Quality Assurance Project Plan

Project 16 – 031
Condensed Chemical Mechanisms for Ozone and Particulate Matter Incorporating the Latest in Isoprene Chemistry

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

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The University of North Carolina at Chapel Hill has prepared this QAPP following EPA guidelines for a Quality Assurance (QA) Category III Project: Measurement and Modeling. It is submitted to the Texas Air Quality Research Program (AQRP) as required in the Work Plan requirements.

QAPP Requirements: Project description and objectives, organization and responsibilities, model selection, model calibration, model verification, model documentation, scientific approach, sampling procedures, measurement procedures, quality metrics, data analysis, interpretation, and management, reporting, and references, prescribed in the applicable NMRL QAPP Requirements template (https://www.tceq.texas.gov/airquality/airmod/project/quality-assurance).

QA Requirements: Technical Systems Audits - Not Required for the Project
Audits of Data Quality – 10% Required
Report of Findings – Required in Final Report

This document is a Category III Quality Assurance Project Plan for Project 16 – 031 Condensed Chemical Mechanisms for Ozone and Particulate Matter Incorporating the Latest in Isoprene Chemistry. The Principal Investigator for the project is William Vizuete and Co-PI is Jason Surratt.

Electronic Approvals:

This QAPP was approved electronically on 10/13/2016 by Elena McDonald Buller, The University of Texas at Austin.

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1. Project Description and Objectives

Isoprene, the most emitted non-methane hydrocarbon on the planet, is known to influence ozone (O_3) formation in Houston, Texas. Eastern Texas and northern Louisiana feature some of the largest biogenic emission sources of isoprene in the United States. It is also now known that the photochemical oxidation of isoprene, when mixed with anthropogenic emissions from urban areas like those found in Houston, can produce significant yields of fine particulate matter ($PM_{2.5}$) through acid-catalyzed multiphase chemistry of isoprene epoxydiols (IEPOX) that leads to secondary organic aerosol (SOA) formation. Next-generation regulatory models in Houston will attempt to capture this recent discovery even though there exists great uncertainty in both gas-phase isoprene oxidation and SOA formation chemistry.

This work will produce a fully updated condensed gas-phase mechanism based on SAPRC-07 and PM formation parameters suitable for use in a regulatory air quality model. The updated parameters will be evaluated against an archive of UNC smog chamber experiments, including new isoprene SOA experiments that investigate the effect of organic coatings/mixtures on the acid-catalyzed multiphase chemistry of IEPOX. We will also produce a regulatory air quality-modeling episode focused on Houston to test these new updates in a simulated urban environment. This will be based on an existing air quality-modeling episode developed by the Environmental Protection Agency (EPA) to explore isoprene oxidation chemistry. EPA developed the CMAQ modeling episode for a 12 km grid resolution over Houston and spans May through June 2013. This episode uses SAPRC07tic and aero6i to predict isoprene oxidation and SOA formation. Details of the implementation, model performance, meteorological inputs, and the emission inventory can be found in Pye et al., 2015.

2. Organization And Responsibilities

2.1 Project Personnel and Responsibilities

This collaborative project will be conducted under a grant from the Texas Air Quality Research Program with UNC as the lead organization. Dr. William Vizuete of UNC is serving as Principal Investigator with overall responsibility for the research and associated quality assurance. The project will be overseen by AQRP Project Manager Dr. Elena C. McDonald-Buller. The scientists working on this project and their specific responsibilities are listed in Table 1.

Table 1. Project participants and their responsibilities.

Participant	Project Responsibility
Dr. William Vizuete	Principal Investigator, air quality model guidance, data analysis and reporting; Mechanism development
Dr. Jason Surratt	Co-Principal Investigator, Mechanism development; Manage smog chamber experiments, data analysis, and reporting
Dr. Avram Gold	Lead organic synthetic efforts, data analysis and reporting
Dr. Zhenfa Zhang	Conduct the synthetic chemical production
UNC Graduate Students	Conduct smog chamber experiments, simulation runs and data analysis

2.2 Project Schedule And Milestones

The specific tasks for this project were detailed in the Statement of Work (Section 1) of the project Work Plan. Table 2 summarizes the overall project schedule and Table 3 lists specific project milestones and associated deliverables.

Table 2. Project schedule

Deliverable	Due Date
Submit Work Plan with detailed budget (including Quality Assurance Performance Plan) to AQRP	September 15, 2016
Task 1- Update SAPRC-07 and Aerosol Module for Isoprene Oxidation	February 28, 2017
Task 2- Chamber Experiments: Interplay of Particle-Phase Composition, Phase, and Viscosity on IEPOX Multiphase Chemistry	February 28, 2017
Task 3- Implementation in a regulatory air quality model	June 30, 2017
Task 4a- Draft Final Report	July 30, 2017
Task 4b- Final Report acceptable to TX AQRP	August 30, 2017

Table 3. Project Timeline

Project Task	2016				2017							
	9	10	11	12	1	2	3	4	5	6	7	8
Submit Work Plan with detailed budget (including Quality Assurance Performance Plan) to AQRP	██											
Task 1- Update SAPRC-07 and Aerosol Module for Isoprene Oxidation	██	██	██	██	██	██						
Task 2- Chamber Experiments: Interplay of Particle-Phase Composition, Phase, and Viscosity on IEPOX Multiphase Chemistry	██	██	██	██	██							
Task 3- Implementation in a regulatory air quality model							██	██	██			
Task 4a- Draft Final Report										██		
Task 4b- Final Report acceptable to TX AQRP											██	

3. Model Selection

To help mitigate the risk of implementation we have chosen a regulatory CMAQ modeling episode already developed by the Environmental Protection Agency (EPA) to explore isoprene oxidation chemistry[1]. EPA developed the CMAQ modeling episode for the horizontal domain shown in Figure 1. The simulation has a 12 km grid resolution over Houston and spans May through June 2013. This episode uses SAPRC07tic and aero6i to predict isoprene oxidation and SOA formation. Details of the implementation, model performance, meteorological inputs, and the emission inventory can be found in Pye et al., 2015. With this modeling platform it is our goal to quantify the impacts on gas
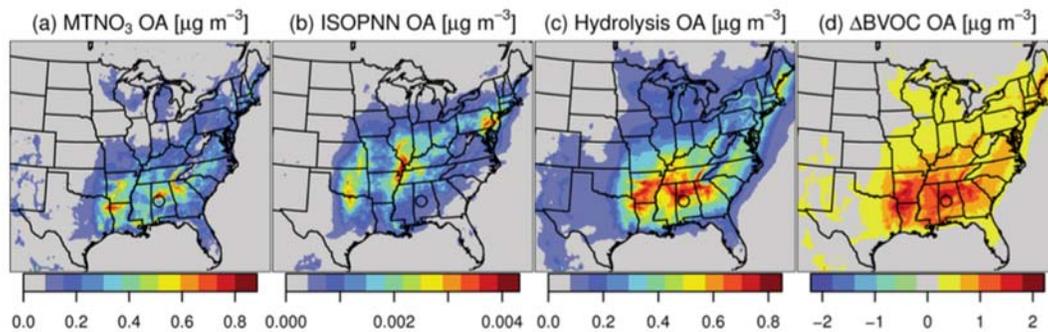

