GoAmazon: Exploring the Impacts of a Metropolis on Amazonian Air with an Explicit Organic Chemistry Scheme

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Observations and Modeling of the Green Ocean Amazon.

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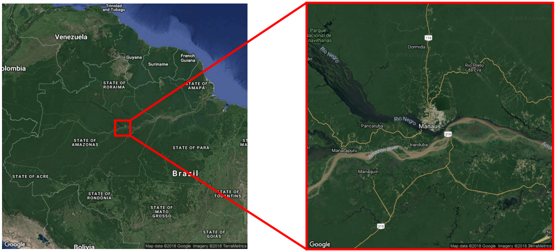

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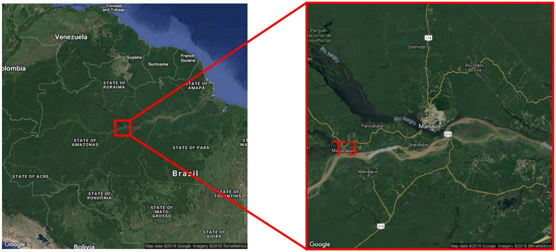

Manaus, Brazil

Growing, isolated urban area of 2.1 million inhabitants in the middle of 1000 km of Amazonian forest.

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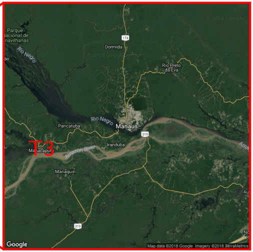
- Better understand Aerosols-Clouds-Precipitations interactions.
- How are chemical, hydrological, energetical and ecological cycles perturbed by climate change and anthropogenic pollution?



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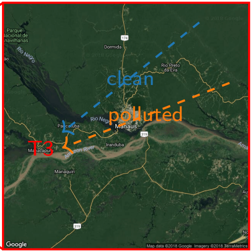

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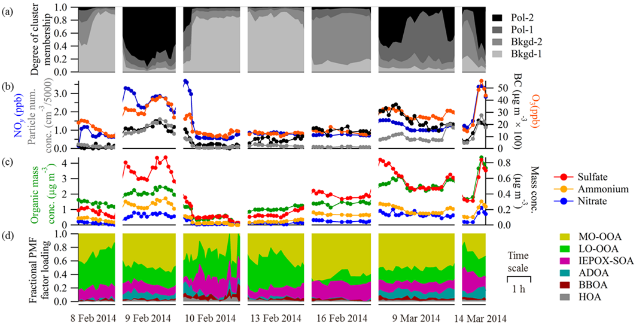
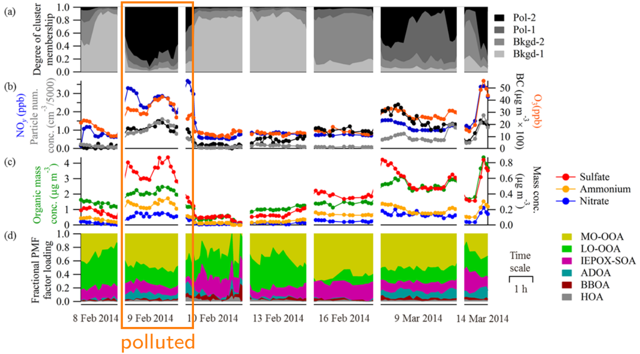
Experimental Data



de Sá et al. (2018)



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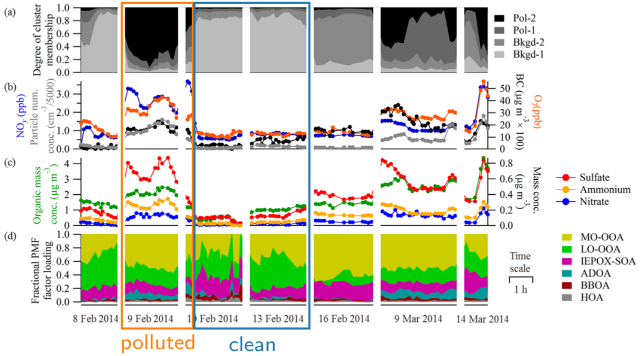

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- High variability of particles composition linked to the origin of air masses.

