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**	9/8/2014
REPORTING PERIOD	**From:** August 1, 2014 **To:** August 30, 2014	**REPORT #**	3

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.

Detailed Accomplishments by Task

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

Preliminary Analysis

This month we have completed our analysis of the gas phase simulations using the SAPRAC07TC chemical mechanism of our chamber experiments. We have analyzed these results and in the process of writing up results for submission to peer review journal.

We have continued our implementation of the multiphase chemistry of isoprene-derived epoxides. In the past month we continue to refine the box model, which simulates the uptake of gaseous IEPOX onto an aerosol of variable acidity, temperature, and relative humidity. These refinements have been evaluated using test experiments.

We have also made a list of essential measurements shown below in Table 1.

Table 1. Model Inputs to be measured from Indoor Smog Chamber Experiments

Variable	Description	Purpose	Instrumentation at UNC to Measure Variable
r_p	particle radius	Equations for calculating change in [$IEPOX_{gas}$] or [MAE_{gas}] for each time step	Scanning Mobility Particle Sizer (SMPS) (TSI, Inc.)[a]
A	particle surface area	Equation for heterogeneous uptake rate constant (k_{het}) for IEPOX and MAE	SMPS[a]
T	temperature	Equations for mean molecular speed of epoxides, uptake coefficient (g), and 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)

Data Collected

We have generated simulations necessary for the gas phase evaluation of the SAPRAC07TC chemical mechanism. We have also generated QA data for the multiphase box model.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

Some numerical stability issues in our calculations of model parameters that we solved.

Goals and Anticipated Issues for the Succeeding Reporting Period

We will continue to test the entire box model to verify that all portions are working together. We will use the QA code to model experiments listed in the table 2. We plan to compare the final measured concentrations of these aerosol species to the model using different proposed rate constants for the acid-catalyzed ring opening reactions.

Table 2. 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

Detailed Analysis of the Progress of the Task Order to Date
We are finishing the development of the box model needed for the rest of the project. This task is progressing as expected.

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

Preliminary Analysis
We have completed synthesis of our 2-methylglyceric acid and 2-methyltetrol standards as shown in Figure 1.

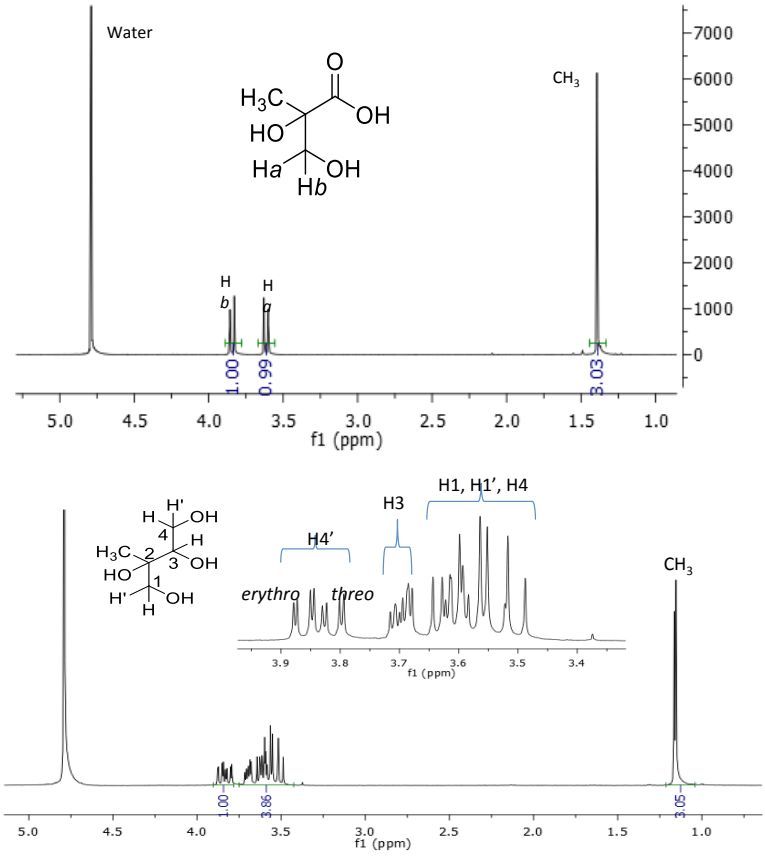


Figure 1. 1H NMR data of our (a) synthesized 2-methylglyceric acid standard and (b) 1H NMR data of our racemic standard of the 2-methyltetrols (i.e., 2-methylerythritol and 2-methylthreitol).

We have also generated GC/MS data for these two standards as shown in Figure 2.

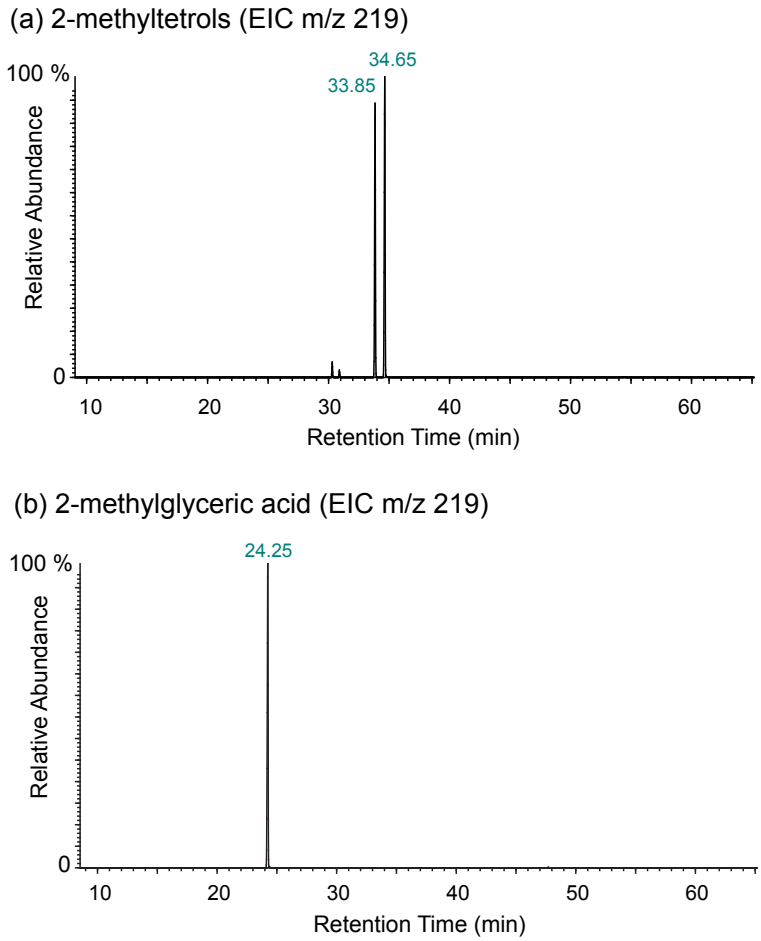


Figure 2. GC/MS data of (a) 2-methltetrols and (b) 2-methylglyceric acid.

Both the 1H NMR and GC/MS data show that these compounds are synthesized in very high purity (> 99%). We will use these next for calibration of GC/MS for quantification of SOA that we will generate in our indoor chamber. We have now completed all of our synthesis products except for the organosulfate derivatives of 2-methyltetrols and 2-methylglyceric acid.

Data Collected
From the original proposal we have completed Scheme 1 and 2.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments
None

Goals and Anticipated Issues for the Succeeding Reporting Period
We will continue to work on synthesizing Schemes 3 and 4 from the original proposal.

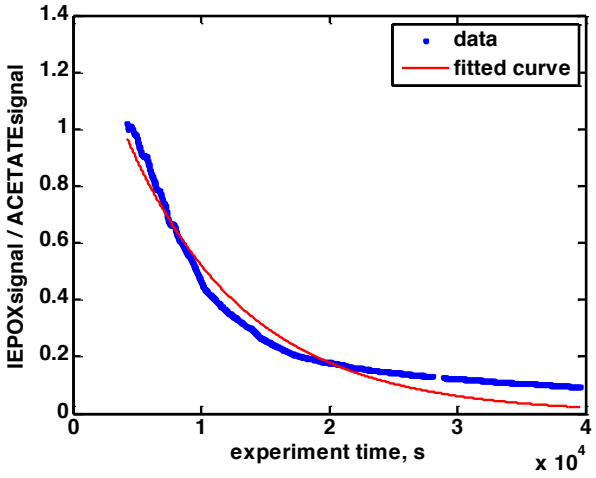
Detailed Analysis of the Progress of the Task Order to Date
Given the synthesis protocol in timing we are confident this task being completed in time for our experiments.

Detailed Accomplishments by Task

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

Preliminary Analysis

Our experimental plan is listed in Table 2. Each experiment shown in the table will be done in triplicate. In the past month we have completed 1 run each for experiments 7 and 8 listed in Table 2. The purpose of these experiments is to characterize the wall loss of gas-phase IEPOX and MAE inside our 10-m3 chamber. Figure 3 shows the measured wall loss of trans-beta-IEPOX. This was done at 50% RH under dark conditions without the presence of seed aerosol.



General model Exp1 for fit curve:
f(x) = a*exp(b*x)
Coefficients (with 95% confidence bounds):
a = 1.518 (1.49, 1.545)
b = **-0.0001067 s^{-1}** (-0.0001085, -0.0001048)

Figure 3. Characterization of Trans-b-IEPOX Wall Loss in UNC 10-m3 Indoor Smog Chamber at ~ 50% RH.

These wall loss experiments will help us account for wall losses of gaseous isoprene-derived epoxides in our box modeling of the SOA production.

Data Collected

We have collected data for experiments 7 and 8 in table 2.

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 by the model. These will include repeating the wall-loss experiments (including for IEPOX and MAE), as well as experiments outlined in Table 2.

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

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

Preliminary Analysis
N/A

Data Collected
N/A

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

Submitted to AQRP by:
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