Figure 1. Predicted concentration (a) of monoterpene nitrate SOA, (b) of isoprene nitrate SOA, (c) of SOA from hydrolysis of nitrates, and (d) change in BVOC SOA compared to base CMAQ v5.0.2+ without explicit pON SOA. τ = 3 h pseudohydrolysis (Pye et al. 2015).

and particle phase concentrations from our proposed changes in the gas and aerosol algorithms relative to this base simulation. Our analysis will look at absolute changes in

species concentration and PM concentrations similar to what is shown in Figure 1. Since CMAQ is process analysis enabled, we will also use UNC process analysis software to quantify changes in radical and nitrogen budgets.

Ideally, we would use the Comprehensive Air quality Model with extensions (CAMx) system for episodes developed for Texas. This path would require more time and resources, development work to ensure implementation of new parameters, and has a greater risk of encountering unknown barriers. Members of this team have had extensive experience with the CMAQ model and its output is compatible with all UNC advanced analysis software. By leveraging the EPA work we can focus on analysis of the sensitivity to changes in parameters from our proposed work. As shown in Figure 1 this modeling system is sensitive to changes in isoprene oxidation chemistry. When compared with the base simulation there was an increase in predicted concentration of isoprene nitrate SOA and a change in total biogenic derived (BVOC) SOA by as much as 2 μg m^{-3} [1]. Members of this proposal have ongoing collaborations with EPA scientists involved in this research and we have gained permission by EPA to use the model. Given our current working relationship and existing modeling framework we feel we can accomplish this task in the timeframe provided.

4. Model Calibration

The following describes our calibration approach to produce a condensed gas-phase chemical mechanism suitable for use in a regulatory air quality model. For this work the Morphocule kinetics simulation software (Morpho) will simulate all archived and new UNC smog chamber gas phase experiments. These archived smog chamber experiments are needed to complete Task 2 and evaluate the results of our new mechanism. The data produced by these experiments have already been used to evaluate a chemical mechanism's ability to predict ozone and other chemical formation products. The experiments include a mixture of nitrogen oxides (NOx) and various volatile organic carbons (VOCs) ranging from single species to urban mixtures. These urban mixtures each contain 16 to 54 species, ranging in varying complexity from simple alkanes and alkenes to various carbonyls and aromatics The average urban atmosphere is Overall, 40 experiments (16 characterization runs and 24 isoprene runs) were conducted in the UNC Dual Gas-phase Chamber (Pittsboro, NC), where the real-time concentration of NO$_x$, VOCs and O$_3$ can be measured accurately. Environmental parameters including temperature, relative humidity, and light intensity were also monitored to compute chemical and photochemical reaction rates.

In these comparisons we will complete an operational evaluation including statistical and graphical analyses that does a comparison of predicted and observed concentrations of ozone, nitrogen oxide (NO), nitrogen dioxide (NO$_2$), and the NO to NO$_2$ crossover time. For this analysis we will produce mean bias (MB), mean (gross) error (ME/MGE), root mean square error (RMSE), normalized mean bias (NMB), normalized mean error (NME), (mean fraction bias (MFB/FB), (Mean) fractional error (MFE/FE), and correlation

coefficient (R^2). These metrics and their formulas were based on recommendations made by the U.S. EPA in their 2014 "Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5, and Regional Haze" document. The formulas are listed in Table 4. We will also represent data graphically as time series and scatter plots.

The goal of this analysis is to calibrate the new chemical mechanism using the metrics described above. The calibration will be made by comparing the performance of the new mechanism against the original unmodified SAPRC07 mechanism. Previous additions of isoprene chemistry to SAPRC07 have resulted in increases in bias of ozone by up to 9.4%. Our goal will be to reduce this increase in bias by half. This model performance should be sufficient to achieve our stated goal of using this mechanism in a CMAQ model.

Table 4. Definition of statistical metrics excerpted from the U.S. EPA in their 2014 "Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5, and Regional Haze" document.

Abbreviation	Term	Definition
MB	mean bias	$\dfrac{1}{N}\sum (M_i - O_i)$
ME	mean error	$\dfrac{1}{N}\sum |M_i - O_i|$
RMSE	root mean squared error	$\sqrt{\dfrac{\sum (M_i - O_i)^2}{N}}$
FB	fractional bias	$100\% \times \dfrac{2}{N}\sum \dfrac{(M_i - O_i)}{(M_i + O_i)}$
FE	fractional error	$100\% \times \dfrac{2}{N}\sum \dfrac{|M_i - O_i|}{(M_i + O_i)}$
NMB	normalized mean bias	$100\% \times \dfrac{\sum (M_i - O_i)}{\sum O_i}$
NME	normalized mean error	$100\% \times \dfrac{\sum |M_i - O_i|}{\sum O_i}$
r^2	coefficient of determination	$\left(\dfrac{\sum_1^N \big((M_i - \bar{M}) \times (O_i - \bar{O})\big)}{\sqrt{\sum_1^N (M_i - \bar{M})^2 \sum_1^N (O_i - \bar{O})^2}}\right)^2$

M_i = modeled concentration i. O_i = observed concentration i. N = number of paired obs/model concentrations. $\bar{M}$ = mean modeled concentration. $\bar{O}$ = mean observed concentration.

For this work we will also rely on box models developed at UNC to determine updates in aerosol algorithms. In these comparisons we will complete an operational evaluation including statistical and graphical analyses that does a comparison of predicted and observed concentrations of chamber-generated IEPOX SOA, as recently demonstrated

in our published work (Riedel et al., 2016). For this analysis we will produce mean bias (MB), mean (gross) error (ME/MGE), root mean square error (RMSE), normalized mean bias (NMB), normalized mean error (NME), (mean fraction bias (MFB/FB), (Mean) fractional error (MFE/FE), and correlation coefficient (R^2). We will also represent data graphically as time series and scatter plots. These metrics and their formulas were based on recommendations made by the U.S. EPA in their 2014 "Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5, and Regional Haze" document. The formulas are listed in Table 4.