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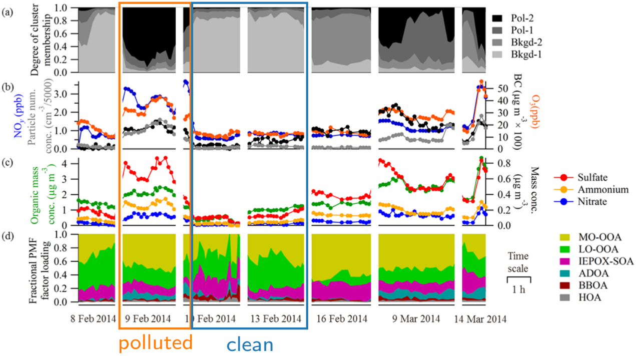

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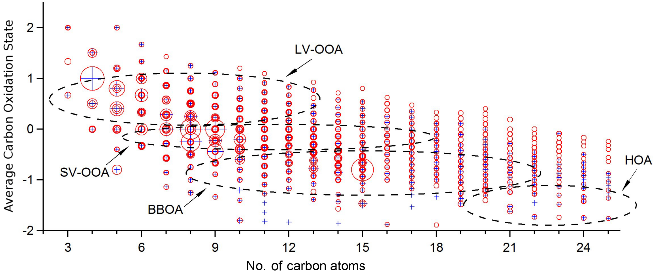
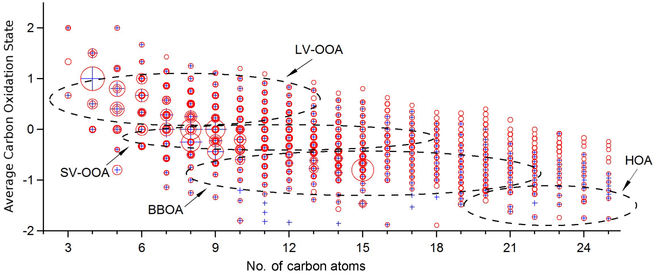
Questions

- Do we understand the processes that lead to SOA formation and variability?
- Are we able to model these processes?



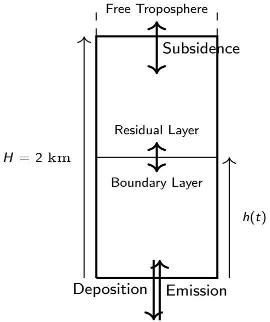
Kourtchev et al. (2016)

- Approx. 2100 elemental formulae identified in field samples during the **GoAmazon** campaign.

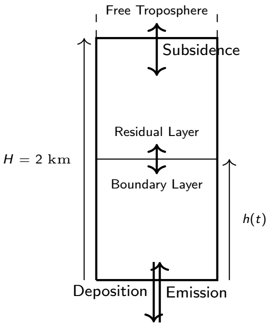


Kourtchev et al. (2016)

- Approx. 2100 elemental formulae identified in field samples during the **GoAmazon** campaign.
- Explicit modeling is needed to represent the complex organic mixture making Secondary Organic Aerosol.



- Diurnal evolution of the PBL.
- The upper box is a residual layer that is progressively mixed with the PBL during the day. This allows retention of previous days products.
- Primary VOCs are emitted in the lower box.
- Deposition is parameterized according to Wesely (1989).



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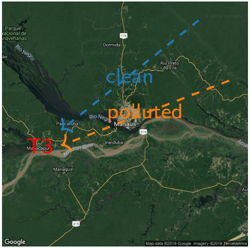

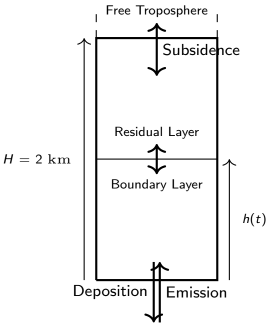

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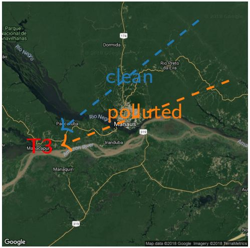

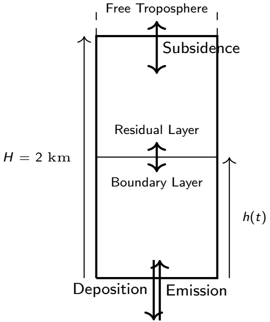

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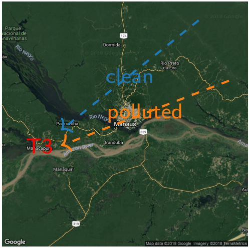
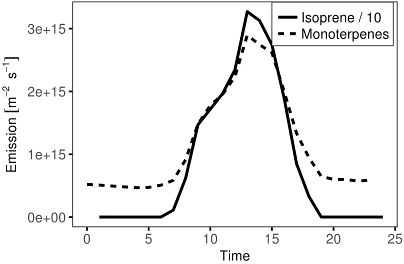
Scenario

- Rainforest emissions.
- Manaus emissions for 1 hour (12pm).
- Back to rainforest emissions.



