Modeling Secondary Organic Aerosol Formation from Photooxidation of Isoprene in California

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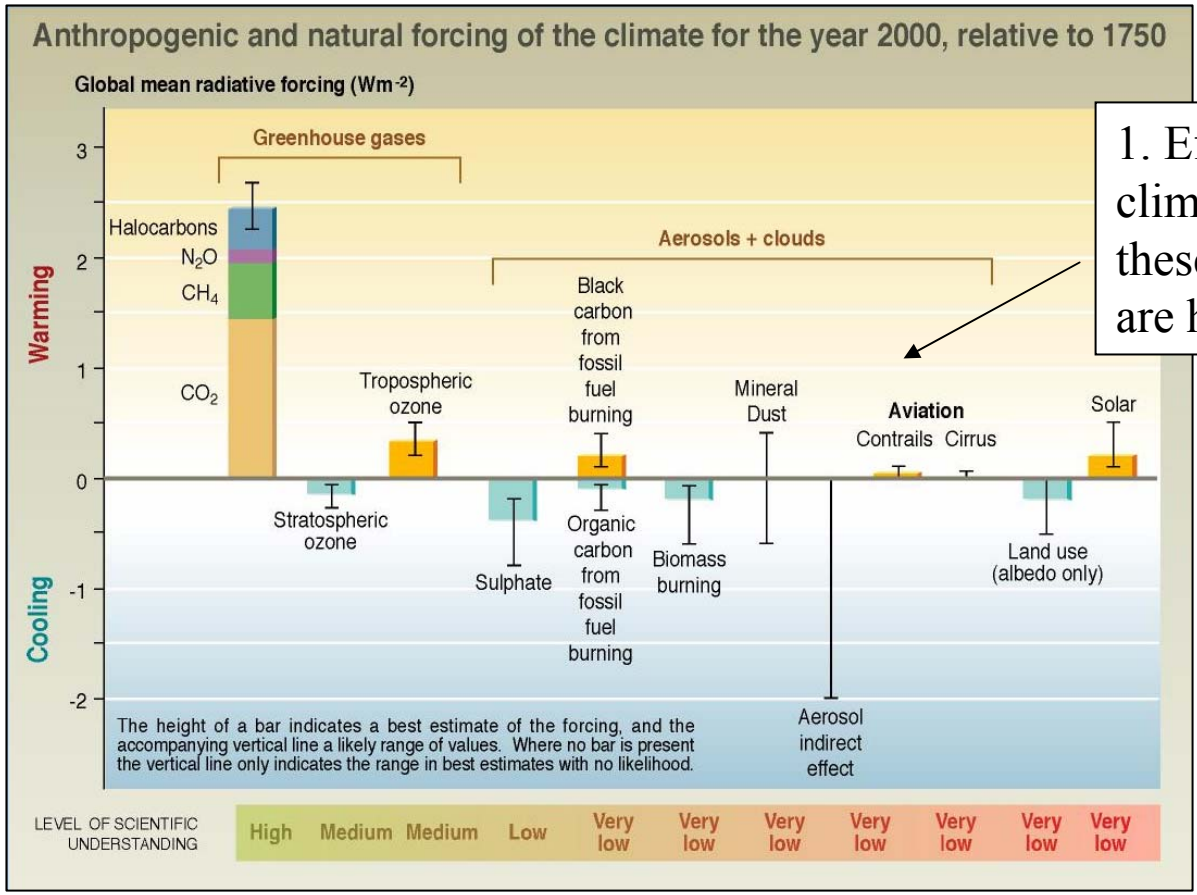
Why study aerosols?

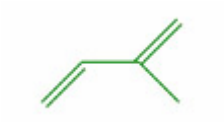


1. Effect on climate change: these error bars are huge!

2. Mitigation: Isotopic studies are suggesting that a large proportion of secondary aerosols are the product of anthropogenic oxidants *and already existent biogenic compounds*!