5. Model Verification

CMAQ output will be evaluated against all measurements collected during the May-June 2013 time frame. This includes all gas- and particle-phase measurements from the TCEQ surface-monitoring network in the Houston Galveston Brazoria non-attainment region. For our gas-phase analysis we will include hourly averages of NO, NO_2, and ozone. For the particle analysis we will rely on $PM_{2.5}$ concentrations and particulate OC measurements if they are available. For this analysis we will first complete an operational analysis and produce mean bias (MB), mean (gross) error (ME/MGE), root mean square error (RMSE), normalized mean bias (NMB), normalized mean error (NME), (mean fraction bias (MFB/FB), (Mean) fractional error (MFE/FE), and correlation coefficient (R^2). We will also represent data graphically as time series and scatter plots.

In addition to this operational analysis we will also do a preliminary diagnostic evaluation. The goal will be to determine whether the model correctly represented the chemical processes. We will extract the diagnostic chemical processing information through the use of process analysis tools already included in the air quality model. The output of process analysis will be inputted into our UNC developed software so that we can quantify changes in radical and nitrogen budgets.

We will also evaluate model output against particle-phase measurements taken during the Southeast Atmosphere Study (SAS) that took place during the summer of 2013. This project will include documentation that will include where the SAS data was obtained and references used for QA/QC protocols. From SAS we will use SOA tracers of IEPOX chemistry as well as total $PM_{2.5}$ and particulate OC data collected at three ground sites during the Southern Oxidant and Aerosol Study (SOAS). The three ground sites include the Centreville (CTR), AL and Birmingham (BHM), AL ground sites, which are apart of the SouthEastern Aerosol Research and Characterization (SEARCH) Network, as well as the Look Rock (LRK), TN site. SOA tracer data of IEPOX chemistry as well as $PM_{2.5}$ and particulate OC mass have been published by our group (Rattanavaraha et al., 2016; Budisulistiorini et al., 2015). CTR is a regionally representative rural site to the southwest of BHM. The BHM site is located in downtown BHM. Finally, LRK is a ridge-top site located on the northwestern edge of the Great Smoky Mountains National Park (GSMNP) downwind of Maryville and Knoxville and small farms with animal grazing area. LRK is also considered a regional background site like that of CTR. Comparisons will be made of predicted and observed concentrations of organic carbon and IEPOX SOA tracers for all sites. It is worth noting that all of the IEPOX-SOA tracers will be quantified using synthesized standards or surrogate standards, as previously described by Rattanavaraha et al. (2016). For this particle phase analysis we will first complete an

operational analysis and produce mean bias (MB), mean (gross) error (ME/MGE), root mean square error (RMSE), normalized mean bias (NMB), normalized mean error (NME), (mean fraction bias (MFB/FB), (Mean) fractional error (MFE/FE), and correlation coefficient (R^2). We will also represent data graphically as time series and scatter plots.

The objective of this task is implementation of an updated isoprene aerosol and gas phase parameters in a regulatory air quality model. Verification will include quality assurance of the implemented parameters and model evaluation. The quality assurance and model evaluation process will consist of evaluation of expected model behavior when comparison with observed values using the metrics described above. Should large deviations from expected behavior, or observed phenomena, occur we will then complete a more detailed analysis of model processes to ensure that the result is not an implementation artifact.

6. Model Documentation

Details of the implementation, model performance, meteorological inputs, and the emission inventory of the base model can be found in Pye et al., 2015. We will provide documentation justifying the changes in gas phase and particle phase algorithms. This will include underlying assumptions, parameter values, and output of model runs and interpretation. We will also ensure that model documentation includes summaries of the input file values that were changed, the boundary conditions, and why the changes were made; the analysis of the output files, and any other important instructions required for replicating each run.

7. Scientific Approach

7.1 Experimental Design

Chamber experiments needed to evaluate the project objectives will be conducted in an indoor 10-m^3 flexible Teflon chamber at UNC. Prior to the start of each experiment, the chamber will be flushed continuously with clean house air for over 24 h corresponding to a minimum of 5 chamber volumes. A scanning mobility particle sizer (SMPS) system equipped with a cylindrical differential mobility analyzer (DMA, Model 3081, TSI, Inc.) and a condensation particle counter (CPC, Model 3022, TSI, Inc.) will be used to measure aerosol size distributions and particle volume concentrations inside the chamber. Chamber background aerosol concentrations will be monitored before all experiments to ensure that there is no pre-existing aerosol in the chamber.

To investigate the impact of organic coatings/mixtures on reactive uptake of IEPOX, stabilized acidified ammonium sulfate aerosol will then be coated by the condensation of oxidized products of either α-pinene (Sigma-Aldrich; > 99%) ozonolysis, OH-initated oxidation of toluene (Sigma-Aldrich; > 99%) (a model aromatic VOC typically most abundant in urban air)[2], or OH-initiated oxidation of dodecane (Sigma-Aldrich) (a model alkane VOC typically quite abundant in urban air) prior to IEPOX injection[3]. The

oxidation of these VOCs were selected since they will lead to varying O:C ratios, resulting in varying viscosities of the aerosol mixtures[2]. Since organics can affect the phase state (viscosity) of pre-existing aerosol, their presence within acidic sulfate aerosol could lower the diffusion rate of gaseous IEPOX and therefore determine whether if it is confined to the surface region of a particle or alternatively can proceed in the interior. As a result, the presence of organics within acidic sulfate aerosol could lower the aerosol yields previously measured on pure inorganic aerosols[4]. For -pinene ozonolysis, approximately 300 ppb of ozone will be added after the acidic sulfate aerosol injection, then 2 or 5 0.15 μL injections of -pinene will be made. Nucleation of α-pinene ozonolysis products is prevented by multiple injections of -pinene[5]. For OH-initiated oxidation of toluene and dodecane, OH radicals will be formed from the ozonolysis of tetramethylethylene (TME, Matheson) in darkness, as done in previous studies[6-8]; specifically, O_3 (1.4−1.6 ppm) will be injected into the chamber using an O_3 generator (Model L21, Pacific ozone) and followed by addition of a continuous flow of TME (1×10^9 molecule cm^{-3} s^{-1}). Under these conditions we can produce $3-4 \times 10^6$ molecule cm^{-3} of OH radicals in our chamber, which is an atmospherically relevant level.