- MEGAN emission inventory (Guenther et al., 2012): isoprene, total monoterpenes.



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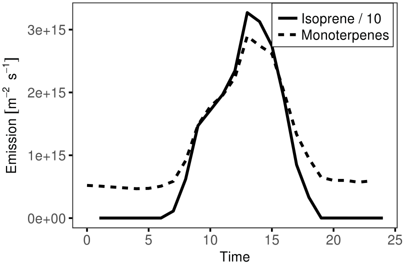
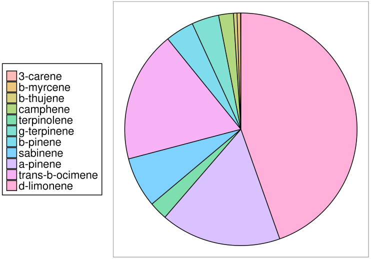


- Jardine et al. (2015) provide the speciation of monoterpenes in the rainforest.



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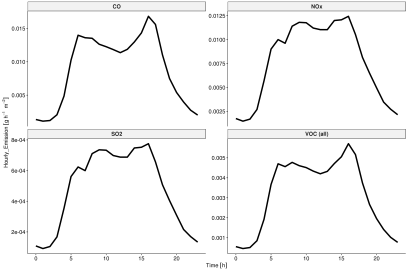
- Andrade et al. (2015): Vehicles use statistics in São Paulo.



Urban Emissions

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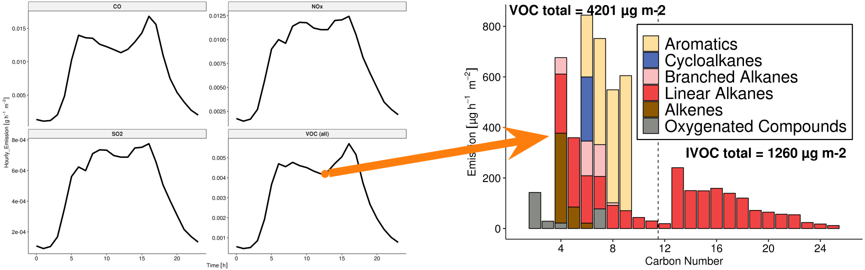
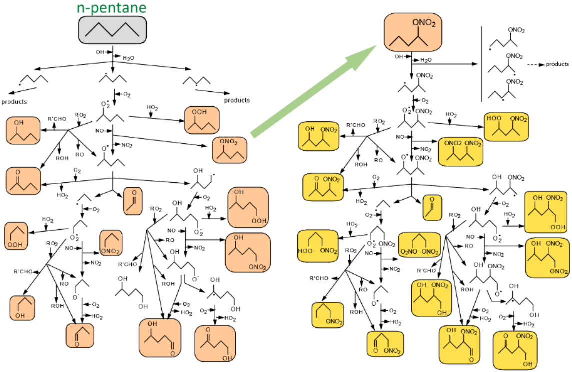
- Andrade et al. (2015): Vehicles use statistics in São Paulo.
- Martins et al. (2006): VOC speciation of São Paulo trafic emissions.
- Gentner et al. (2012); Zhao et al. (2015, 2016); Lee-Taylor et al. (2015): Extrapolate unmeasured diesel vehicles emissions.

