# A Global Perspective on Aerosol from Low-Volatility Organic Compounds

**Havala O. T. Pye and John H. Seinfeld**

Departments of Chemical Engineering and Environmental Science and Engineering
California Institute of Technology

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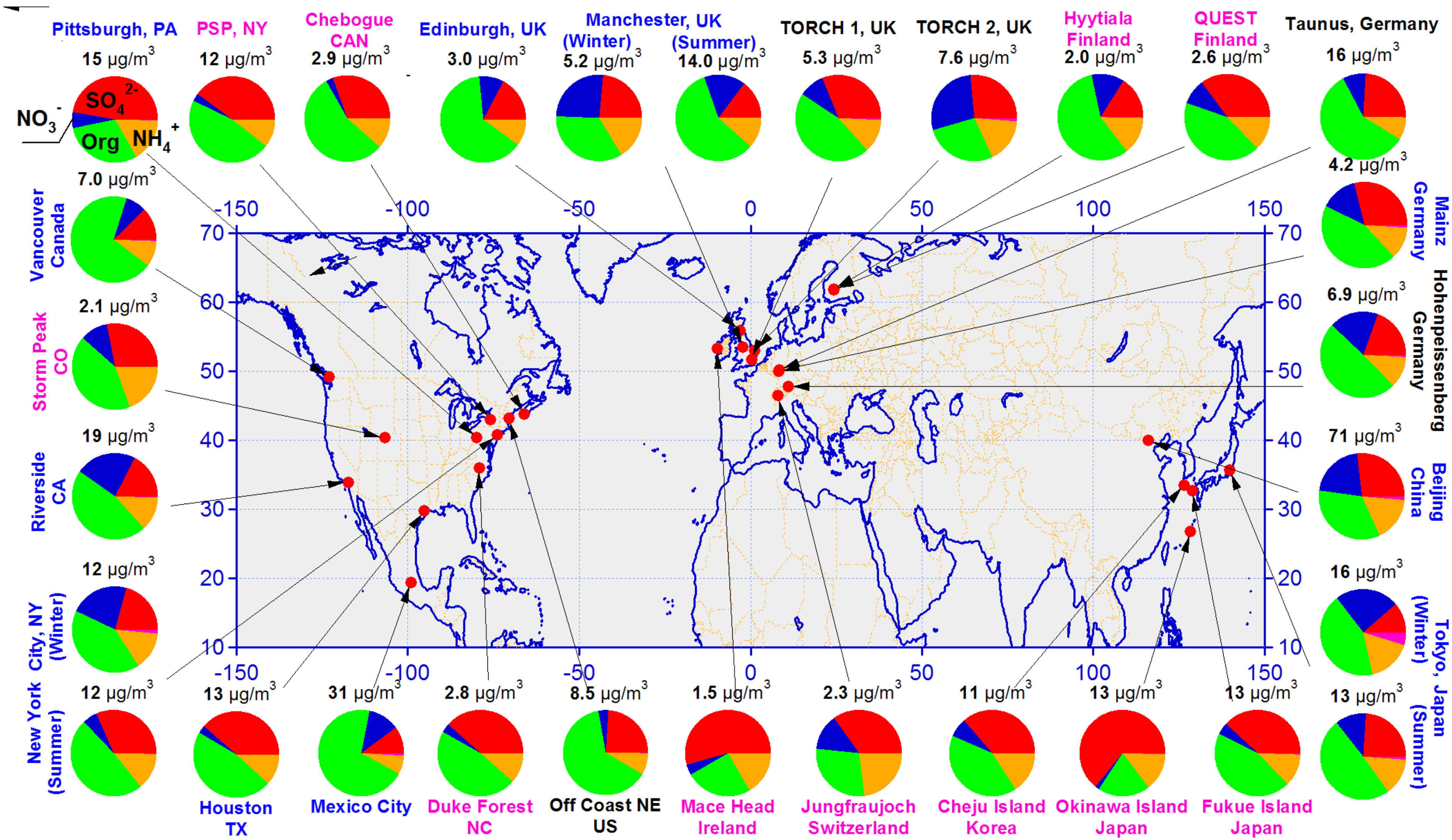
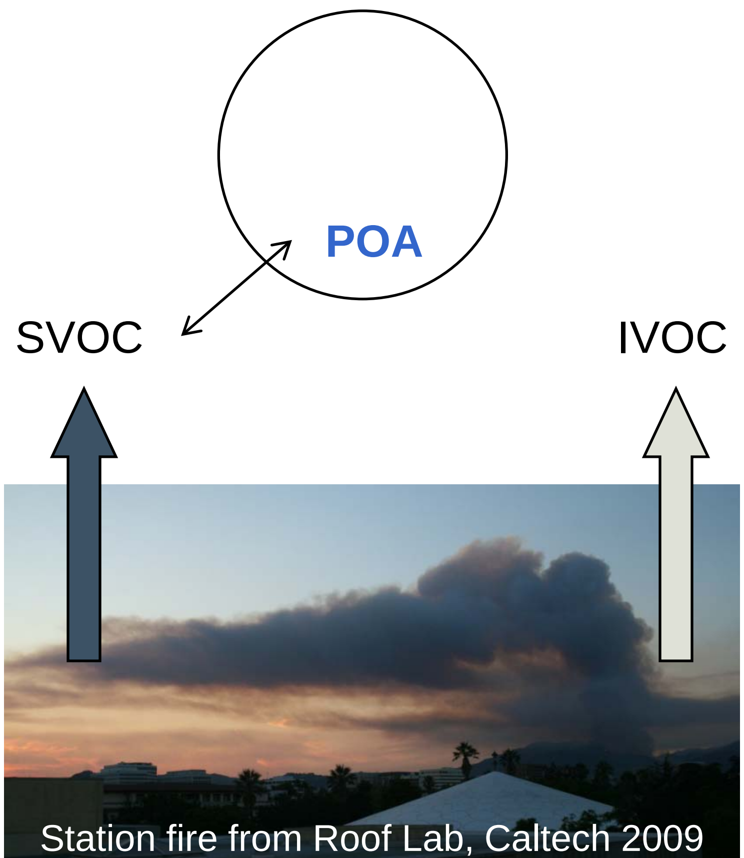
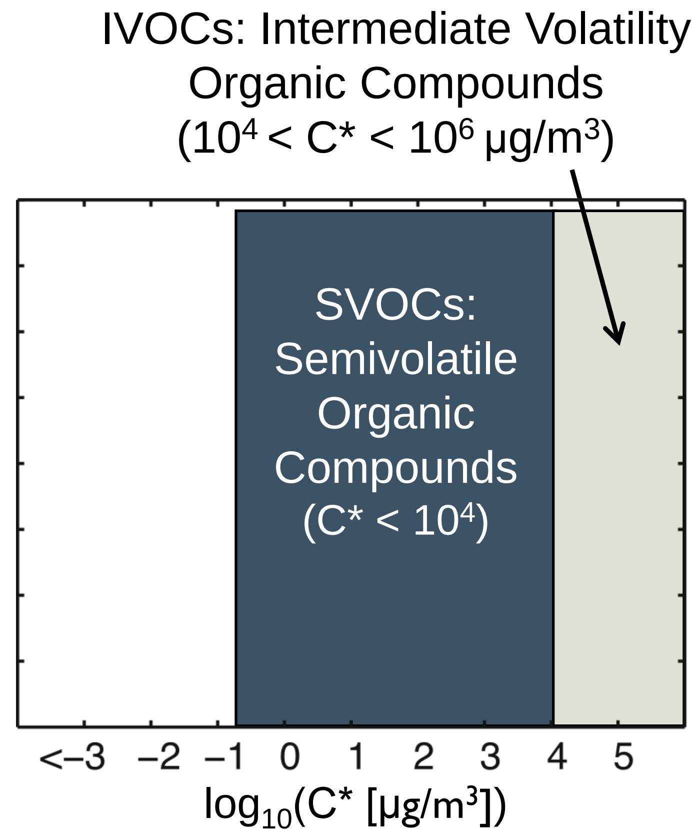