After the acidic sulfate aerosol are coated/mixed with their respective SOA types described above and stabilized (well mixed), IEPOX will then be injected into the chamber for 2 h by passing 4 L min^{-1} of N_2(g) through a glass manifold heated at 60 ⁰C containing 50–300   L of a 100 mg mL^{-1} ethyl acetate solution of *trans*- -IEPOX, the predominant IEPOX isomer[9]. Chamber aerosol number distributions, which will be subsequently converted to total aerosol surface area and volume concentrations, will be measured by a scanning electrical mobility system (SEMS v5.0, Brechtel Manufacturing Inc.– BMI) containing a differential mobility analyzer (DMA, BMI) coupled to a mixing condensation particle counter (MCPC Model 1710, BMI). On completion of IEPOX injection and stabilization of aerosol size distribution, a filter sample will be collected for offline chemical analysis of the chamber-generated SOA. Aerosols will be collected onto 46.2mm Teflon filters (part no.: SF17471, Tisch Scientific) in a stainless-steel filter holder for 2 h at 15 L min^{-1} with a carbon strip denuder (Sunset Labs) upstream of the filter holder. Filters will be stored in 20 mL scintillation vials at -20 ⁰C prior to extraction and chemical analysis. An iodide-adduct high-resolution time-of-flight chemical ionization mass spectrometer (HR-TOF-CIMS, Aerodyne Research Inc.) will be used to continuously monitor IEPOX gas-phase concentrations as well as oxidation products of   -pinene, toluene, or dodecane[4, 10]. Recently, we demonstrated that the Filter Inlet for Gases and AEROsol (FIGAERO) coupled to HR-TOF-CIMS can measure the volatility of IEPOX-derived SOA[11], which will also add in assessing the effect of organic coatings/mixtures on IEPOX uptake. As described in our previous studies[4], IEPOX-derived SOA components will be extracted from filters with high-purity methanol prior to chemical analysis by GC/EI-MS and UPLC/ESI-HR-QTOFMS.

Control experiments will be conducted to determine wall losses of aerosol and of IEPOX. Further, we will conduct uptake experiments of IEPOX on pure organic aerosols derived from   -pinene ozonolysis and OH-initiated oxidations of toluene and dodecane. These experiments will provide further insights into the affect of organics on IEPOX multiphase chemistry, especially when compared to our previous AQRP work on pure inorganic aerosols and on the newly proposed mixed organic/sulfate aerosol.

All of the experimental parameters to be measured from the proposed set of indoor chamber experiments are described in Table 5 and are needed for the proposed model development and testing. These experiments will be conducted in the Surratt Lab at

UNC in the Department of Environmental Sciences & Engineering, which is located in 0016 Michael Hooker Research Center.

7.2 Process Measurements

Specific target analytes include aerosol size distributions, gaseous IEPOX, inorganic aerosol composition (i.e., sulfate, ammonium, and magnesium), and SOA chemical composition. For the latter this includes known molecular tracers for IEPOX-derived SOA (i.e., 2-methyltetrols, C_5-alkene triols, organosulfates, 3-methyltetrahydrofuran-3,4-diols, and dimers). For all of these analytes, we will use the instrumentation, which has been used successfully in prior work, listed in Table 5.

Table 5. Measurements from Proposed Indoor 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 calcualting aeosol 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]

[a]Described in detail in Zhang et al. (2011, ACP)

[b]Described in detail in Lund et al. (2013, Inhal. Toxic.)

[c]Described in detail in Bertram et al. (2011, AMT)

[d]Described in detail in Lin et al. (2012, ES&T) and Lin et al. (2013, PNAS)

7.3 Test Conditions

Shown in Figure 2 is a schematic simply highlighting our general approach in conducting the indoor chamber experiments needed to accomplish the project objectives outlined in the proposal. In this schematic we show IEPOX as an example. Step 1 in all of our experiments is to inject a known amount of seed aerosol. We do this by atomizing (nebulizing) an aqueous solution of 0.6 M $(NH_4)_2SO_4$ or 0.6 M $(NH_4)_2SO_4$ + H_2SO_4, representing the more "neutral" and "acidic" aerosol cases, respectively.
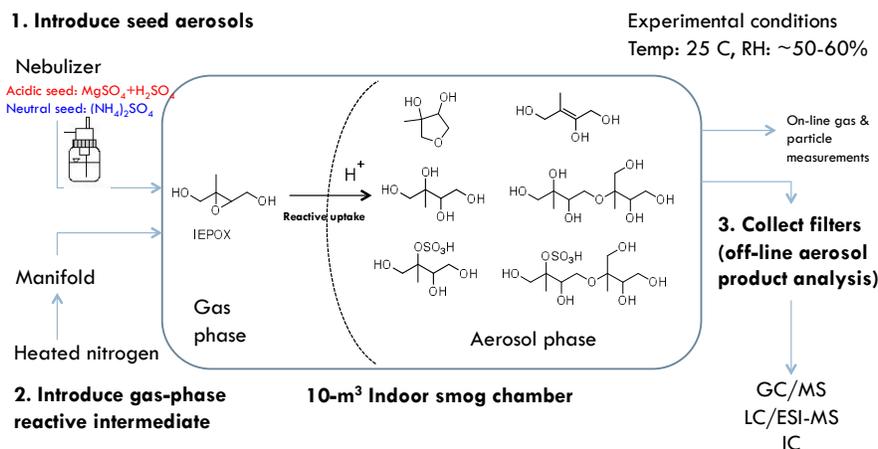
Figure 2. Schematic summarizing our general approach and test conditions using IEPOX as an example.

Seed aerosol will be atomized into the chamber using a home-built nebulizer at a flow rate of 4 L min^{-1} until a total aerosol mass concentration of 20-30 μg m^{-3} is achieved. Experiments will be conducted at a relative humidity of 50-60%. Temperature and RH inside the chamber will be monitored using an OM-62 temperature relative humidity data logger (OMEGA Engineering, Inc.). Synthesized *trans*-β-IEPOX (15 mg) will next be introduced (step 2 from Figure 2 above) into the chamber by flowing high-purity N_2 gas through a warm manifold heated to ~70 °C (manifold wrapped in aluminum foil, heating tape and heat resistant fabric) at 2 L min^{-1} for 4 hours. Synthesis procedures for *trans*-β-IEPOX have been published by from our research group [12, 13]. Following 4 hours of reaction after SOA stabilizes, aerosol samples will be collected onto Teflon membrane filters (47 mm diameter, 1.0 μm pore size; Pall Life Science). Filter sampling (Step three above in Figure 2) will be conducted at a flow rate of 25 L min^{-1} for two hours. Exact mass loadings on the filters will be determined based on calculations of total volume sampled multiplying by the average mass concentrations of aerosols during the sampling period, assuming a density of 1.25 g cm^{-3} for IEPOX-derived SOA (i.e. isoprene low-NO_x SOA) to convert measured volume concentrations to mass concentrations [14]. Following collection, filter samples will be stored in 20 mL scintillation vials at -20°C and under darkness until analysis. Samples from the filters will be extracted with methanol, and subsequently analyzed chemical measurements to examine and quantify the molecular features of resultant SOA constituents.

