A Global Perspective on Aerosol from Low-volatility Organic Compounds

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Introduction

Recent work indicates that what has traditionally been considered non-volatile primary organic aerosol (POA) is actually a dynamic system of semivolatile species that partition between gas and aerosol phases. Low-volatility organic compounds (saturation concentrations, C*, less than 10^6 $\mu g/m^3$) in the gas phase can also undergo oxidation resulting in lower volatility species that partition to form secondary organic aerosol (SOA).

Objective

A chemical transport model, GEOS-Chem, incorporating recent chamber data is employed to estimate the contribution of aerosol from low-volatility organic compounds. Two types of compounds are considered:

• SVOCs: semivolatile organic compounds, $0.1 < C^* < 10^4$ $\mu g/m^3$, emissions partition between the gas and aerosol phase under ambient conditions, includes traditional non-volatile POA, emissions can oxidize to form SOA

• IVOCs: intermediate volatility organic compounds, $10^4 < C^* < 10^6$ $\mu g/m^3$, emitted entirely in the gas-phase, oxidation products form SOA

Method

Emission Inventories

SVOC Emissions:
• Traditional non-volatile POA inventory scaled up 27% to represent missing SVOCs
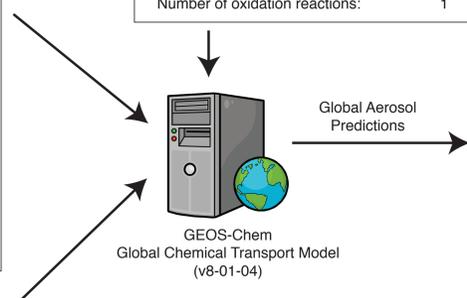• SVOCs emitted as 2 species with different volatilities (based on Shrivastava et al. 2006)

SVOC	Fraction of Emissions [fraction]	C* [$\mu g/m^3$]
SVOC1	0.49	1646
SVOC2	0.51	20

IVOC Emissions:
• Spatially distributed like naphthalene
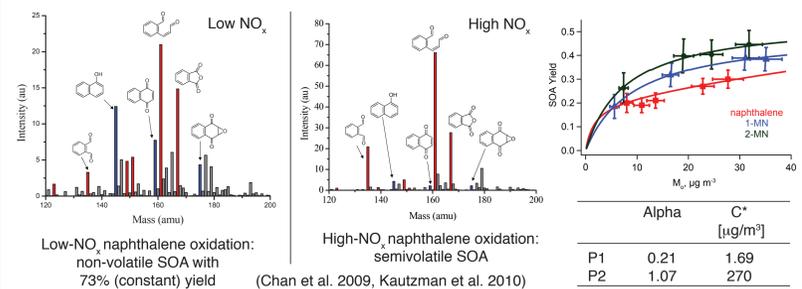• Naphthalene emissions scaled up based on wood burning inventory

SVOC SOA Parameterization

Based on Grieshop et al. 2009:
Gas-phase k_{OH} (cm³ molec⁻¹ s⁻¹): 2×10^{-11}
Reduction in volatility per reaction: 100x
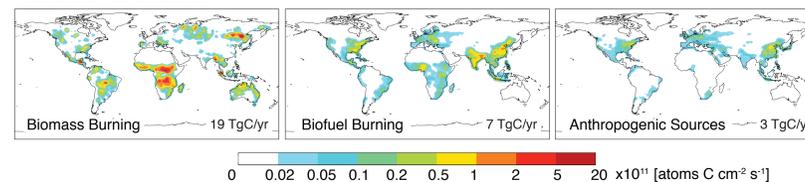Increase in mass per reaction: 50%
Number of oxidation reactions: 1

GEOS-Chem
Global Chemical Transport Model
(v8-01-04)

Global Aerosol Predictions

IVOC-surrogate (Naphthalene) SOA Yields

Low-NO_x
High-NO_x

naphthalene
1-MN
2-MN

Low-NO_x naphthalene oxidation: non-volatile SOA with 73% (constant) yield

High-NO_x naphthalene oxidation: semivolatile SOA

(Chan et al. 2009, Kautzman et al. 2010)

	Alpha	C* [$\mu g/m^3$]
P1	0.21	1.69
P2	1.07	270

Aerosol from Primary SVOCs

Globally, biomass burning is the largest source of SVOCs followed by biofuel burning and other anthropogenic sources (i.e. fossil fuel combustion).