Zhang, Jimenez et al., *GRL*, 2007

# Low-Volatility Organics

Recent work indicates there is a large potential for low-volatility organic compounds ( $C^* < 10^6\ \mu g/m^3$ ) to form organic aerosol




See Robinson et al., 2007 Science; Shrivastava et al., 2008 JGR

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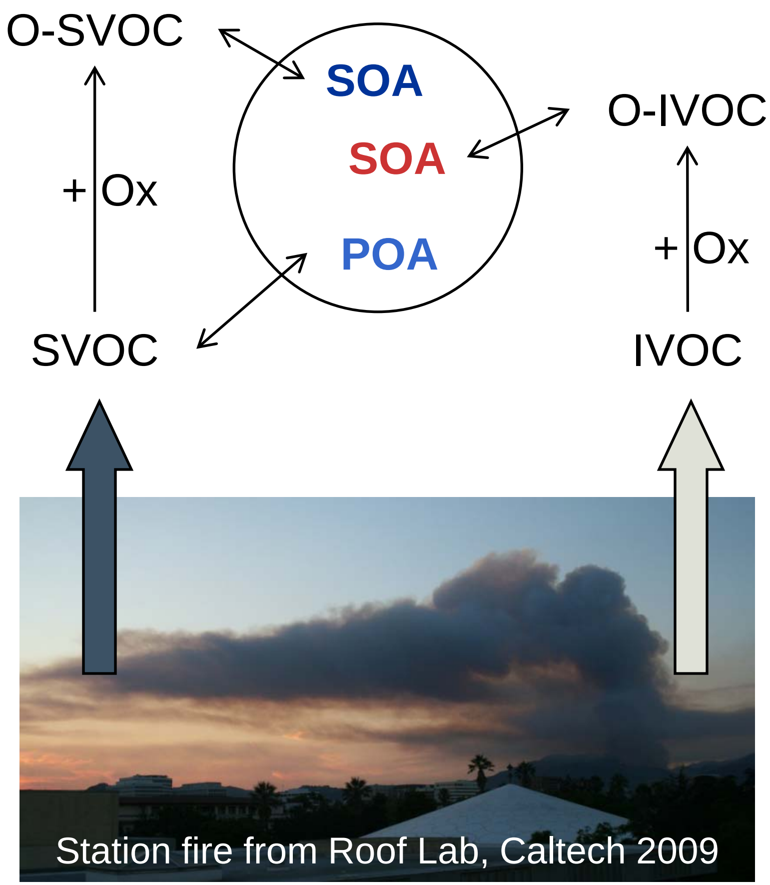
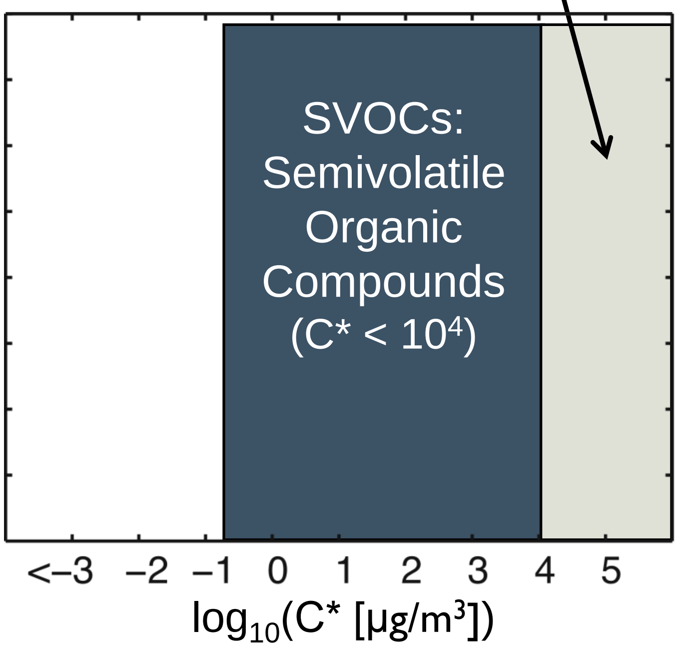



IVOCs: Intermediate Volatility Organic Compounds ($10^4 < C^* < 10^6$ µg/m$^3$)