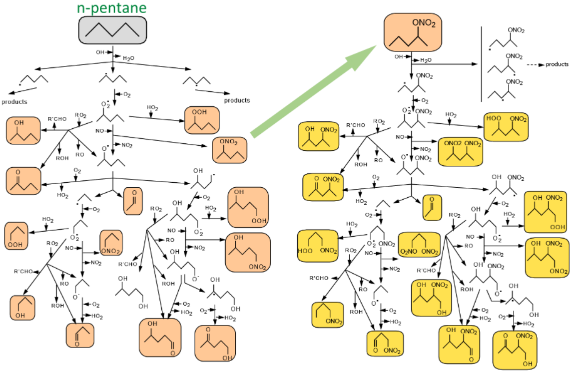




Parent Hydrocarbon

Chemical Scheme

Chemical Mechanism: GECKO-A



Parent Hydrocarbon → 1st generation species

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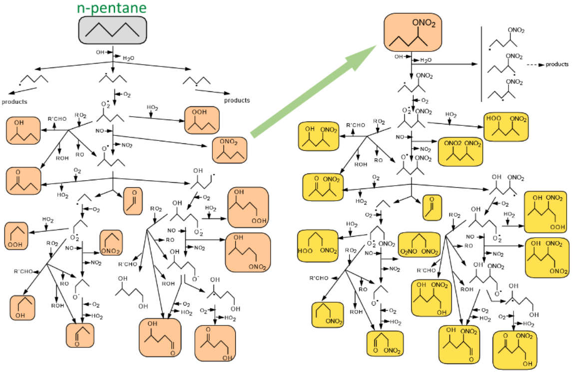

Parent Hydrocarbon → 1^{st} generation species → 2^{nd} generation species

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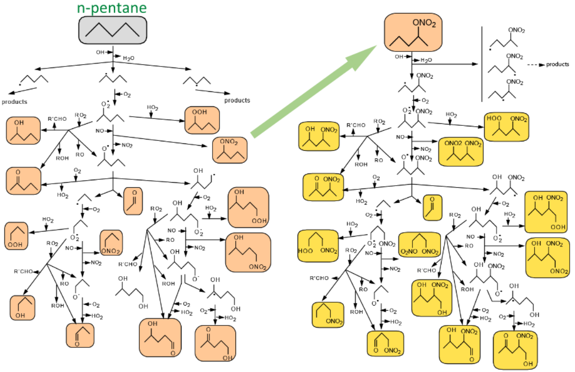

Parent Hydrocarbon → 1st generation species → 2nd generation species --→ CO_2

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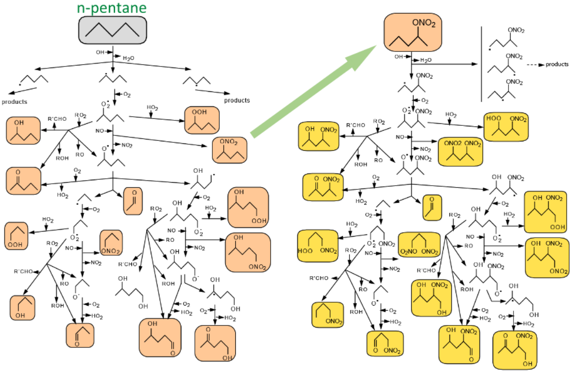

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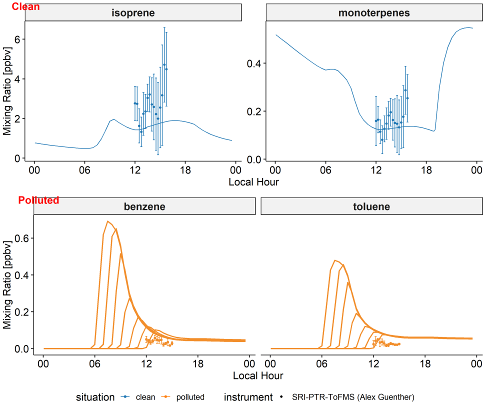
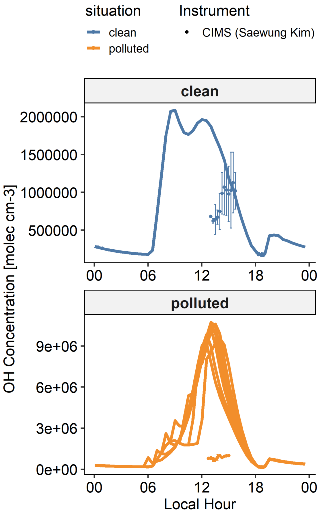
Chemical Scheme

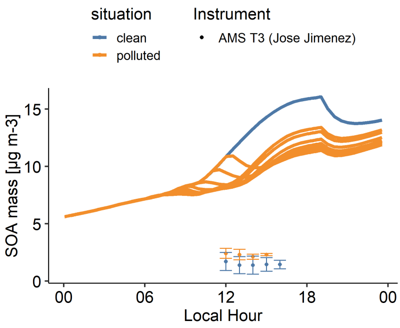
- The Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (**GECKO-A**) is used to automatically generate the fully explicit oxidation of all primary organic species (9 biogenics, 50 anthropogenics).
- Isoprene chemistry follows MCM 3.3.1 (2 generations) and isoprene soa formation is parameterized according to Marais et al. (2016).
- 4.3M Species, 14M Reactions.