Traditional SVOC Emissions

Biomass Burning   19 TgC/yr
Biofuel Burning   7 TgC/yr
Anthropogenic Sources   3 TgC/yr

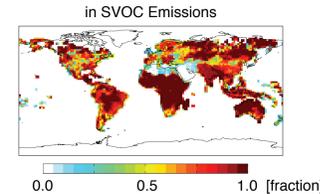0 0.02 0.05 0.1 0.2 0.5 1 2 5 20 x10¹¹ [atoms C cm⁻² s⁻¹]

Although most of the SVOC emissions evaporate, some form POA. Primary SVOCs oxidized in the gas phase form more regionally distributed SOA.

SVOCs are predicted to produce aerosol with significant amounts of modern C even in the United States.
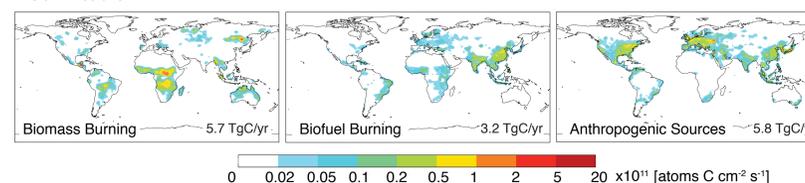
Surface Level Aerosol from SVOCs

Winter POA   Summer POA
Winter SOA   Summer SOA

0 0.02 0.05 0.1 0.2 0.5 1 2 5 10 17 [$\mu g C/m^3$]
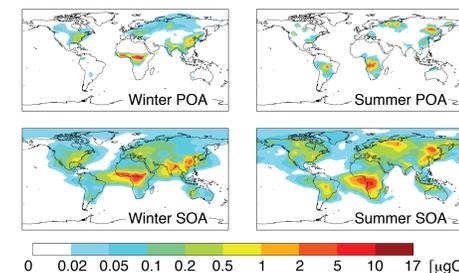
Fraction of Modern C in SVOC Emissions

0.0   0.5   1.0 [fraction]

Aerosol from IVOCs

Globally, biomass burning and anthropogenic sources are predicted to contribute roughly equal amounts of IVOCs.
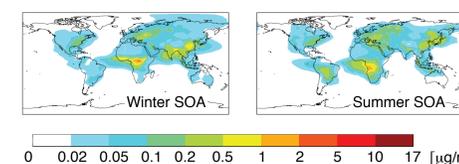
IVOC Emissions

Biomass Burning   5.7 TgC/yr
Biofuel Burning   3.2 TgC/yr
Anthropogenic Sources   5.8 TgC/yr

0 0.02 0.05 0.1 0.2 0.5 1 2 5 20 x10¹¹ [atoms C cm⁻² s⁻¹]

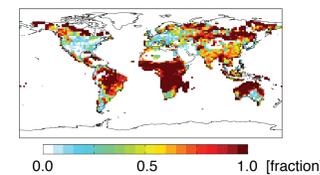IVOCs are predicted to produce about 5 Tg/yr of SOA.

• High-NO_x oxidation (more dominant in anthropogenic source regions) leads to semivolatile SOA.

• Low-NO_x oxidation (more dominant in remote regions) leads to non-volatile SOA.

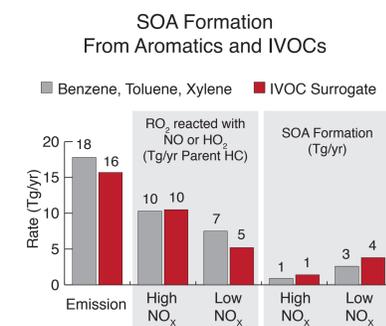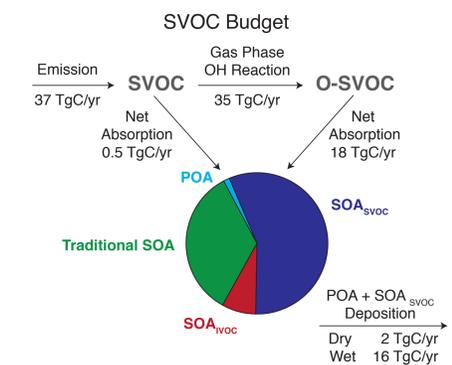IVOCs are predicted to produce aerosol with significant amounts of fossil carbon in the United States.