Secondary Organic Aerosols

Product of reactions with volatile compounds, rather than directly emitted as aerosol

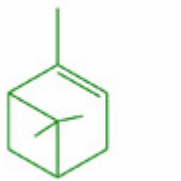


Volatile Organic Compounds (biogenic or anthropogenic)

Oxidation (OH, O_3, NO_3)

Oxidation Products

Volatile Products



Semi-volatile Products

Gas-Particle Partitioning

Polymerization

Nucleation

Secondary Aerosol

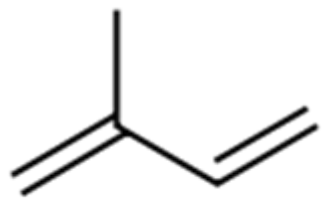
Adapted from Seinfeld, JH

Isoprene:

A Biogenic Volatile Organic Compound (VOC)

Both anthropogenic and biogenic sources

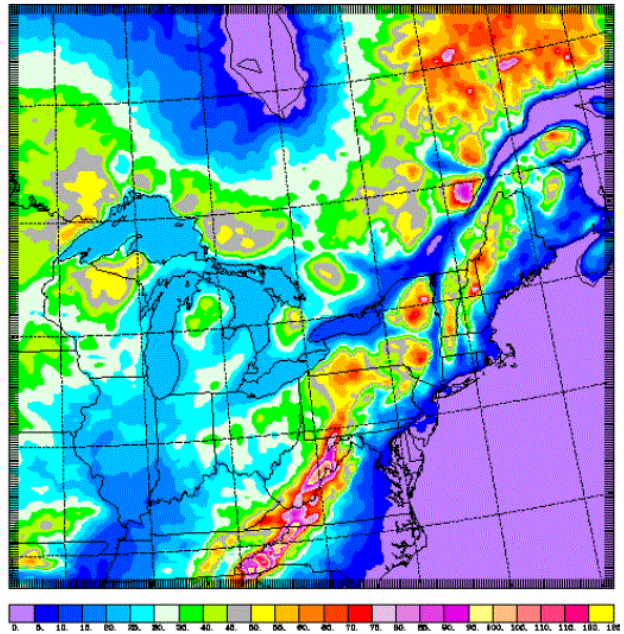
- global emissions estimated to be ~500 TgC/yr[1]
  - 44% of annual global VOC flux and more than all anthropogenic non-methane hydrocarbons combined[2]
- predominant VOC emitted by poplar, oak, willow, eucalyptus, and sycamore
  - emissions a function of land use, light and temperature



- Isoprene oxidized by OH and O_3 (day), NO_3 (night)
  - First generation products are highly volatile—don't form aerosol[1]
  - Oxidation of first generation products (like methacrolein) may lead to semi-volatile compounds [3]
- Recent work suggests heterogeneous reactions (oxidization of reaction products, polymerization, etc.) may produce a low yield of SOA[1]
  - Pathways that lead to SOA formation undetermined
    - Yield a complex function of NO_x concentration, enhanced by presence of acid

WRF-Chem

- Fully coupled meteorology and chemistry
  - emissions, transport, meteorology, chemical reactions all calculated within the same time step
  - (hopefully) provides more accurate feedback between chemistry and meteorology and therefore concentrations of chemical species