8. Sampling Procedures

8.1 Site Specific Factors

The only site-specific factor that needs to be considered is regarding the use of a 10-m^3 Teflon smog chamber. Other labs might use larger or small smog chambers, and thus, rates of aerosol wall loss and epoxide wall loss could be different. As a result, this is why we proposed the need to conduct epoxide only and seed aerosol only experiments. Our chamber is operated as a batch reactor, and thus, if other labs were to try and reproduce our conditions, they would need to refrain from using a steady-state reactor. For aerosol sampling, all of our sampling ports are stainless steel and our sampling lines for gaseous epoxide sampling are Teflon lines. For the collection of aerosol samples for post chemical analyses, we use Teflon membranes.

8.2 Sampling Procedures
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Gas Chromatography/Mass Spectrometry (GC/MS) Analysis for IEPOX-derived SOA tracers: Samples from teflon filters collected from the indoor chamber experiments will be extracted with 20 mL of high-purity methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) under 45 min of sonication. Filter extracts will be blown dry under a gentle N_2 stream at room temperature. When the extraction solvents are completely

removed, the residues will be trimethylsilylated by reacting with 100 µL of BSTFA + TMCS (99:1 (v/v), Supelco) and 50 µL of pyridine (99.8%, Sigma-Aldrich). The reaction mixture will be allowed to heat at 70 °C for 1 hr, and followed by subsequent GC/EI-MS analysis within 24 hr after extractions. An HP 5890 Series II Gas Chromatograph interfaced to an HP 5971A Mass Selective Detector will be used for the GC/EI-MS analyses. An *Econo-Cap™-EC™-5* Capillary Column (30m×0.25mm i.d.; 0.25µm film thickness) is used to separate the trimethylsilyl(TMS)-derivatives before MS detection. Approximately 1 µL of each derivatized sample will be injected onto this GC column. Detailed operating conditions of the GC/EI-technique are described previously in a number of publications from our lab [13, 15]. This technique will be used to quantify all observed non-organosulfate SOA compounds. Isoprene-derived SOA standards (including the 2-methyltetrols, cis- and trans-3-MeTHF-3,4-diols, and the IEPOX-derived organosulfate) produced by our lab will be used to generate 6-point calibration curves.

Ultra Performance Liquid Chromatography interfaced to Electrospray Ionization High-Resolution Quadrupole Time-of-Flight Mass Spectrometry (UPLC/ESI-HR-QTOFMS): Organosulfates from IEPOX reactive uptake on sulfate aerosol will be chemically characterized by UPLC/ESI-HR-Q-TOFMS [13, 15]. An Agilent 6500 Series Accurate-Mass Q-TOF LC/MS will be operated in the negative ion mode. A Waters ACQUITY ultra performance liquid chromatography (UPLC) high-strength silica (HSS) T3 column (2.1×100mm, 1.8 µm) will be used for chromatographic separations. Samples from teflon filters are extracted in the same manner as those for GC/EI-MS analysis. After the filter extracts are blown dry using high-purity N_2 gas at room temperature, the extract residues will be reconstituted with 150 µL of a 50:50 (v/v) solvent mixture of methanol containing 0.1% acetic acid (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and water containing 0.1% acetic acid (LC-MS CHROMASOLV-grade, Sigma-Aldrich), as the same composition of liquid chromatography/mass spectrometry (LC/MS) mobile phase solutions. Detailed UPLC/ESI-HR-Q-TOFMS operating conditions can be found in Zhang et al. (2011)[16] and in Appendix 1. At the beginning of each analysis period, the Q-TOFMS instrument will be calibrated using a commercially available electrospray ionization-low (ESI-L) concentration tuning mixture (Agilent Technologies), which is composed of a 95:5 (v/v) solvent mixture of acetonitrile and water. This external calibration will be done in the low-mass range (m/z< 1700). Six specific ions will be used from the commercial tuning mixture during calibration, and include: 112.985587, 301.998139, 601.978977, 1033.988109, 1333.968947, and 1633.949786 Da. During the chromatographic runs, the Q-TOFMS will be continually calibrated by the constant injection of the following reference compounds in the ESI source: purine, leucine enkephalin, and HP-0921 acetate adduct (Agilent Technologies). Furthermore, synthetic organosulfates standards will be used to generate 6-point calibration curves for the compounds we observe from chamber experiments. Data will be acquired and analyzed by Mass Hunter Version B.03.01 Build 3.1.346.0 software.

Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometry (CI-HR-TOFMS): Teflon sampling lines will be short to ensure IEPOX are measured with minimal losses from the indoor chamber. CI-HR-TOFMS pressure is checked before collection of IEPOX to ensure no leaking is occurring. Ion molecule reaction (IMR) and short-segment quadrupole (SSQ) pressures are set to 74 and 1.8 mbar respectively before measurements then checked right before injection ("sweet spot" for reagent ion signal). All pressures within the MS are also recorded during measurements. Turbo pump power and temperature are recorded and checked before measurements. The MS will be mass calibrated, baseline set, threshold set, and single ion area checked to make

sure we are within 80% (threshold area/raw area); if not within 80% MCP voltage is changed. One hour of background/clean air is regularly (every day) recorded to provide blank controls. Post-processing controls: mass calibration is adjusted to exact masses (accuracy is +/- < 4ppm); peak shape is defined for each MS set; resolution is defined for each MS set; baseline is calculated for each MS set. The CI-HR-TOFMS will be calibrated using synthetic *trans-* -IEPOX standards. The calibration will be done by injecting known amounts of these epoxides into the indoor chamber and then diluting down to make a 6-point calibration curve. Furthermore, we will also use a home-built diffusion system to check the accuracy of our calibrations. Before each experiment, we will sample from the clean chamber (nothing injected) to ensure there is no background organic or inorganic gaseous present in the chamber.