- Isoprene and Σmonoterpenes emissions have been scaled to match measurements.
- The model matches measured benzene and toluene without scaling.



- Modeled OH levels match measurements in the clean case.
- Overestimated after pollution events by an order of magnitude.



- The model overestimates SOA mass ($\times$ 7–10).
- Modeled SOA mass decreases after pollution event, contrary to observations.

	clean		polluted	
	model	exp	model	exp
Total SOA [μg m^{-3}]	15	1.4	10 (-5)	2.2 ($+0.8$)
anthropogenic part (HOA + ADOA) [μg m^{-3}]	0	0.04	0.3 ($+0.3$)	0.09 ($+0.05$)

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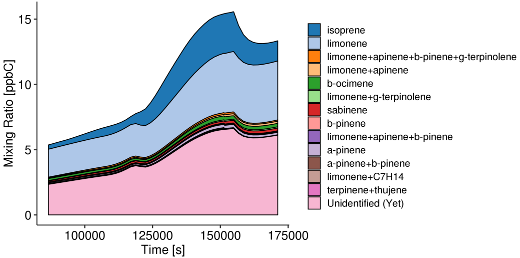
- Most of the discrepancy between model and experiment is not caused by anthropogenic chemistry.
- Lower SOA yield in the temporary high NO_x regime brought by Manaus cause the modeled SOA mass drop.
- Anthropogenic SOA formation doesn't compensate for that biogenic SOA decrease.
- Experimentally, anthropogenic SOA production is not enough to explain experimental total SOA mass increase
- Experimental biogenic SOA yield increases in the polluted environment.

Secondary Organic Aerosol Atomic Composition

- Precursors of the 50 most important species in the aerosol phase for the polluted case.



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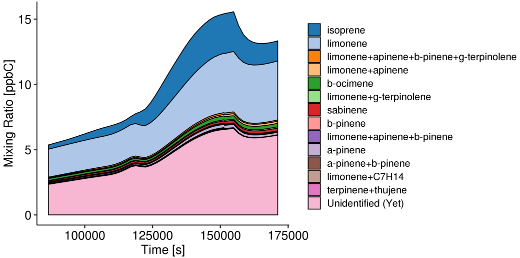
- $\approx$ half of modeled SOA comes from isoprene and limonene.



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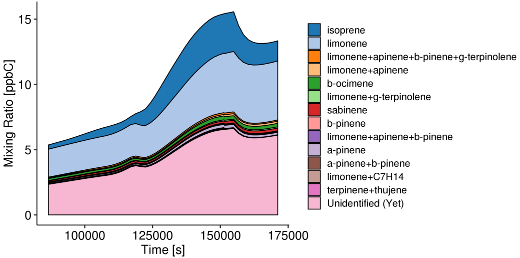

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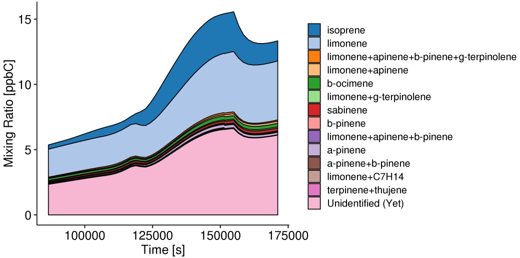

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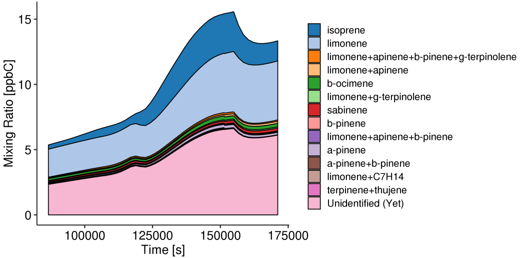

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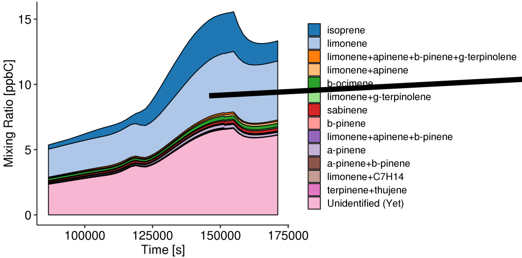