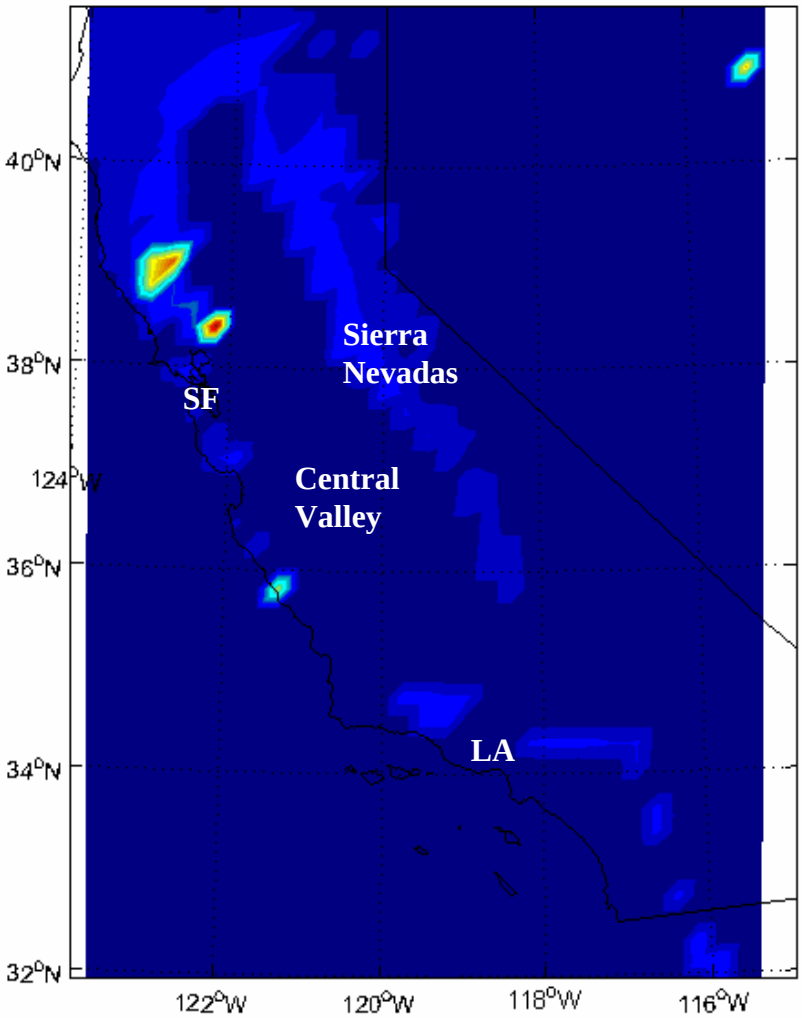


Questions

- What is the estimated yield of SOA in California from reactions of isoprene?
- Where is isoprene-derived SOA formed in California?
- Are these patterns confirmed by observational data?

What is the estimated yield?

1. Isoprene Emissions



WRF-CHEM

-200 MgC/day (**240 tonsC**) emitted during summer

- At most 0.075 TgC emitted/year (does not correct for reduced winter emissions)

California Air Resources Board (CARB)[4]

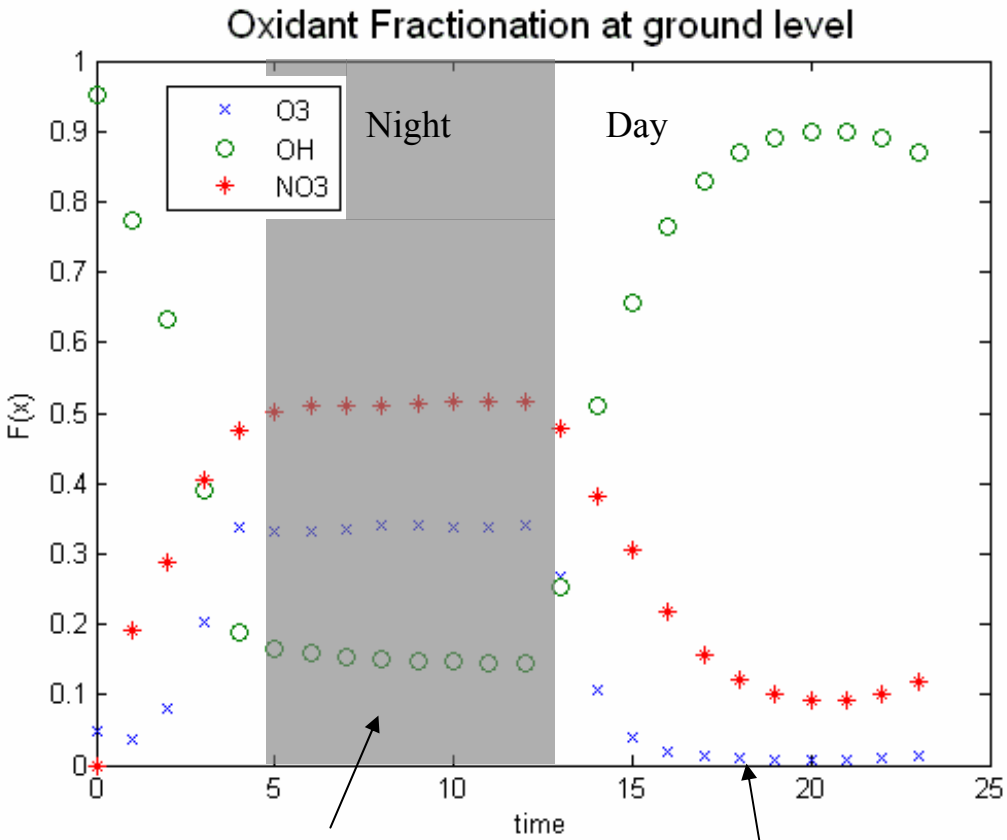
-Annual average of 700 tons isoprene (**620 tonsC**) emitted/day

-0.2 TgC emitted/year

Discrepancy between WRF model and CARB model!

