC under clear natural sunlight. The smog chamber is divided by a Teflon film curtain into two separated sides: a 136 m³ side referred as “North” and a 138 m³ side referred as “South”. Both sides of the chamber were vented with rural North Carolina background air for at least 6 hours before each experiment. A subsequent drying process was performed with a 250 L min⁻¹ Aadco clean air generator at a flow rate of 6-m³ hr⁻¹ to each side of the chamber. The extent of drying time depended on the specific needs of a given experiment.

Simulations of these experiments will be evaluated against experimental measurements and also compared with simulations using the base SAPRC07 chemical mechanism and Odum method [36]. Ambient air composition and chamber wall reactions will be consistent with UNC smog chamber simulation system.

Deliverable: This task will produce data that quantifies performance of the updated SAPRC07 mechanism and SOA algorithms to predict ozone, its precursors, isoprene oxidation products, and SOA. Recommendation will also be made on key parameters in the modeling algorithms.

3. KEY PERSONNEL

3.1 DR. WILLIAM VIZUETE

Dr. William Vizuete is a professor in the Department of Environmental Science and Engineering in the Gillings School of Global Public Health and his research interests have focused on atmospheric chemistry and atmospheric modeling. Dr. Vizuete has, for the last nine years, been working with Texas State regulators in support of their attainment demonstration of the ozone National Ambient Air Quality Standard including being PI on three projects funded by the Houston Advanced Research Center. Dr. Vizuete was also co-PI in a project that is assessing air quality risk in the United Arab Emirates through the use of regulatory air quality models, satellite data, and surface measurements.

3.2 DR. JASON SURRETT

Jason Surratt has ten years of experience in studying SOA formation from isoprene oxidation, as well as from other SOA precursors. This work has helped to lead to the recognition of the importance of isoprene-derived epoxides in forming SOA from isoprene oxidation in the presence of anthropogenic pollutants [8-12, 14, 37, 38]. Some of this work involved Dr. Surratt serving as PI on two projects funded by the U.S. EPA and the Electric Power Research Institute (EPRI).

3.3 DR. AVRAM GOLD

Dr. Gold will lead the proposed organic synthetic efforts at UNC. He will also collaborate in the preparation of manuscripts for publication. Prof. Gold has an ongoing collaboration with Dr. Surratt that has led to 6 recent co-authored peer-reviewed publications.

3.4 DR. ZHENFA ZHANG

Dr. Zhang will be directly responsible for the synthetic work. He will use our published synthetic routes for the epoxide intermediates (IEPOX and MAE) and marker compounds required for this proposal. He will apply state-of-the-art spectroscopic methods for structural characterization of all synthetic targets and additional photoproducts. Dr. Zhang will be continuing a collaborative effort with UNC Co-PIs Surratt and Gold that has led to 4 recent peer-reviewed publications.

4. DELIVERABLES

4.1 DELIVERABLES

Deliverable	Due Date
Task 1- Submit Work Plan with detailed budget (including Quality Assurance Performance Plan) to AQRP	April 15, 2014
Task 2- Integration of Gas-Phase Epoxide Formation and Subsequent SOA Formation into UNC MORPHO Box Model	October 31, 2014
Task 3- Synthesis of Isoprene-derived Epoxides and Known SOA Tracers	October 31, 2014
Task 4- Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides	January 31, 2015
Task 5- Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers	May 30, 2015
Task 6a- Draft Final Report	May 30, 2015
Task 6b- Final Report acceptable to TX AQRP	June 30, 2015

AQRP requires certain reports to be submitted on a timely basis and at regular intervals. A description of the specific reports to be submitted and their due dates are outlined below. One report per project will be submitted (collaborators will not submit separate reports), with the exception of the Financial Status Reports (FSRs). The lead PI will submit the reports, unless that responsibility is otherwise delegated with the approval of the Project Manager. All reports will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. Report templates and accessibility guidelines found on the AQRP website at <http://aqrp.ceer.utexas.edu/> will be followed.

Executive Summary

At the beginning of the project, an Executive Summary will be submitted to the Project Manager for use on the AQRP website. The Executive Summary will provide a brief description of the planned project activities, and will be written for a non-technical audience.