Ion Chromatography (IC): Samples from teflon filters used for IC analyses will be extracted in 15 mL of high-purity water (Milli-Q, 18.2 MW). Inorganic (NO_3^-, NO_2^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}) species will be quantified with commercially available standards using a conductivity detector (Dionex, Model CDM-1). A Dionex ASM-2 autosampler will deliver samples from 0.5-mL vials to the anion (IonPac AS-11 column 4 x 250 mm, anion self-regenerating suppressor (ASRS) 300 4-mm suppressor, and sodium hydroxide eluent) or cation systems (IonPac CS12 column 4 x 250 mm, cation self-regenerating suppressor (CSRS) 300 4-mm suppressor, and methanesulfonic acid eluent). Samples will be injected onto either the anion or cation system via 50-mL sample loops. Anion chromatography will be conducted using a Dionex GPM-1 gradient pump, where the eluents consisted of (A) water (Milli-Q, 18.2 MW   B   mM NaOH, and (C) 30 mM NaOH. The applied 30-min gradient elution program will be as follows: the concentration of eluent A will be at 90% and eluent B will be at 10% for first 4 min, eluent B will then be increased to 100% for the next three minutes, and then eluent C will be increased to 100% for the final 23 min. The regenerant for anion chromatography will be 25 mM sulfuric acid (H_2SO_4). Cation chromatography will be conducted using isocratic elution, where 20 mM methanesulfonic acid will be used as the eluent. The regenerent for cation chromatography will be 100 mM tetrabutylammonium hydroxide (TBAOH). For all ions of interest for these experiments, commercially available standards will be used to generate 6-point calibration curves needed for quantification.

Scanning Mobility Particle Sizer Coupled to Condensation Particle Counter (SMPS-CPC): The SMPS-CPC will set to size particles between 10–1000 nm in diameter for both up and down scans. The SMPS sheath airflow rate will be set to 5 L min^{-1} and particles will be sampled at 0.5 L min^{-1}. Particle volume concentration from each scan will be collected every 120 s, and both up and down scans were averaged to get one data point every 4 min and 30 s, which includes the scanning delay time. Monodisperse solid-particle aerosols will be generated in order to calibrate this instrument by nebulizing (or atomizing) a liquid suspension containing monodisperse solid particles of known size. Liquid suspensions of monodisperse polystyrene latex spheres (PSLs) (Duke Scientific, Palo Alto, CA) will be used for this purpose. The spheres have relative standard deviations of a few percent, are perfect spheres, and have homogeneous properties. We will use 150, 250, 300, and 450 nm standard PSLs to make sure the sizing instrument is calibrated and working properly before each experiment.

8.3 Sample Lists

We will then use 20 mL scintillation vials to store and extract the Teflon filter samples for chemical analyses by IC, GC/MS, and UPLC/ESI-HR-QTOFMS described in Table 5. These vials are also used for storing calibration standards, blanks, and laboratory controls. In addition we will use 300 L HPLC vials for storing filter extracts prepared for GC/MS or UPLC/ESI-HR-QTOFMS analyses. We will pull 1 L for sample, calibration standard, and control sample (i.e., blank filters) for the GC/MS with at least 5 repeat injections (total 5 L needed for each type). For the UPLC/ESI-HR-QTOFMS we will pull 5 L, with at least 5 repeat injections (total 25 L needed for each), for sample, calibration standard, and control sample (i.e., blank filters). The sample, calibration standard, and control sample (i.e., blank filters) amount for the IC is 0.5 mL, with at least 5 repeat injections (total 2.5 mL needed for each). The sample, calibration standard, and control sample (i.e., clean chamber) amount for the CI-HR-TOFMS is around 1 ppb of IEPOX to be above our detection limits. We sample at 1 L min^{-1} from our chamber.

8.4 Sample Preservation

Aerosol samples will be preserved by storing all collected filters under dark and frozen (-20 ^{o}C) conditions until the time of extraction and chemical analyses. These samples will be stored for no more than 2 months. Isoprene-derived SOA standards synthesized in our lab are stored under the exact same conditions. Once aerosol samples are extracted from filter samples, they will be analyzed within 1-4 days by the analytical methods described above. During this time, the extracts are kept dark and frozen until analyzed.

8.5 Sample tracking

Sample security and accountability are assured during each stage of sample processing. Each sample is assigned a unique laboratory sample number and name so that it can be identified and traced throughout the laboratory. Laboratory documentation assures analysis results traceable to valid calibrations, optimal instrument conditions, and appropriate reagents.

8.6 Shipping Samples

We will not be shipping samples outside of our lab. We label all samples with a unique laboratory sample number and name. These are then stored in our freezers until time of analyses. HPLC vials specific to GC/MS and UPLC/ESI-HR-QTOFMS are generated for the same samples to prevent cross contamination. All samples are listed in our lab notebooks, on our group Google docs page, and also backed up on each of the computers interfaced to each of our analytical methods.

9. Measurement Procedures

9.1 Process Measurements

For GC/MS we have described the process measurement procedures in detail in Lin et al. (2012, 2013) as well as in Appendix 2. For UPLC/ESI-HR-QTOFMS we have described these procedures in detail in Zhang et al. (2011) as well as in Appendix 1. For IC we have described these procedures in detail in Lund et al. (2013)[17] as well as in Section 8.2.

9.2 Calibration Procedures

If not provided in Section 9.1 or the referenced method, include specific calibration procedures, including linearity checks and initial and continuing calibration checks.

These details have been described in section 9.1.

10. Quality Metrics (QA/QC Checks)

10.1 QA/QC checks

Analytical data collected in this proposal does not fall into the TCEQ's general provisions of environmental testing laboratory accreditation and certification. The reason for this is that this project provides unique analytical data for which the commission does not offer accreditation. Specifically, this project utilizes a novel high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) equipped with iodide reagent ion chemistry to quantitatively measure in real-time the reactive uptake of isoprene epoxydiols (IEPOX) on submicron aerosols generated in a smog chamber at UNC. Furthermore, UNC is the first lab in the world to publish on the organic synthesis of IEPOX for use in the proposed studies, and thus, this compound is not commercially available

QC samples of known standards are run at standard intervals (i.e., at the beginning and ending of operation) to assure stable calibration conditions for all instrumentation. Filter blanks and filter blanks spiked with known concentrations of target analytes are prepared and handled in the same manner as samples to assure accuracy at every stage of sample testing. Surrogate spikes are performed to quantify the recovery without introducing target analytes into the process. Triplicate samples are run at standard intervals to measure precision and reproducibility of the results. Laboratory blanks provide assurance that positive results are not from sources other than the one being tested. Laboratory blanks ensure that the sampling device has been effectively cleaned. Laboratory blanks monitor lab reagents for analyte contamination.

For all processes, calibrations are done prior to all experiments and chemical analyses. Furthermore, a post-calibration is done to ensure that the calibration remains acceptable at the end of the experimental/analysis time period.

10.2 QA Objectives

No additional project-specific QA objectives are applicable to this project.

11. Data Analysis, Interpretation, And Management

11.1 Reporting Requirements

The project team will conduct experiments and collect data to help develop uptake coefficients. These tasks and underlying analyses will be summarized in the Final Report. All data obtained for this project will be stored in electronic excel format. If data are provided on paper, the paper documents will be scanned to electronic PDF files for storage.

