Quality Assurance Project Plan
Project 14-003

Update and evaluation of model algorithms needed to predict particulate matter from isoprene

Dr. William Vizuete
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599
airquality@unc.edu
919-966-0693

Summary of Project

QAPP Category Number: III
Type of Project: Measurement

QAPP Requirements: This QAPP requires descriptions of project description and objectives; organization and responsibilities; scientific approach; quality metrics; data analysis, interpretation, and management; reporting; and references.

QAPP Requirements:
Audits of Data Quality: 10% Required
Report of QA Findings: Required in final report

May 29, 2014

0. TITLE AND APPROVAL SHEET

This document is a Level III Quality Assurance Project Plan for Update and evaluation of model algorithms needed to predict particulate matter from isoprene. The staff at University of North Carolina – Chapel Hill, manages this project.

QAPP was approved electronically on May 12, 2014 by UNC-CH Principal Investigator William Vizuete.

1. PROJECT DESCRIPTION AND OBJECTIVES

Terrestrial vegetation emits large quantities (~500 teragrams C) of isoprene (C_5H_8) to the atmosphere each year. Eastern Texas and northern Louisiana features some of the largest biogenic emissions of isoprene in the United States. Photochemical oxidation of isoprene leads to significant yields of gas-phase epoxide intermediates that then undergo uptake and multiphase (heterogeneous) chemistry producing low-volatility organic compounds that contribute to fine particulate matter ($PM_{2.5}$) through secondary organic aerosol (SOA) formation. The production of isoprene-derived SOA on $PM_{2.5}$ is enhanced when mixed with anthropogenic emissions from urban areas like those found in Houston. To predict SOA production from isoprene requires fundamental parameters needed to describe the efficiency with which its epoxides react on the surface or in the bulk of atmospheric particles. Recently, EPA updated the SAPRC mechanism to include the formation of known gas-phase isoprene-derived epoxides. Furthermore, we recently collaborated with the EPA to update the Community Multi-scale Air Quality (CMAQ) model to predict isoprene-derived SOA explicitly from these known isoprene-derived epoxides. This updated gas- and aerosol-phase modeling framework, however, remains to be validated against systematically conducted chamber experiments.

1.2 Project Objectives

We first propose to conduct a series of new experiments at the University of North Carolina at Chapel Hill (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 will produce a fully updated gas- and aerosol-phase box model (Morpho) and a model evaluation of isoprene SOA formation against existing UNC outdoor smog chamber experiments. This project will also deliver performance data needed to bound uncertainties in key parameters used by the Comprehensive Air Quality Model with extensions (CAMx) to predict isoprene derived SOA. This work directly addresses the stated priority area of investigating the transformation of gas-phase pollutants to particulate matter that impact Texas air quality.

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 and Texas Commission on Environmental Quality (TCEQ) Project Liaison Doug Boyer. 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, box model guidance, data analysis and reporting
Dr. Jason Surratt	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 Student	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
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

Table 3. Project Timeline

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															

3. SCIENTIFIC APPROACH

3.1 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. Either acidic or neutral seed aerosols will be introduced into the chamber by atomizing 0.06 M magnesium sulfate ($MgSO_4$)+ 0.06 M sulfuric acid (H_2SO_4) (aq) and 0.06 M ammonium sulfate ($(NH_4)_2SO_4$) (aq) solutions, respectively. Glass microliter syringes will be used to inject known amounts of reactive intermediates (*trans*-β- IEPOX and MAE) into a 10 mL glass manifold. Approximately 15 mg of IEPOX will be injected for each experiment (the mixing ratios of *trans*-β-IEPOX were □ 300 ppbv). The manifold will be wrapped with calibrated heating tapes heated to 60 ºC, and will be flushed with N_2 (preheated to 60 ºC) at 5 L min^{-1} for at least 2 h until no additional increase in aerosol volume is observed by the SMPS. After stabilization of particle

