Modeling the Explicit Chemistry of Organic Aerosols: Formation, Removal, and Properties

Sasha Madronich,[1] Camille Mouchel-Vallon,[1] Alma Hodzic,[1] Julia Lee-Taylor McMillan,[2] Jose Jimenez [2] and Bernard Aumont [3]
[1]NCAR, [2]U. Colorado, [3]U. Paris

OVERVIEW

This new project will use observational data from three DOE-led field campaigns (GoAmazon [1], BBOP [2], and HI-SCALE [3]) to evaluate and improve our hyper-explicit chemical model GECKO-A (the Generator of Chemistry and Kinetics of Organics in the Atmosphere [4]), and specifically to evaluate its ability to predict the amounts and properties of organic aerosols (OA). Each campaign offers specific challenges and opportunities to evaluate and improve GECKO-A: **GoAmazon** sampled at the interface of regions dominated by biogenic or anthropogenic hydrocarbons, providing a contrast between chemical regimes that should be within the current predictive capability of GECKO-A. **BBOP** provides an opportunity to test and improve the chemistry of light-absorbing compounds, important to radiative forcing (brown carbon) and OA lifetimes (photolysis), with updates based on our Tropospheric Ultraviolet Visible model. **HI-SCALE** provides simultaneous measurements of organic molecules in air, aerosols, and cloud droplet residuals, and will be used to test our extension of GECKO-A to cloud chemistry. We anticipate that this will elucidate the formation of carboxylic acids, which observations show to be ubiquitous but are not fully explained; and the formation of OA particles when cloud droplets evaporate, which some (but not all) previous studies have suggested as major contributors to the global burden of organic aerosols. Successful improvements will be parameterized for implementation in a three-dimensional regional chemistry-transport model WRF-Chem and will be made available to the community.

Biogenic & Anthropogenic Precursors

We plan explicit chemistry simulations of the GoAmazon field campaign for:
(i) pristine conditions dominated by biogenic VOCs,
(ii) polluted urban plumes from Manaus, and
(iii) mixed situations.
Precursor VOCs include dozens of biogenic and anthropogenic hydrocarbons, each having distinct chemical degradation pathways leading to products having different chemical, thermodynamic, and optical properties. In preparation for these complex simulations, we are using the GECKO-A model to develop an on-line data base, or "library", for many common individual hydrocarbon precursors to SOA formation, under a small number of standard representative environmental conditions (see Table 1):

TABLE 1: Scenarios (Aumont et al. 2016)[5]	Remote	Remote Continental	Continental	Polluted Continental	Urban
Constrained					
NOx [ppb] [(a)]	0.02	0.025	0.5	2	20
CO [ppb]	120	120	150	200	300
NMHC K_{oh} [s^{-1}] [(b)]	0	1	6	9	13
CO+NMHC K_{oh} [s^{-1}]	0.7	1.7	6.9	10.2	14.8
HCHO [ppb]	0	0	2	5	10

(a) NOx fixed, NO/NO2 varying.
(b) Surrogate to maintain VOC/NOx ratio.
All: O_3 = 40 ppb, CH_4 = 1850 ppb, T = 298K, RH = 70%, sza = 45 deg, SOA seed 10 μg m^{-3}.

A Library of Precursors and Their Products

Both gas and particle-phase properties will be inventoried. For each precursor, we can compute

- the explicit molecular identity of major (e.g. top ten) oxidation products in both phases, and the average molecular mass in the particle phase
- atomic ratios (O/C, N/C, H/C, van Krevelen diagrams) summed over any subset of species (e.g. condensed or gas phase)
- functional group statistics (the number of ketones, aldehydes, di-carbonyls, nitrates, peroxides, acids, alcohols, etc., divided by the number of carbons) for the particle phase
- spectral absorption cross sections in the gas phase and mass absorption coefficients and indices of refraction for the particle phase
- volatility spectra of the gas-particle ensemble (mass as function of vapor pressure), and volatility averaged over the particle distribution
- correlations between volatility and solubility (Henry's law constant) for the oxidation products.

The library will be made available online to the research community.

Example: n-dodecane (n-$C_{12}H_{26}$), Continental

The GECKO-A model computes the identity and amounts of all molecules plausibly derived from a precursor VOC. This large output can be "sliced and diced" to synthesize important gas and particle properties, including measurable quantities (e.g. O/C ratios). Below are some of the products that can be made available for each precursor, and each environmental scenario.

