Chemically Explicit Model of Secondary Organic Aerosol (SOA) Formation in Mexico

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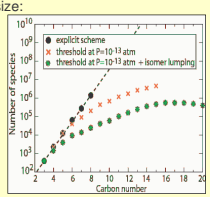
A. Context

Secondary Organic Aerosols (SOA) are major constituents of the troposphere, with mass often exceeding sulfate, nitrate, and soot combined[1], and with impacts on human health[2], urban and regional photochemistry[3], precipitation patterns[4], and directly or indirectly on climate[5]. SOA are by-products of the photo-oxidation of hydrocarbons, both anthropogenic and biogenic[6,7], but attempts to describe the chemistry of their formation have fallen short by 0.5-2 orders of magnitude[8]. Implementation of SOA in atmospheric models is still in its infancy and recently[9,10] include parameterizations of chamber-derived yields and volatility distributions without specific information on SOA chemical composition[11-14].

We are developing a model of the explicit gas phase chemistry of hydrocarbons leading to the formation of SOA[15,16]. Chemical pathways and kinetics are obtained from compilations of laboratory measurements, or derived from these using various structure-activity relations. The model predicts the chemical identity of the products as well as their properties relevant to gas/particle partitioning. The model is being evaluated with observations in Mexico City (MILAGRO, 2006) of SOA mass (μg m^{-3}) and atomic ratios (oxygen and nitrogen to carbon ratios, O/C and N/C). The major chemical constituents of SOA are identified as δ-hydroxy nitrates and ketones from long-chain alkanes as observed in chamber studies[17], and nitro-catechols from aromatics. The importance of nitrogen-containing molecules is noteworthy in our model results, although measurements by aerosol mass spectrometry (AMS) suggest lower values[18].

B. Model: The "Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere" (GECKO-A)

- Aliphatic chemistry is represented explicitly via structure-activity relationships[15].
- Aromatic chemistry to ring-opening is from Leeds MCM[19] mechanism.
- Saturation vapor pressures are computed using group contributions.[20]
- Equilibrium gas/aerosol partitioning[21] using Raoult's law.
- No in-aerosol chemistry.
- 2 sets of assumptions reduce mechanism size:
  a) Species with vapor pressures < 10^{-13} atm partition exclusively to aerosol phase → no further gas phase reactions
  b) Longer-chain species lumped into chemically-similar isomers

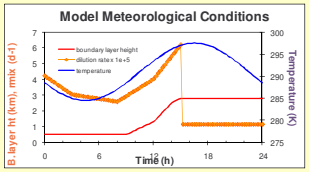


Mechanism size for Mexico simulations:

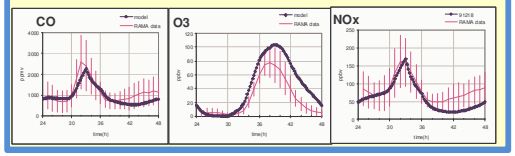
- 1.15 M species (~ 300 K non-radicals)
- 6.3 M gas-phase reactions
- Computational time on workstation ~ 0.5x real time

C. Mexico City Model

- The explicit mechanism is used in a 0-D (box) model with diurnally-varying temperature, solar cycle, emissions , deposition, and boundary layer height.



Model-obs comparison: inorganic species in Mexico City, March 2006

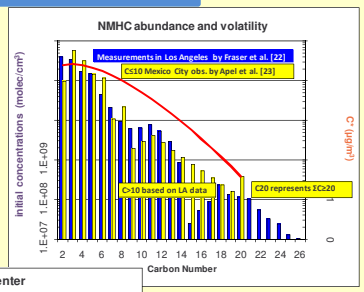


D. Aerosol Mass Yields and Carbon

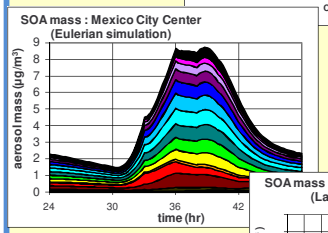
As carbon number rises,

gas-phase NMHC abundance drops.

Volatility also drops ….

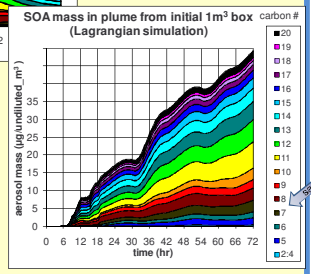


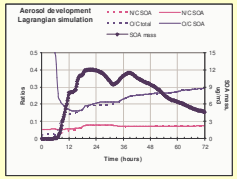
…. resulting aerosol mixture is highly diverse in terms of chain length.



Eulerian simulation: Afternoon ventilation reduces aerosol mass in the city, giving a daily cycle.

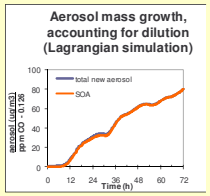
Lagrangian simulation: Aerosol mass production continues as plume expands downwind from city

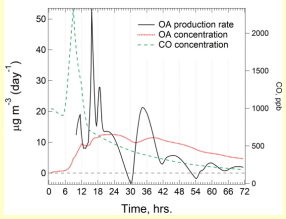




O/C ratios are smaller than observed[24] from AMS (0.4-0.9)
N/C ratios are larger than observed[18] from AMS (≤0.01)

Large regional impacts: Net production continues for several days despite dilution and evaporation.