volume concentrations, aerosol samples will be collected on 47 mm diameter, 1.0-μm pore size Teflon membrane filters (Pall Life Science) for product analyses, at a sampling flow rate of □ 20 L min^{-1} for 2 h. For each experiment, two Teflon filters will be stacked in the filter holder. The front filter will be collected to examine particle-phase reaction products, whereas the back filter will be collected to correct for any gas-phase IEPOX absorption on the filters. All experiments will be carried out in the dark at a constant temperature (20–25 ºC) under dry (RH ~ 50–60%) conditions. Control experiments will also be performed to rule out potential artifacts. These will include chamber blank experiments along with addition of reactive intermediates (*trans*-β-IEPOX and MAE) or seed aerosol (i.e., acidic and neutral seed) to the chamber in isolation.

Key to the experimental approach is the availability of IEPOX, MAE, and SOA marker compounds. 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 the proposed indoor chamber experiments have been developed by the UNC group. The UNC group has published routes to the racemic IEPOX geometric isomers and IEPOX-derived SOA racers, *cis*- and *trans*-3-MeTHF-3,4-diols, as well as for MAE [1-3]. All reported syntheses yield products in high purity (> 99%), as characterized and confirmed by Nuclear Magnetic Resonance (NMR) and Mass Spectrometry (MS) analytical techniques in those studies.

All of the experimental parameters to be measured from the proposed set of indoor chamber experiments are described in Table 4 and are needed for the proposed model development and testing.

Table 4. 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)

The reason for using this experimental design is we have successfully used this to elucidate the chemical formation mechanism of isoprene SOA from reactive uptake of epoxides (i.e., IEPOX and MAE) [1, 3]. SOA constituents we generated from these indoor chamber experiments have also been detected in large quantities from ambient $PM_{2.5}$ samples collected in isoprene-rich regions. 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. The set of experiments we will conduct are summarized in Table 5 below.

Table 5. Proposed Indoor Chamber Experiments to be Conducted at UNC

Expt. #	Epoxide	[Epoxide] (ppb)	Seed Aerosol Type	Initial Seed Aerosol ($\mu g/m^3$)	RH (%)	T (^oC)
1	IEPOX	300	$(NH_4)_2SO_4$	~20-30	~50-60	~20-25
2		300	$(NH_4)_2SO_4 + H_2SO_4$	~20-30	~50-60	~20-25
3	MAE	300	$(NH_4)_2SO_4$	~20-30	~50-60	~20-25
4		300	$(NH_4)_2SO_4 + H_2SO_4$	~20-30	~50-60	~20-25
5	none		$(NH_4)_2SO_4$	~20-30	~50-60	~20-25
6	none		$(NH_4)_2SO_4 + H_2SO_4$	~20-30	~50-60	~20-25
7	IEPOX	300	none	none	~50-60	~20-25
8	MAE	300	none	none	~50-60	~20-25

Experiments 1-4 are needed to evaluate the model development proposed in this study. In addition, experiments 5-8 are control experiments needed to evaluate the wall losses of seed aerosol injected into the chamber and also the wall losses of the reactive epoxides themselves. All experiments listed in Table 5 will be conducted under dark conditions, and thus, no photochemistry will occur. Experiments will be conducted with either aqueous ammonium sulfate or acidified ammonium sulfate particles with a relative humidity of ~50-60% in the chamber to create a deliquesced less or more acidic seed aerosol type. Inorganic seed aerosol loadings will be 20-30 $\mu g\ m^{-3}$. These loadings are similar to those used previously to study IEPOX and MAE SOA formation, and are similar to atmospheric levels [3]. Epoxides will be injected into the chamber using 300 ppb as a target mixing ratio. This concentration 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 chemical ionization (CI) high-resolution time-of-flight mass spectrometer (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 will be characterized by gas chromatography (GC/MS) and liquid chromatography interfaced to both a diode array detector and a quadruopole time-of-flight mass spectrometer equipped with electrospray ionization (LC/DAD-ESI-QTOFMS), as previously demonstrated by our group [1, 3]. ***For statistical purposes, we will conduct all experiments listed in Table 5 in triplicate.*** If there is enough time remaining in the project period, we will also aim to conduct some IEPOX and MAE reactive uptake experiments (i.e., Experiments 1-4 in Table 5) at lower mixing ratios (e.g., 10-50 ppb) in order to mimic closer to atmospheric conditions. The reason we will aim for 300 ppb for