Distribution of biogenic isoprene emissions for one day in July, 2005

What is the estimated yield?
2. The First Reaction: oxidation



Nighttime not as significant because isoprene primarily emitted during day

Ozone not a significant daytime oxidant

- Typical oxidant fractionation for July
- Fraction OH increases with height

Isoprene primarily oxidized by OH—can disregard ozonolysis in SOA formation mechanism

What is the estimated yield?

Isoprene photooxidation (isoprene+OH+*hv*) has a SOA mass yield of ~4% in chamber studies[1]

- Isoprene 9.3% of total VOC emissions, but only 0.7% of total VOC-derived SOA[4]
- Isoprene 35% of total biogenic VOC emissions but only 2.5% of total biogenic VOC-derived SOA[4]

WRF: 3500 tonsC of aerosol/year from isoprene in California
9.5 tonsC aerosol/day from isoprene in California
CARB: 9000 tonsC aerosol/year from isoprene in California
25 tonsC aerosol/day from isoprene in California

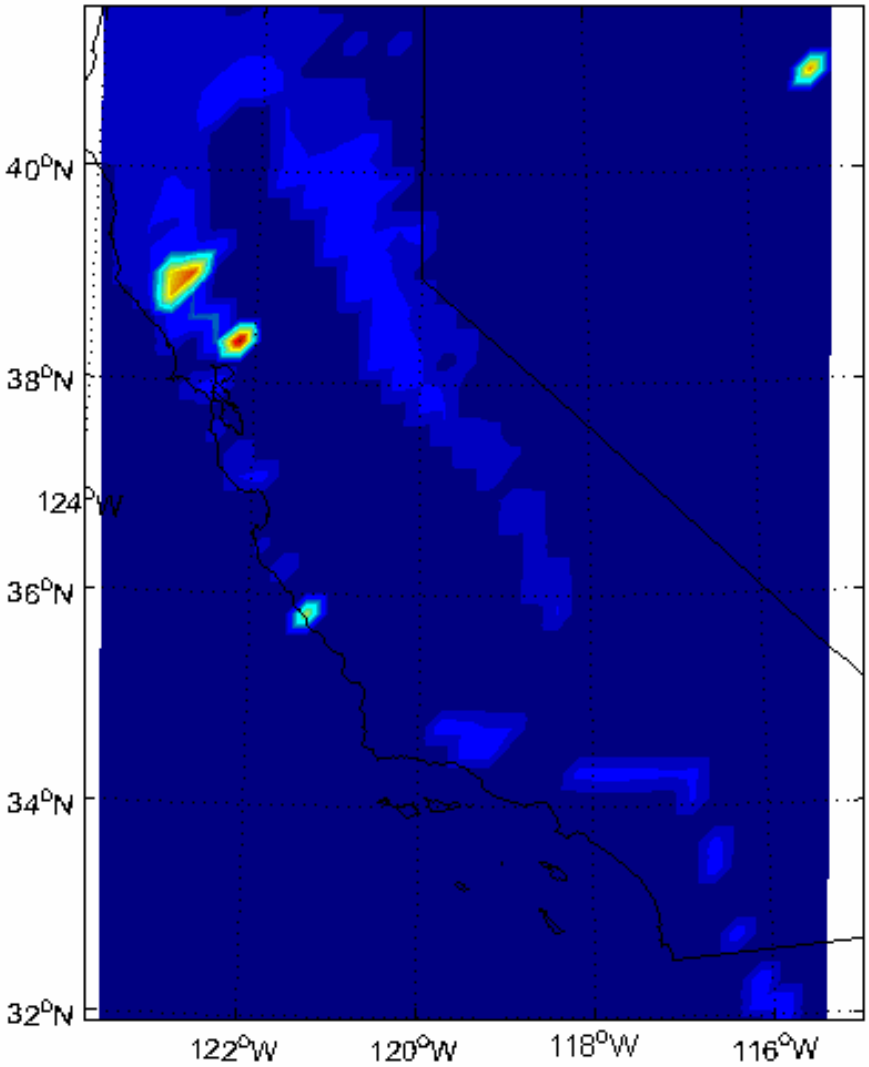
By comparison, in California

- On-road vehicles release 34 tons $PM_{2.5}$/day[4]
- Other vehicles release 114 tons $PM_{2.5}$/day[4]
- Fires release 215 tons $PM_{2.5}$/day[4]