The project team will issue a monthly report to the project management at UT and TCEQ, and a draft and fully revised final report at the end of the project. The reports will summarize the steps that have been taken for quality assurance project data and results.

11.2 Data Validation

Daily backups of all measurement data will be copied to and stored in at least two additional mediums besides the main data collection medium. Data management activities for the acquisition of new data will include procedures similar to those used for ICARTT 2004 and MILAGRO 2006, requiring reporting of the QC level of all data and documentation of all revisions. These procedures allow for documented exchange of data within the project, in order to initiate comparisons of results and to provide a second level of QA by comparison to independent measurements. All data will be archived by the PI, with appropriate time-stamping to indicate the time increment of the data. Data reporting forms will be in excel format and will contain a column for flagging and indicating the validity of quality data. Model output and other electronic data will be backed up so that the raw data is maintained for future reference. Results of this proposal will be published in the peer-reviewed literature and in the project report in order to provide broad dissemination of the final results. Proposed timelines for data sharing, policies, and formats for the SOAS study are provided in detail in the Data Plan section of this proposal. Data validation will be confirmed by the consistency of measurements against isoprene-derived SOA calibration standards and also between different experiments.

11.3 Data Summary

The data measurements will be summarized in a table that lists each physical and/or chemical parameter. The required 10% data audit will be conducted by Dr. Surratt and results reported in the final report. The audit will consist of protocols to ensure data is saved properly on our data acquisition computers and also stored in our lab notebooks and followed calibration and blank subtraction procedures.

11.3.1 Descriptive Statistics

IEPOX-SOA tracers quantified from chamber experiments will be done using isoprene-derived SOA and surrogate standards, as previously described by our group (Rattanavaraha et al., 2016; Budisulistiorini et al., 2015). Tables will be used to summarize the data, which will include mean, median, standard error, minimum and maximum values of measured IEPOX-SOA tracers produced during the new chamber experiments.

11.3.2 Inferential Method
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We will be testing the hypothesis that the pre-existing organic coatings on acidic sulfate aerosol will reduce the uptake coefficient of IEPOX compared to its uptake on pure acidic sulfate aerosol.   Comparisons between data sets will be made using an unpaired t-test with Welch's correction. Significance will be defined as $p < 0.05$

11.4 Data Storage

Data generated for this project will be securely archived during the project and stored for a period of at least five years following the completion of the project. All data obtained for this project will be stored in electronic format. If data are provided on paper, the paper documents will be scanned to electronic PDF files for storage. The University of Texas will receive an electronic copy of all data sets.

12. Reporting

12.1 List of project deliverables by participant.

Table 6. Participants and deliverables

Deliverable	Participant
Submit Work Plan with detailed budget (including Quality Assurance Performance Plan) to AQRP	Dr. Vizuete
Task 1- Update SAPRC-07 and Aerosol Module for Isoprene Oxidation	Dr. Vizuete, Dr. Surratt

Task 2- Chamber Experiments: Interplay of Particle-Phase Composition, Phase, and Viscosity on IEPOX Multiphase Chemistry	Dr. Surratt
Task 3- Implementation in a regulatory air quality model	Dr. Vizuete

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.

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

Abstract Due Date: Wednesday, August 31, 2016

Quarterly Reports: Each Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Microsoft Word 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.

Quarterly Report Due Dates:

Report	Period Covered	Due Date
Aug2016 Quarterly Report	June, July, August 2016	Wednesday, August 31, 2016
Nov2016 Quarterly Report	September, October, November 2016	Wednesday, November 30, 2016
Feb2017 Quarterly Report	December 2016, January & February 2017	Tuesday, February 28, 2017
May2017 Quarterly Report	March, April, May 2017	Friday, May 31, 2017
Aug2017 Quarterly Report	June, July, August 2017	Thursday, August 31, 2017
Nov2017 Quarterly Report	September, October, November 2017	Thursday, November 30, 2017

Monthly Technical Reports (MTRs): Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison in Microsoft Word format using the AQRP FY16-17 MTR Template found on the AQRP website.

MTR Due Dates:

Report	Period Covered	Due Date
Aug2016 MTR	Project Start - August 31, 2016	Thursday, September 8, 2016
Sep2016 MTR	September 1 - 30, 2016	Monday, October 10, 2016
Oct2016 MTR	October 1 - 31, 2016	Tuesday, November 8, 2016
Nov2016 MTR	November 1 - 30 2016	Thursday, December 8, 2016
Dec2016 MTR	December 1 - 31, 2016	Monday, January 9, 2017
Jan2017 MTR	January 1 - 31, 2017	Wednesday, February 8, 2017
Feb2017 MTR	February 1 - 28, 2017	Wednesday, March 8, 2017
Mar2017 MTR	March 1 - 31, 2017	Monday, April 10, 2017
Apr2017 MTR	April 1 - 28, 2017	Monday, May 8, 2017
May2017 MTR	May 1 - 31, 2017	Thursday, June 8, 2017
Jun2017 MTR	June 1 - 30, 2017	Monday, July 10, 2017
Jul2017 MTR	July 1 - 31, 2017	Tuesday, August 8, 2017

Financial Status Reports (FSRs): Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzione) by each institution on the project using the AQRP FY16-17 FSR Template found on the AQRP website.

FSR Due Dates:

Report	Period Covered	Due Date
Aug2016 FSR	Project Start - August 31	Thursday, September 15, 2016
Sep2016 FSR	September 1 - 30, 2016	Monday, October 17, 2016
Oct2016 FSR	October 1 - 31, 2016	Tuesday, November 15, 2016
Nov2016 FSR	November 1 - 30 2016	Thursday, December 15, 2016
Dec2016 FSR	December 1 - 31, 2016	Tuesday, January 17, 2017
Jan2017 FSR	January 1 - 31, 2017	Wednesday, February 15, 2017
Feb2017 FSR	February 1 - 28, 2017	Wednesday, March 15, 2017
Mar2017 FSR	March 1 - 31, 2017	Monday, April 17, 2017
Apr2017 FSR	April 1 - 28, 2017	Monday, May 15, 2017
May2017 FSR	May 1 - 31, 2017	Thursday, June 15, 2017
Jun2017 FSR	June 1 - 30, 2017	Monday, July 17, 2017
Jul2017 FSR	July 1 - 31, 2017	Tuesday, August 15, 2017
Aug2017 FSR	August 1 - 31, 2017	Friday, September 15, 2017
FINAL FSR	Final FSR	Monday, October 16, 2017

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. It will also include a report of the QA findings.

Draft Final Report Due Date: Tuesday, August 1, 2017

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.