these epoxides is due to our recent work showing we produce ample amounts of SOA needed for providing ample material for the chemical characterization efforts.

3.2 Process Measurements

Process measurements include flow rate, temperature, relative humidity, aerosol size distributions, mixing ratios of *trans*-β-IEPOX and MAE, inorganic aerosol composition, SOA chemical composition and purity of synthesized standards.

Specific target analytes include aerosol size distributions, gaseous MAE and 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) and MAE-derived SOA (i.e., 2-methylglyceric acid, dimers, and organosulfates). For all of these analytes, we will use the instrumentation, which has been used successfully in prior work, listed in Table 4.

3.3 General Approach

Shown in Figure 1 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

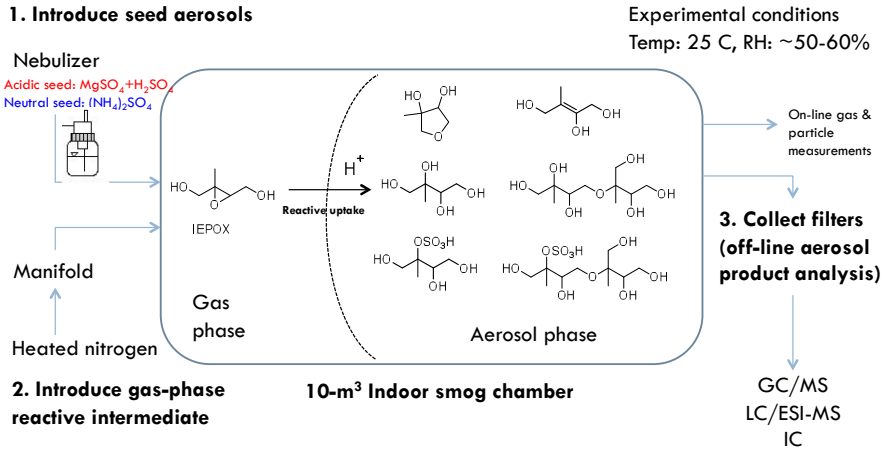

Figure 1. Schematic summarizing our general approach and test conditions using IEPOX as an example

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. 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 and MAE (15 mg) will next be introduced (step 2 from Figure 1 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 and MAE have been published by Zhang et al. (2012) and Lin et al. (2013) from our research group. 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 1) 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 [4]. 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.

4. SAMPLING PROCEDURES

4.1 Describe any known site-specific factors that may affect sampling procedures as well as all site preparation (e.g., sampling device installation, sampling port modifications, achievement of steady-state) needed prior to sampling.

The only site-specific factor that needs to be considered is we are using 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 (Experiments 5-8) listed in Table 5. 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 fro 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.

4.2 Describe or reference each sampling procedure (including a list of equipment needed and the calibration of this equipment as appropriate) to be used. Include procedures for homogenizing, compositing, or splitting of samples, as applicable.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis for IEPOX- and MAE-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 (Lin et al., 2012; Lin et al., 2013). This technique will be used to quantify all observed non-organosulfate SOA compounds. Authentic standards 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 and MAE reactive uptake on sulfate aerosol will be chemically characterized by UPLC/ESI-HR-Q-TOFMS (Lin et al., 2012; Lin et al., 2013). 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, 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). 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 these 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 and MAE are measured with minimal losses from the indoor chamber. CI-HR-TOFMS pressure is checked before collection of IEPOX or MAE 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*-β-IEPOX and MAE 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. These calibrations will be done near the time of the indoor experiments described in Table 5. 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 authentic 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, authentic 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.