Due Date: Friday, May 30, 2014

Quarterly Reports

The Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Word doc file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ.

Due Dates:

Report	Period Covered	Due Date
Quarterly Report #1	March, April, May 2014	Friday, May 30, 2014
Quarterly Report #2	June, July, August 2014	Friday, August 30, 2014
Quarterly Report #3	September, October, November 2014	Monday, December 1, 2014
Quarterly Report #4	December 2015, January & February 2015	Friday, February 27, 2015
Quarterly Report #5	March, April, May 2015	Friday, May 29, 2015
Quarterly Report #6	June, July, August 2015	Monday, August 31, 2015
Quarterly Report #7	September, October, November 2015	Monday, November 30, 2015

Technical Reports

Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison as a Word doc using the AQRP FY14-15 MTR Template found on the AQRP website.

Due Dates:

Report	Period Covered	Due Date
Technical Report #1	Project Start - May 31	Monday, June 9, 2014
Technical Report #2	June 1 - 30, 2014	Tuesday, July 8, 2014
Technical Report #3	July 1 - 31, 2014	Friday, August 8, 2014
Technical Report #4	August 1 - 31, 2014	Monday, September 8, 2014
Technical Report #5	September 1 - 30, 2014	Wednesday, October 8, 2014
Technical Report #6	October 1 - 31, 2014	Monday, November 10, 2014
Technical Report #7	November 1 - 30 2014	Monday, December 8, 2014
Technical Report #8	December 1 - 31, 2014	Thursday, January 8, 2015
Technical Report #9	January 1 - 31, 2015	Monday, February 9, 2015
Technical Report #10	February 1 - 28, 2015	Monday, March 9, 2015
Technical Report #11	March 1 - 31, 2015	Wednesday, April 8, 2015
Technical Report #12	April 1 - 28, 2015	Friday, May 8, 2015
Technical Report #13	May 1 - 31, 2015	Monday, June 8, 2015

Financial Status Reports

Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzione) by each institution on the project using the AQRP FY14-15 FSR Template found on the AQRP website.

Due Dates:

Report	Period Covered	Due Date
FSR #1	Project Start - May 31	Monday, June 16, 2014
FSR #2	June 1 - 30, 2014	Tuesday, July 15, 2014
FSR #3	July 1 - 31, 2014	Friday, August 15, 2014
FSR #4	August 1 - 31, 2014	Monday, September 15, 2014
FSR #5	September 1 - 30, 2014	Wednesday, October 15, 2014
FSR #6	October 1 - 31, 2014	Monday, November 17, 2014
FSR #7	November 1 - 30 2014	Monday, December 15, 2014
FSR #8	December 1 - 31, 2014	Thursday, January 15, 2015
FSR #9	January 1 - 31, 2015	Monday, February 16, 2015
FSR #10	February 1 - 28, 2015	Monday, March 16, 2015
FSR #11	March 1 - 31, 2015	Wednesday, April 15, 2015
FSR #12	April 1 - 28, 2015	Friday, May 15, 2015
FSR #13	May 1 - 31, 2015	Monday, June 15, 2015
FSR #14	June 1 - 30, 2015	Wednesday, July 15, 2015
FSR #15	Final FSR	Wednesday, August 15, 2015

Draft Final Report

A Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Due Date: Monday, May 18, 2015

Final Report

A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Due Date: Tuesday, June 30, 2015

Project Data

All project data including but not limited to QA/QC measurement data, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion. The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information. This database will include observational data from all experiments conducted in the workplan and then box model input and output data.

AQRP Workshop

A representative from the project will present at the AQRP Workshop in June 2015.

4.2 SCHEDULE

Project Task	2014											2015					
	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6		
Task 1- Submit Work Plan with detailed budget (including Quality Assurance Performance Plan) to AQRP																	
Task 2- Integration of Gas-Phase Epoxide Formation and Subsequent SOA Formation into UNC MORPHO Box Model																	
Task 3- Synthesis of Isoprene-derived Epoxides and Known SOA Tracers																	
Task 4- Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides																	
Task 5- Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers																	
Task 6a- Draft Final Report																	
Task 6b- Final Report acceptable to TX AQRP																	

5. REFERENCES:

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