Final Report Due Date: Thursday, August 31, 2017

Project Data: All project data including but not limited to QA/QC measurement data, metadata, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion (September 29, 2017). The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information. It will also include a report of the QA findings. Dr. Vizuete will retain all project data and it will be retained for a period of five years.

AQRP Workshop: A representative from the project will present at the AQRP Workshop in the first half of August 2017.

Presentations and Publications/Posters: All data and other information developed under this project which is included in **published papers, symposia, presentations, press releases, websites and/or other publications** shall be submitted to the AQRP Project Manager and the TCEQ Liaison per the Publication/Publicity Guidelines included in Attachment G of the Subaward.

13. References

1.   Pye, H.O.T., et al., *Modeling the Current and Future Roles of Particulate Organic Nitrates in the Southeastern United States.* Environmental Science & Technology, 2015. **49**(24): p. 14195-14203.
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9.   Bates, K.H., et al., *Gas Phase Production and Loss of Isoprene Epoxydiols.* Journal of Physical Chemistry A, 2014. **118**(7): p. 1237-1246.
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12.   Zhang, H.F. and R.M. Kamens, *The influence of isoprene peroxy radical isomerization mechanisms on ozone simulation with the presence of NOx.* Journal of Atmospheric Chemistry, 2012. **69**(1): p. 67-81.

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15.   Lin, Y.-H., et al., *Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive Uptake Studies with Authentic Compounds.* Environmental Science & Technology, 2012. **46**(1): p. 250-258.

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17.   Lund, A.K., et al., *The effects of alpha-pinene versus toluene-derived secondary organic aerosol exposure on the expression of markers associated with vascular disease.* Inhalation Toxicology, 2013. **25**(6): p. 309-324.

Appendix 1: Detailed Operating Conditions for Ultra Performance Liquid Chromatography interfaced to Electrospray Ionization High-Resolution Quadrupole Time-of-Flight Mass Spectrometry (UPLC/ESI-HR-QTOFMS)

Polar and oligomeric compounds found in isoprene SOA will be analyzed by UPLC/ESI-HR-Q-TOFMS. Dried residues from filter extracts will be reconstituted with 150 µL of 50:50 (v/v) solvent mixture of 0.1% acetic acid in methanol (LCMS ChromaSolv-Grade, Sigma-Aldrich) and 0.1% acetic acid in water (LC-MS ChromaSolv-Grade, Sigma-Aldrich). The reconstituted residues will be shaken and sonicated for 5 min and then stored at − 20 °C before analysis. An Agilent 6520 Series Accurate Mass Q-TOFMS instrument, equipped with an ESI source operated in the negative (−) ion mode, will be used to chemically characterize and quantify polar and acidic compounds in the filter extracts. Optimum ESI conditions require using a 3500 V capillary voltage, 100 V fragmentor voltage, 62 V skimmer voltage, 300 °C gas temperature, 10 L min⁻¹ drying gas flow rate, 35 psig nebulizer, 10 psig reference nebulizer, and 35 psig reference mass feed. The ESI-Q-TOFMS instrument will acquire mass spectra from m/z 63 to 1000. The high resolution (i.e., mass resolution will be ~ 5,000-9,000) and accurate mass capabilities in both MS and MS/MS modes make this instrument a powerful tool of structural elucidation of unknown and known isoprene-derived SOA constituents. The chromatographic separations will be carried out using a Waters ACQUITY UPLC HSS (high-strength silica) column (2.1 x 100 mm, 1.8 µm particle size) at 45 °C. The mobile phases wiil consist of eluent (A) 0.1% acetic acid in water (LC-MS ChromaSolv-Grade, Sigma-Aldrich) and eluent (B) 0.1% acetic acid in methanol (LC-MS ChromaSolv-Grade, Sigma-Aldrich). The applied 12 min gradient elution program will be as follows: the concentration of eluent B will be at 0% for the first 2 min, increased to 90% from 2 to 10 min, held at 90% from 10 to 10.2 min, and then decreased back to 0% from 10.2 to 12 min. The flow rate and sample injection volume will be 0.3 mL min⁻¹ and 5 µL, respectively. Data will be acquired and analyzed by Mass Hunter Version B.03.01 Build 3.1.346.0 software. At the beginning of each analysis period, the Q-TOFMS instrument will be calibrated using a commercially available ESI-L low concentration tuning mixture (Agilent Technologies), which will be composed of a 95:5 (v/v) solvent mixture of acetonitrile and water. This external calibration will be done in the low-mass range (m/z< 1700). Six specific ions will be used from a commercial tuning mixture during calibration, and include: 112.985587, 301.998139, 601.978977, 1033.988109, 1333.968947, and 1633.949786 Da. During the chromatographic runs, the Q-TOFMS will be continually calibrated by the constant injection of the following reference compounds in the ESI source: purine, leucine enkephalin, and HP-0921 acetate adduct (Agilent Technologies).

Appendix 2: Detailed Operating Conditions for Gas Chromatography/Mass Spectrometry (GC/MS)

Teflon filters collected from the chamber experiments will be extracted with 20 mL high-purity methanol (LC-MS CHROMASOLVgrade, Sigma-Aldrich) under 45 min of sonication. The filter extracts will be blown dry under a gentle N₂ gas stream at room

temperature. Residues will then be trimethylsilylated by reacting with 100 µL of BSTFA + TMCS (99:1 v/v, Supelco) and 50 µL of pyridine (anhydrous, 99.8%, Sigma-Aldrich). The reaction mixture will be heated at 70 °C for 1 h, and analyzed by GC/MS within 24 h after extraction. GC/MS analysis will be performed using a Hewlett-Packard (HP) 5890 Series II Gas Chromatograph coupled to a HP 5971A Mass Selective Detector. An Econo-Cap-EC- 5 Capillary Column (30 m x 0.25 mm i.d.; 0.25 µm film thickness) will be used to separate the trimethylsilyl (TMS) derivatives before MS detection. One µL of each derivatized sample will be injected onto the GC column. Helium will be used as the carrier gas at a flow rate of 0.8 mL min^{-1}. The 65.17-min temperature program of the GC will be as follows: isothermal hold at 60 °C for 1 min, temperature ramp of 3 °C min^{-1} up to 200 °C, isothermal hold at 200 °C for 2 min, temperature ramp of 20 °C min^{-1} to 310 °C, and isothermal hold at 310 °C for 10 min. The MS scan will be performed in the *m/z* 50–500 range. A solvent delay time of 7.5 min will be employed to protect the electron mulitplier (the detector) from high concentration solvent. The ion source will be operated at an electron energy of 70 eV. The temperatures of both the GC inlet and detector will be held at 250 °C.