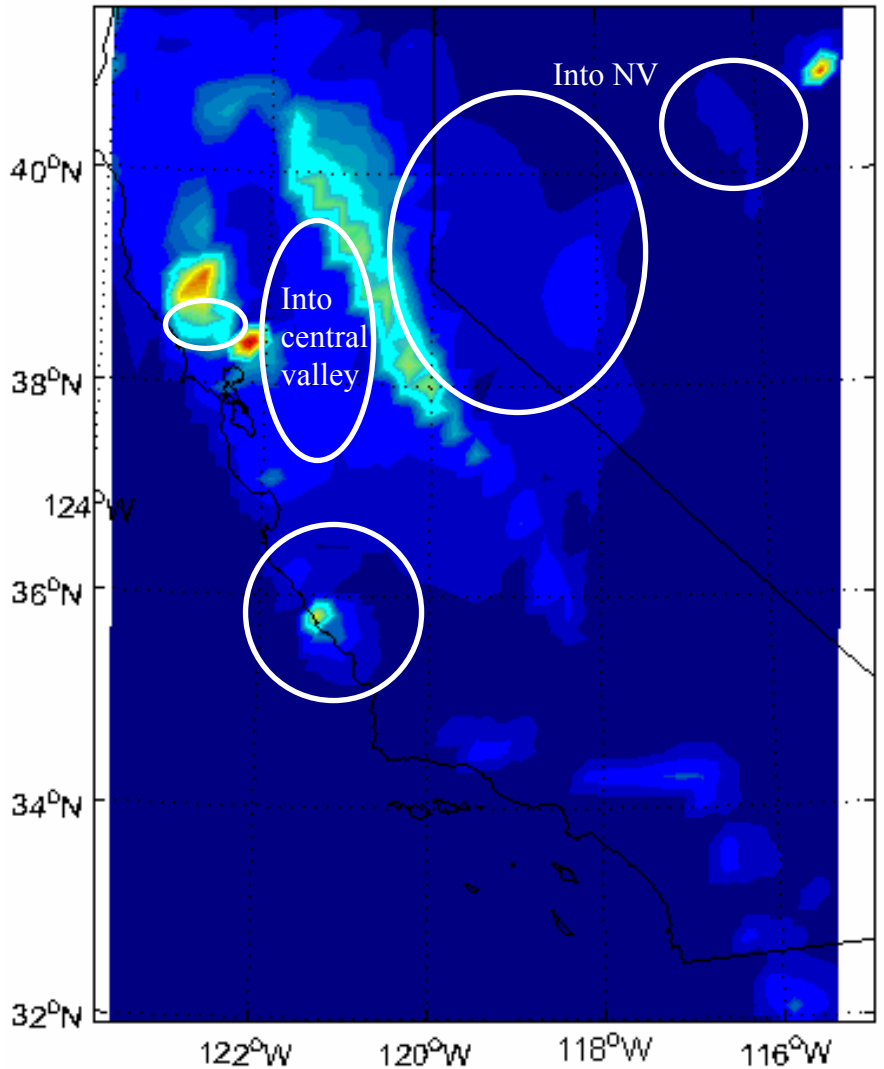
-- IPCC estimates global biogenic SOA 8-40 TgC/yr[5]




Where is the SOA?



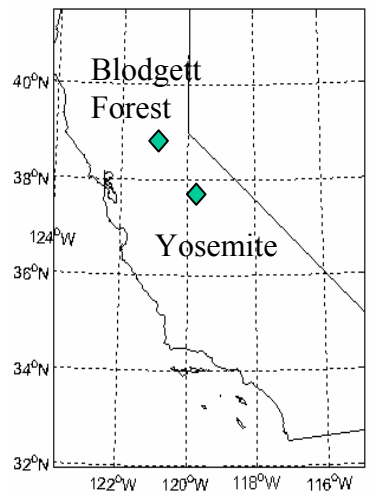
Isoprene emitted for day 6, hour 18 (approx 9 am)



Isoprene tracer at day 6, hour 18

What does the literature say?