Surface Level Aerosol from IVOCs

Winter SOA   Summer SOA

0 0.02 0.05 0.1 0.2 0.5 1 2 5 10 17 [$\mu g/m^3$]

Fraction of Modern C in IVOC Emissions

0.0   0.5   1.0 [fraction]

Global Organic Aerosol Production

SVOC Budget

Emission 37 TgC/yr → SVOC — Gas Phase OH Reaction 35 TgC/yr → O-SVOC

Net Absorption 0.5 TgC/yr   Net Absorption 18 TgC/yr

POA
SOA$_{SVOC}$
Traditional SOA
SOA$_{IVOC}$

POA + SOA$_{SVOC}$ Deposition
Dry 2 TgC/yr
Wet 16 TgC/yr

Only 0.5 TgC/yr (net) of the SVOCs emitted form POA. Most of the SVOCs are oxidized in the gas phase.

SOA Formation From Aromatics and IVOCs

Benzene, Toluene, Xylene
IVOC Surrogate

RO_2 reacted with NO or HO_2 (Tg/yr Parent HC)
SOA Formation (Tg/yr)

Emission: 18, 16
High NO_x: 10, 10
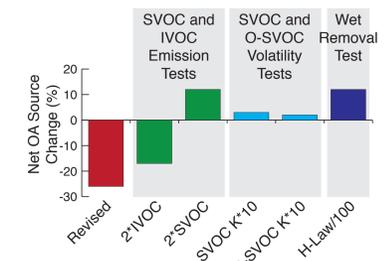Low NO_x: 7, 5
High NO_x: 1, 1
Low NO_x: 3, 4

Most of the IVOC reacts through the high-NO_x pathway, but more aerosol forms through the low-NO_x pathway due to the high yield of a non-volatile product.

Sensitivity of Global OA Source to Model Parameters Relative to Traditional Simulation

Simulations:
Traditional: non-volatile POA
Revised: semivolatile POA, SOA from SVOCs and IVOCs
*2*IVOC*: Double IVOC emissions compared to *Revised*
*2*SVOC*: Double SVOC emissions compared to *Traditional*
*SVOC K*10*: SVOC emissions and oxidation products are a factor of 10 less volatile than in the *Revised* simulation
*O-SVOC K*10*: SVOC oxidation products are a factor of 10 less volatile than in the *Revised* simulation
H-Law/100: *Revised* simulation with less aggressive wet removal

SVOC and IVOC Emission Tests
SVOC and O-SVOC Volatility Tests
Wet Removal Test

Revised, 2*IVOC, 2*SVOC, SVOC K*10, O-SVOC K*10, H-Law/100

Summary and Conclusions

Aerosol formation from SVOCs and IVOCs has been introduced into the global chemical transport model GEOS-Chem. Making POA semivolatile leads to decreases in surface aerosol concentrations due to evaporation of a large portion of the SVOC emissions. A significant portion of the primary SVOCs are oxidized in the gas phase leading to formation of SOA. SVOC oxidation is predicted to be the largest global source of organic aerosol, larger than traditional organic aerosol sources such as biogenic hydrocarbon oxidation.

SVOC and IVOC emissions are predicted to have different contributions of modern and fossil carbon over the U.S. and Europe which can provide constraints on estimates of SVOC and IVOC aerosol. In the U.S., SVOC emissions have a significant biofuel component which, along with biomass burning emissions, leads to a significant fraction of modern C. U.S. IVOC emissions however, are predicted to be predominantly fossil.

The prediction of the global net organic aerosol source ranges from about 60 Tg/yr (for the *Revised* simulation) to 100 Tg/yr (for the *2*SVOC* or *H-Law/100* simulations). Additional model constraints are needed to sharpen these estimates.

References

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Kautzman, K. E., Surratt, J., Chan, M. N., Chan, A. W. H., Hersey, S. P., Chhabra, P. S., Dalleska, N. F., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of gas- and aerosol-phase products from the photooxidation of naphthalene, J. Phys. Chem. A, J. Phys. Chem. A, 114, 913--934, 2010.

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