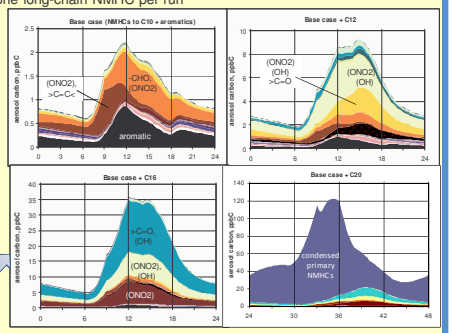
References: [1] Q. Zhang et al., *Geophys. Res. Lett.*, **34**, L13801, 2007. [2] C.A. Pope, D. W. Dockery, *J. Air & Waste Manage. Assoc.*, **56**, 709, 2006. [3] M.Z. Jacobson, *J. Geophys. Res.*, **104**, 3527, 1999. [4] D. Rosenfeld et al., *Science*, **321**, 1309, 2008. [5] M. Kanakidou et al., *Atmos. Chem. Phys.*, **5**, 1053, 2005. [6] A.H. Goldstein, I.E. Galbally, *Environ. Sci. Tech.*, **14**, 1514, 2007. [7] J. De Gouw, J.L. Jimenez, *Environ. Sci. Tech.*, **43**, 7614, 2009. [8] R. Volkamer et al., *Geophys. Res. Lett.*, **33**, L17811, 2006. [9] K. Dzepina et al., *Atmos. Chem. Phys.*, **9**, 5681, 2009. [10] A. Hodzic et al., *Atmos. Chem. Phys. Discuss.*, **10**, 657, 2010. [11] N.L. Ng et al., *Atmos. Chem. Phys.*, **7**, 3909, 2007. [12] A.L. Robinson et al., *Science*, **315**, 1529, 2007. [13] A.P. Grieshop et al., *Atmos. Chem. Phys.*, **9**, 1263, 2009. [14] J.L. Jimenez et al., *Science*, **326**, 1525, 2009. [15] B. Aumont et al., *Atmos. Chem. Phys.*, **5**, 2497, 2005. [16] M. Camredon et al., *Atmos. Chem. Phys.*, **7**, 5599, 2007. [17] Y.B. Lim and P.J. Ziemann, *Environ. Sci. Technol.*, **39**, 9229, 2005. [18] A.C Aiken et al., *Environ. Sci. Technol.*, **42**, 4478, 2008. [19] C. Bloss et al., *Atmos. Chem. Phys.*, **5** 623, 2005. [20] P.B. Myrdal, S.H. Yalkowsky, *Ind. Eng. Chem. Res.*, **36**, 2494, 1997. [21] J.F. Pankow, *Atmos. Environ.*, **28**, 185, 1994. [22] M.P. Fraser et al., *Environ. Sci. Tech.*, **31**, 2356, 1997. [23] E. C. Apel et al., *Atmos. Chem. Phys.*, **10**, 2353, 2010. [24] P.F. DeCarlo et al., *Atmos. Chem. Phys. Discuss.*, **10**, 2445, 2010.

E. Predicted Aerosol Functionality

Conversion factor: 1 ppbC ≈ 0.5 μg/m³

Sensitivity Study : all species with C>10 are represented by one long-chain NMHC per run

Each run (except base case) adds the same quantity of NMHC carbon.



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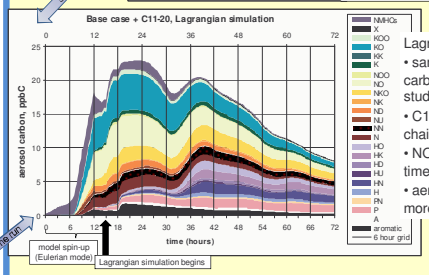
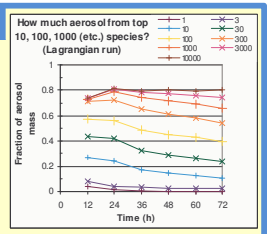


Lagrangian simulation:
- same quantity of carbon as sensitivity study
- C11-C20 straight-chain NMHCs
- NO_x is depleted with time →
- aerosol becomes more diverse

F. Major Aerosol Constituents



Examples of major contributors

Straight-chain NMHCs
n-eicosane & n-nonadecane

Monofunctional nitrates
e.g. pentadecane-2-nitrate

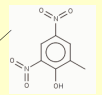
Delta-hydroxy-nitrates
R-CH(ONO_2)-(CH_2)-CH_2(OH)
R-CH(ONO_2)-(CH_2)-CH(OH)-CH_3

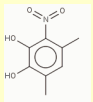
Beta-hydroxy-carbonyls
R-CH(OH)-CH_2-CO-CH3

Tri-functional chains
R-CH(ONO_2)-CO-CH_2-CH_2(OH)
R-CH(OH)-CH_2-CO-CH_2(ONO_2)

Substituted Aromatics
2-methyl-4,6-dinitro-phenol
Precursor: toluene

3,5-dimethyl-6-nitro-catechol.
Precursor: m-xylene

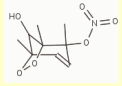




Aromatic ring-opened products

2,3-epoxy-4-hydroxy-2-methyl-5-nitrooxy-6-oxo-heptanal.
Precursor: m-xylene

8-hydroxy-1,4,5-trimethyl-4-nitrooxy-6,7-dioxa-[3.2.1]bicyclo-oct-2-ene
Precursor: 1,2,4-trimethylbenzene



CH_3-C(CO(OH))=C(NO_2)-CHO
Precursor: various aromatics

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