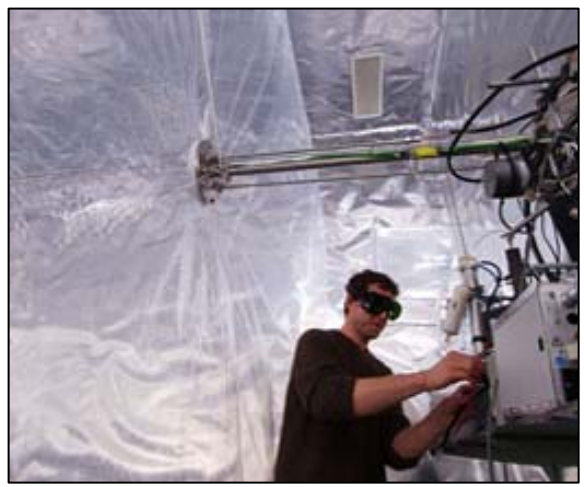
- Blodgett Forest Site[5]: Ponderosa Pine, Live Oak
  - "Aerosol growth sustained over several hours during day"
    - "Oxidation of biogenic emissions significantly contributes to particle growth"
      - Monoterpenes (α- and β-pinene) from pine, isoprene from nearby oak possible
      - Modeled isoprene aerosol mass is 3% of observed aerosol mass
- Yosemite Site[6]
  - "90% of aerosol composed of organic carbon"
    - "Up to 60% by biomass burning"
    - "SOA also a significant component"
      - Identified tracers of monoterpenes (α- and β-pinene)
      - Isoprene precursors not identified;
        Modeled isoprene aerosol mass is 3% of observed aerosol mass



Discussion

Actual SOA formation probably greater than predicted by WRF calculations

- Discrepancy in isoprene emission between WRF-CHEM output and CARB models
- Climate models based on chamber data yields systematically under-estimate SOA formation[2]
  - Chambers run <24 hours but isoprene lifetime 6+ days—time for particle growth and transport
  - Significant loss to walls
  - Unrealistically high concentrations and simplified components changes chemistry
    - Aerosol growth *heterogenous* process



Smog chamber at Paul Scherrer Institut, Switzerland

Conclusions

- At most 0.2 TgC/year of isoprene aerosol produced in California
- Aerosol primarily produced north of SF and in Sierra Nevadas—daytime transport to Central Valley and Nevada
- Isoprene oxidation products probably not a primary aerosol component in California, but may still be an additive component

References

1 Kroll JH, Ng NL, Murphy SM, Flagan RC and Seinfeld JH. Secondary Organic Aerosol Formation from Isoprene Photooxidation, *Environmental Science and Technology* **40** (2006), pp. 1869-1877.

2 Goldstein A.H. and I.E. Galbally, Known and unexplored organic constituents in the earth's atmosphere, *Environmental Science and Technology* **41** (2007), pp. 1514–1521.

3 Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Flagan, R. C.; Seinfeld, J.H. Secondary organic aerosol formation from isoprene photooxidationunder high-NO*x* conditions. *Geophys. Res. Lett.* **32** (2006)

4 Data taken from California Air Resources Board. http://www.arb.ca.gov

5 Lunden M.M., Black D.R., McKay M., Revzan K.L., Goldstein A.H., Brown N.J. Characteristics of Fine Particle Growth Events Observed Above a Forested Ecosystem in the Sierra Nevada Mountains of California. *Aerosol Science and Technology,* **40** (2006) pp.373-388.

6 Engling, G; Herckes, P; Kreidenweis, SM, et al. Composition of the fine organic aerosol in Yosemite National Park during the 2002 Yosemite Aerosol Characterization Study A*tmospheric Environment,* **40** (2006)

Acknowledgements

- DOE-OBER-GCEP-SURE
  - Dr. Jeff Gaffney, Dr. Nancy Marley, Dr. Milton Constantin
- University of California, Berkeley
  - Dr. Ron Cohen, Dr. Juliane Fry, Lukas Valin
- My roommates!
  - Rebecca Callahan, Geeta Persad, Angela Wong
- People who know how to use WRF
  - wrfhelp@ucar.edu, Dr. Serena Chung