AQRP Monthly Technical Report

PROJECT TITLE	**Update and evaluation of model algorithms needed to predict particulate matter from isoprene**	**PROJECT #**	14-003
PROJECT PARTICIPANTS	UNC-CH	**DATE SUBMITTED**	11/8/2014
REPORTING PERIOD	**From:** October 1, 2014 **To:** October 30, 2014	**REPORT #**	5

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

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

Preliminary Analysis
We are confident in the QA/QC testing of the algorithms for the predicted uptake of gaseous IEPOX onto an aerosol of variable acidity, temperature, and relative humidity.

Data Collected
We have generated simulations necessary for QA of data from the model including the predicted bulk SOA formation in our indoor chamber using reactive uptake coefficients we recently derived in flow tube studies (Gaston et al., 2014, ES&T).

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments
N/A

Goals and Anticipated Issues for the Succeeding Reporting Period
N/A

Detailed Analysis of the Progress of the Task Order to Date
N/A

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

Preliminary Analysis
We have completed all syntheses needed for the project.

Data Collected
QA/QC data verifying synthesis.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments
There are some purification issues in the synthesis of the organosulfate standards. These are being addressed and methods have been proposed.

Goals and Anticipated Issues for the Succeeding Reporting Period
We hope to have a purified organosulfate standard.

Detailed Analysis of the Progress of the Task Order to Date
We are confident that this task will be completed in time.

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

Preliminary Analysis
Our experimental plan is listed in Table 1. We continued to complete more experiments.

Table 1. Indoor experiments to be conducted at UNC.

Expt. #	Epoxide	[Epoxide] (ppb)	Seed Aerosol Type	Initial Seed Aerosol ($\mu g/m^3$)	RH (%)	T (°C)
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

0.6 M (NH4)2SO4 + 0.6 M H2SO4

Data Collected
We have collected data for completed experiments.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments
N/A

Goals and Anticipated Issues for the Succeeding Reporting Period
We expect the next 2-3 months will yield enough experimental data to evaluate with the model. This will mean completing all experiments outlined in Table 1.

Detailed Analysis of the Progress of the Task Order to Date
We are currently on schedule to complete this task in time allocated.

Task

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

Preliminary Analysis

We have used a combination of flow reactor studies and smog chamber modeling to constrain two uncertain parameters central to epoxide-derived secondary organic aerosol (SOA): the rates of epoxide heterogeneous reactions with the particle phase and the molar fraction of these uptaken epoxides that go on to contribute to the SOA burden – which we define as the SOA yield (α_{SOA}).

Data Collected

As shown in the table below flow reactor measurements of epoxide-aerosol reaction probability (ɣ) were performed on atomized aerosols. Heterogeneous reactions are often thought of in terms of the reaction probability as it is can be efficiently incorporated into regional and global models. We fit the log of the epoxide decay in the presence and absence of aerosol particles to obtain a pseudo first order rate coefficient for the wall loss and the sum of the wall loss and aerosol loss reactions which can then be converted to ɣ given the aerosol surface area concentration in the flow reactor. We chose aerosol compositions and flow reactor relative humidities to mimic previous smog chamber epoxide SOA experiments. In this way we can use both the flow reactor data and the SOA growth measured in the chamber experiments to constrain α_{SOA}.

As shown in the table below a range in α_{SOA} is estimated through the use of a time-dependent 0-D chemical box model designed to simulate the chamber experiments. We initialize the model with ɣ's from the flow reactor measurements and epoxide mixing ratios, aerosol surface area and mass concentrations from the chamber experiments. Then we vary α_{SOA} in the model to bracket the chamber-measured SOA mass growth and estimate the α_{SOA} range. This range provides an approximation of the fraction of aqueous phase epoxide reactions that produce SOA relative to the total number of aqueous phase reactions. Given these two constraints coupled with ambient measurements of epoxide concentrations and aerosol composition, we can place bounds on the epoxide contribution to SOA in the atmosphere.

Table 2. Modeling results from chamber experiments.

epoxide	aerosol	RH	aerosol [H^+] (M)*	$\gamma \pm 1\sigma$	modeled α_{SOA} range
IEPOX	$(NH_4)_2SO_4$	0.50	7.74E-05	6.5e-4 ± 6.4e-4	0.13 - 0.16
IEPOX	$MgSO_4 + H_2SO_4$	0.08	0.04	0.011 ± 0.003	0.04 - 0.06
IEPOX	$MgSO_4 + H_2SO_4$	0.53	0.73	0.0094 ± 0.003	0.03 - 0.05
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.05	2.78	0.021 ± 0.001	0.09 - 0.11
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.59	2.01	0.019 ± 0.002	0.05 - 0.07
MAE	$MgSO_4 + H_2SO_4$	0.03	0.73	4.9e-4 ± 1e-4	0.05 - 0.11
MAE	$(NH_4)_2SO_4 + H_2SO_4$	0.03	2.78	5.2e-4 ± 1.1e-4	0.14 - 0.22

*Estimated from E-AIM model calculation of moles H^+ and total volume of aqueous phase.

E-AIM RH input must be ≥0.1. Hence the same estimated [H^+] for same aerosol and RH<0.1.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

N/A

Goals and Anticipated Issues for the Succeeding Reporting Period
We will continue to simulate experiments as they become available from Task 3.

Detailed Analysis of the Progress of the Task Order to Date
We are currently on schedule to complete this task in time allocated.

Submitted to AQRP by:
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Principal Investigator: