The Effect of Oceanic Isoprene Emissions on Secondary Organic Aerosol Formation in the Coastal United States

Brett Gantt, Nicholas Meskhidze, Yang Zhang, and Jun Xu

North Carolina State University, Raleigh, NC

Contact Information:

Brett Gantt — bdgantt@ncsu.edu

Dr. Nicholas Meskhidze — nmeskhidze@ncsu.edu

Introduction:

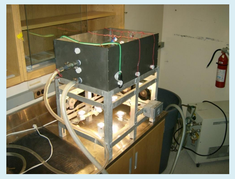
Isoprene (C_5H_8) is the most ubiquitous biogenic volatile organic carbon (BVOC) with annual global emissions estimated of 500 to 750 Tg of carbon (Guenther et al., 2006). Isoprene can be oxidized by several reactants including hydroxyl radical (OH), to form secondary organic aerosols (SOA) (Claeys et al., 2004) with a dry yield of approximately 3% (Kroll et al., 2006) and an aqueous yield of up to 42% (Ervens et al., 2008).

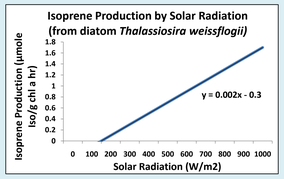
Marine isoprene emissions have been observed over productive areas of the world's oceans with high chlorophyll-a concentrations ([Chl a]). Isoprene production has been shown to be sensitive to light (Sinha et al., 2007) and species of phytoplankton present (Shaw et al, 2003). Today regional and global contributions of marine isoprene to SOA remain poorly defined.

In this study, we carry out laboratory and model simulations to determine the contribution of marine isoprene emissions to SOA concentrations in the coastal regions of the United States. The importance of productive coastal waters on trace gas emissions extends well beyond the regional scale. A study of halocarbons has shown that while coastal and coastally influenced waters make up only 10% of the ocean surface area, make up an estimated 83% of the global flux (Butler et al., 2007)

Laboratory Measurements:

Using a novel approach, we exposed several phytoplankton to various levels of light intensity to assess the effect of changing incoming solar radiation for isoprene production. Using Headspace Gas Chromatography (HS-GC), we measured the isoprene concentrations and converted into isoprene production.





Model Setup:

All simulations performed using the Community Multi-scale Air Quality (CMAQ) model and the following configuration (Zhang et al., 2007):

-Time Period: July 2001

-Domain: Continental US

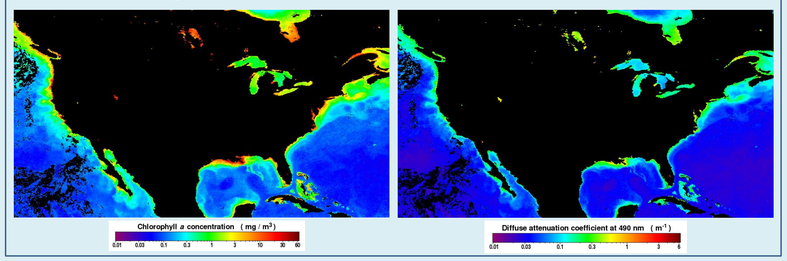
Spatial Resolution: 36 x 36 km^2

-Meteorology: Mesoscale Modeling System Generation 5 (MM5) v. 3.6.1

-Emissions: 2001 National Emissions Inventory (NEI) processed with Sparse Matrix Operator Kernel Emissions (SMOKE) v. 1.4

-Simulations: 1) Control with no marine-source isoprene emissions, 2) Control plus simulated marine-source isoprene emissions, and 3) Control plus 5x simulated marine-source isoprene emissions (to account for inter-annual changes in [Chl *a*])

Emission Inputs:



Marine Isoprene Emissions:

Inputs	Source
Chlorophyll *a* Concentration ([Chl *a*])	SeaWiFS
Diffuse Attenuation (k)	SeaWiFS
Surface Solar Radiation (I_o)	CMAQ

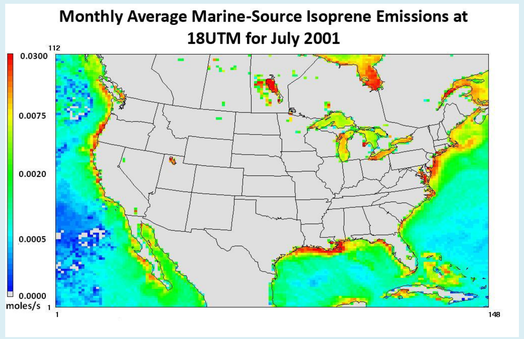
Formulas

$$P_i = 0.002I_i - 0.3$$

$$I_i = I_o \times e^{-kd}$$

$$Emissions\left(\frac{moles}{sec}\right) = 0.00036 \times [Chl\ a] \times \sum_{i=1}^{14} P_i \times D_i$$

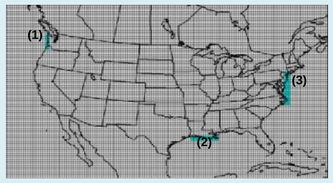
The subscript *i* represents 1 of the 14 sublayers of surface ocean where production *P*, light intensity *I*, and emissions are calculated. The width *D* of each sublayer increases with depth, and the total depth is determined by 90% light attenuation.

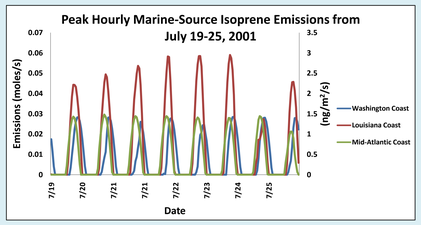


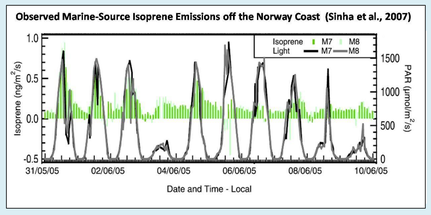
Diurnal Cycle:

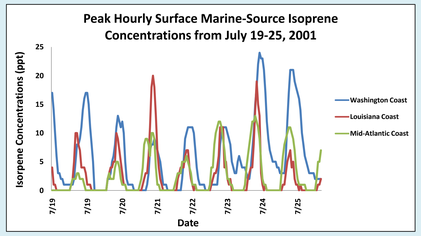
Three productive regions chosen for diurnal analysis:

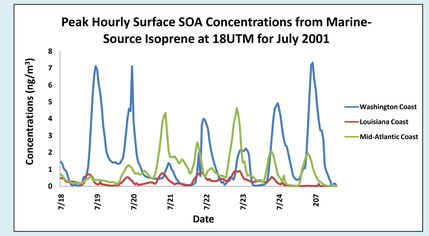
1) Washington Coast
2) Louisiana Coast
3) Mid-Atlantic Coast



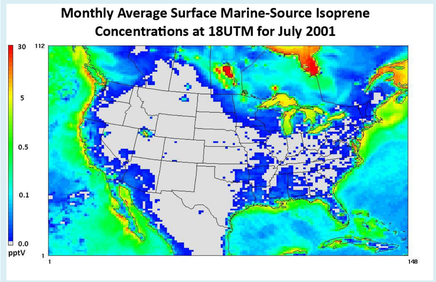


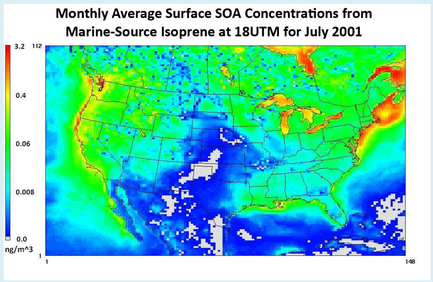




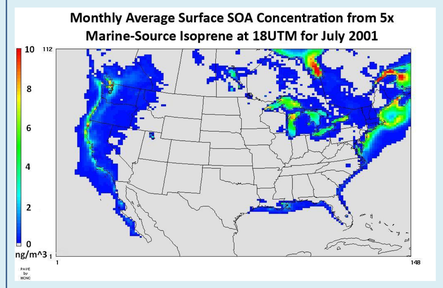


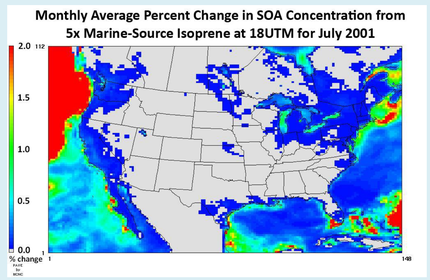
Spatial Distribution:



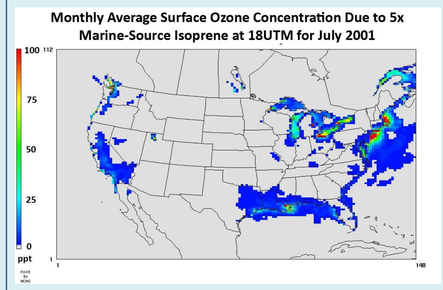


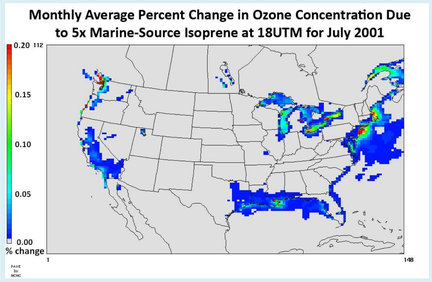
Sensitivity tests (using 5x emissions):





What about Ozone?





Conclusions:

- The model reproduces diurnal changes in isoprene emissions were captured by the model.
- Isoprene and SOA concentrations from marine emissions of isoprene are low with levels ~25 ppt and ~10 ng/m^3, respectively.
- Percent changes in SOA concentrations were low over most terrestrial areas, with modest increases of up to 5% over the coastal regions.
- Very low percent changes in O_3 concentrations occurred over terrestrial areas, with the largest increases of ~0.2% occurring over urban coastal regions.
- Despite identical marine isoprene emissions, the changes in SOA and ozone concentrations were different spatially.

Future work:

- Improve emission estimates with phytoplankton speciation and higher spatial resolution (1x1 km^2) to capture locally high phytoplankton populations such as those in estuaries.
- Examine the effect of SOA from marine-source isoprene emissions on cloud microphysical and radiative properties.

Acknowledgements:

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