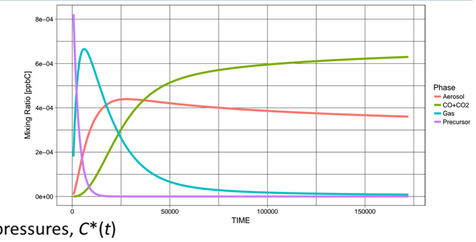


Figure 1: Time evolution of dodecane precursor and its product organic vapors and particles, and inorganic gases.

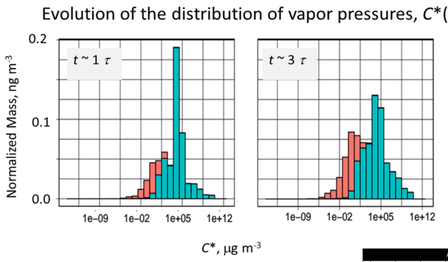


Figure 2: Vapor pressure of dodecane oxidation products, and their phase in the presence of 10 μg m^{-3} seed, at two different times.

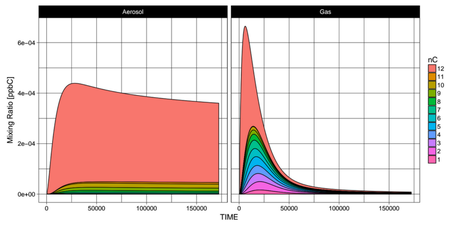


Figure 3: Evolution of molecules with specific number of carbons, from precursor dodecane.

Figure 4: Evolution from dodecane, by element

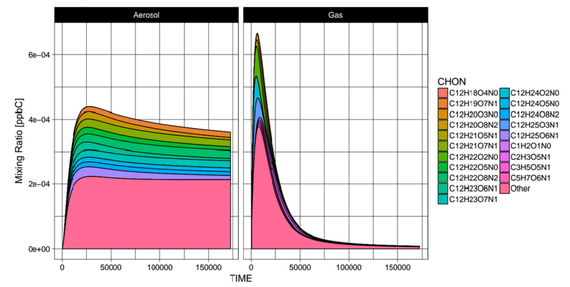


Figure 5: Evolution from dodecane, by functional groups

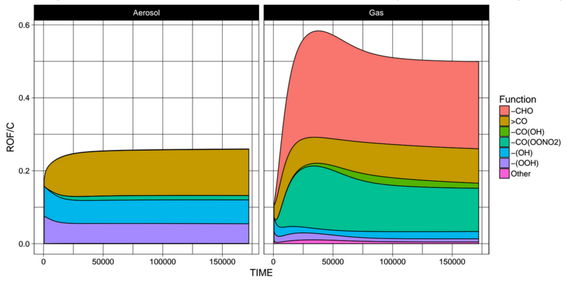
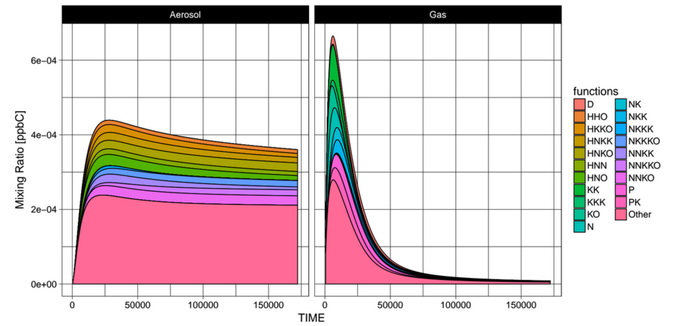


Figure 6: Evolution from dodecane, by polyfunctional molecules



Community Input

The library will be made available online to the research community. To maximize its usefulness, we invite suggestions that enhance our selection of precursors, environmental conditions, molecular-level chemical markers, as well as estimated bulk thermodynamic and optical properties.

Acknowledgements

This work is supported by Department of Energy Office of Science Award No. DE-SC0016331. NCAR is sponsored by the National Science Foundation.

Contact

Sasha Madronich
NCAR
Email: sasha@ucar.edu
Phone: (303) 497-1430

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