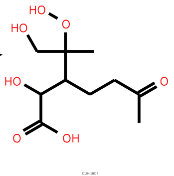

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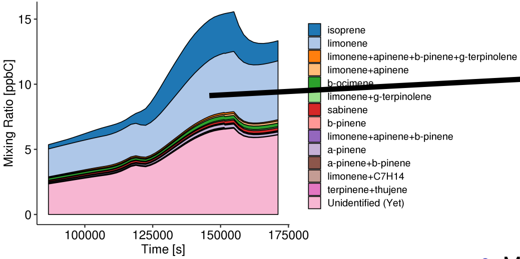

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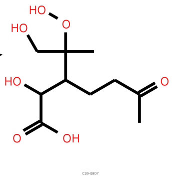

- Missing aerosol phase processes? Photolysis (e.g. Walser et al., 2007)?

- We built a detailed emission inventory for organics in Manaus.
- We generated a detailed chemical scheme to model aerosol formation from biogenic and anthropogenic compounds in a boxmodel.
- Secondary Organic Aerosol formation is overestimated in all cases.
- Bringing GECKO-A closer to field measurements will require better understanding of isoprene and monoterpenes (esp. limonene) SOA formation and destruction pathways especially in low NO_x regimes.

Acknowledgments

- **GECKO-A**
  Julia Lee-Taylor, Sasha Madronich (ACOM/NCAR)
  Marie Camredon, Bernard Aumont (LISA, Paris, France)
- **MEGAN Emissions**
  Louisa Emmons (ACOM/NCAR)
- **Boundary Layer**
  Don Lenschow (MMM/NCAR)
  Dave Gurarie (Case Western Reserve University)
- **Experimental Data**
  ARM Climate Research Facility
  Jose Jimenez (CU Boulder)
  Suzane De Sà, Scot Martin (Harvard)
- **Funding**
  Atmospheric Systems Research Program of the US Department of Energy

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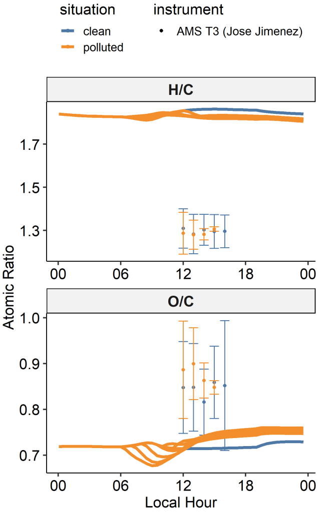
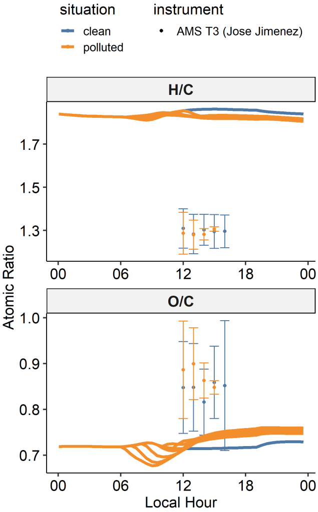
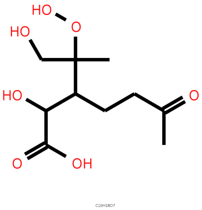
Impact on SOA properties







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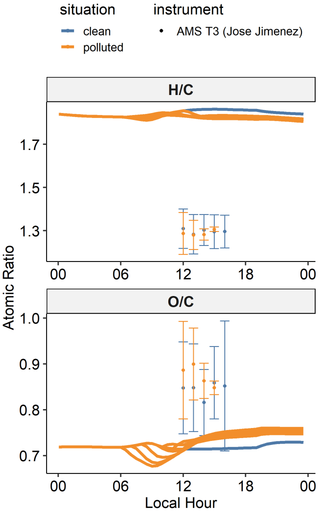

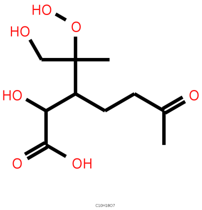

- $C_{10}H_{18}O_7$ and similar species impose clean conditions properties: $H/C = 1.8$,$O/C = 0.7$.
- In clean conditions (epoxydiols and tetrols), $H/C_{\text{isopsoa}} = 2$ and $0.6 < O/C_{\text{isopsoa}} < 0.8$.
- In polluted conditions (organonitrates and sulfates), $H/C_{\text{isopsoa}} = 2$ and $1.2 < O/C_{\text{isopsoa}} < 1.4$.