4.3 Provide a list of sample containers, sample quantities to be collected, and the sample amount required for each analysis, including QC sample analysis.

For this project we will be collecting three Teflon filter samples from each condition listed in Table 5 (24 in total). 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 4. 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 or MAE to be above our detection limits. We sample at 1 L min^{-1} from our chamber.

4.4 Specify sample preservation requirements (e.g., refrigeration, acidification, etc.) and holding times.

Aerosol samples will be preserved by storing all collected filters under dark and frozen (-20 oC) conditions until the time of extraction and chemical analyses. These samples will be stored for no more than 2 months. Authentic standard compounds 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.

4.5 Describe the method for uniquely numbering each sample.

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.

4.6 Describe procedures for packing and shipping samples, including procedures to avoid cross-contamination, and provisions for maintaining chain-of-custody (e.g., custody seals and records), as applicable.

We will not be shipping samples outside of our lab. However, as described above, 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.

5. MEASUREMENT PROCEDURES

5.1. Describe in detail or reference each process measurement or analytical method to be used. If applicable, identify modifications to EPA-approved or similarly validated methods.

Please see section 4.2 for these details. For GC/MS we have described these procedures in detail in Lin et al. (2012, 2013). For UPLC/ESI-HR-QTOFMS we have described these procedures in detail in Zhang et al. (2011). For IC we have described these procedures in detail in Lund et al. (2013).

5.2. If not provided in Section 5.1 or the referenced method, include specific calibration procedures, including linearity checks and initial and continuing calibration checks.

These details have been described in section 4.2.

6. QUALITY METRICS

6.1. For each process measurement and analytical method, identify the required QC checks (e.g., blanks, control samples, duplicates, matrix spikes, surrogates), the frequencies for performing these checks, associated acceptance criteria, and corrective actions to be performed if acceptance criteria are not met.

QA/QC checks: 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.

6.2. Any additional project-specific QA objectives (e.g., completeness, mass balance) shall be presented, including acceptance criteria.

Not applicable to this project.

7. DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

7.1 Data Reporting Requirements

As summarized in Tables 2 and 3, 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.

7.2 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 authentic calibration standards and also between different experiments.

7.3 Data Summary for Reporting

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 procedures.

7.4 Data Storage

Data generated for this project will be securely archived during the project and stored for a period of at least three 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.

8. REPORTING

8.1 List of project deliverables by participant.

Table 4. Participants and deliverables

Deliverable	Participant
Task 1- Submit Work Plan with detailed budget (including Quality Assurance Performance Plan) to AQRP	Dr. Vizuete
Task 2- Integration of Gas-Phase Epoxide Formation and Subsequent SOA Formation into UNC MORPHO Box Model	Dr. Vizuete
Task 3- Synthesis of Isoprene-derived Epoxides and Known SOA Tracers	Dr. Gold
Task 4- Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides	Dr. Surratt
Task 5- Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers	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.

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.

8.2 Expected Outcome

The expected outcome of this project is to provide AQRP and TCEQ a Final Report that will include performance data needed to reduce uncertainties in SOA formation parameters needed for CAMx to simulate isoprene derived SOA. These parameters can then be used by air quality models to develop effective regulatory policies to improve air quality in Houston.

9. REFERENCES

1. 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.
2. Zhang, H. and R. Kamens, *The influence of isoprene peroxy radical isomerization mechanisms on ozone simulation with the presence of NOx.* J Atmos Chem, 2012. **in press**.
3. Lin, Y.H., et al., *Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides.* Proceedings of the National Academy of Sciences of the United States of America, 2013. **110**(17): p. 6718-6723.
4. Kroll, J.H., et al., *Secondary organic aerosol formation from isoprene photooxidation.* Environmental Science & Technology, 2006. **40**(6): p. 1869-1877.