Robinson et al., Science (2007); Shrivastava et al., JGR (2008)

# Gas-Particle Partitioning

A gas phase parent HC reacts to form several semi-volatile compounds:

$$HC + Ox \rightarrow \alpha_1 G_1 + \alpha_2 G_2 + \ldots + \alpha_i G_i$$

$$G_i \leftrightarrow A_i$$

The relative amount in each phase is governed by absorptive partitioning:

$$K_i = \frac{[A_i]}{[G_i][M_O]} = \frac{RT}{\overline{M_w}\,\gamma_i\,P_i^o}$$

$$M_O = \sum_i [A_i] + other$$

$$K_i \approx \frac{1}{C_i*}$$

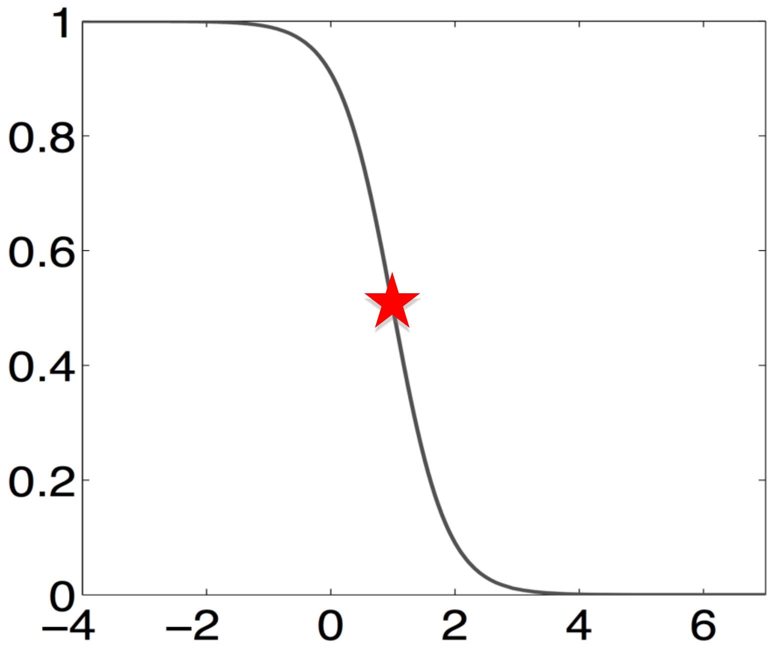
| | |
|---|---|
| $A_i$ | *aerosol-phase concentration* |
| $G_i$ | *gas-phase concentration* |
| $\alpha_i$ | *mass-based stoichiometric coefficient* |
| $M_O$ | *total aerosol mass for partitioning* |
| $K_i$ | *equilibrium partitioning coefficient* |
| $P_i^o$ | *vapor presure of pure species i at T* |
| $C_i*$ | *saturation vapor pressure* |

# Gas-Particle Partitioning

Fraction of Semivolatile in Aerosol Phase vs. Saturation Vapor Pressure
($M_o$ = 10 μg/m$^3$)

Fraction in Aerosol

$$\frac{[A_i]}{[G_i]+[A_i]}$$




$\log_{10}(C^*_i$ [μg/m$^3$])

# Questions

- How much aerosol do SVOCs and IVOCs produce globally?
- Can we simulate reasonable surface concentrations with semivolatile POA in a global model?
- What are the relative contributions of modern and fossil carbon to global organic aerosol?

# Model Overview

Objective: Estimate the contribution of SVOCs and IVOCs to organic aerosol in GEOS-Chem (v8-01-04, 2x2.5 assimilated meteorology and 4x5 GCM meteorology)

| Category | Precursor/description | Oxidants |
|---|---|---|
| **Traditional GEOS-Chem SOA (Henze et al., ACP, 2008):** | | |
| $SOA_1$ | Pinene, sabinene, D3-carene, limonene, terpenes | $O_3$, OH, $NO_3$ |
| $SOA_2$ | Myrcene, linalool, terpene-4-ol, ocimene | $O_3$, OH, $NO_3$ |
| $SOA_3$ | $\beta$-caryophyllene, $\alpha$-humulene | $O_3$, OH |
| $SOA_4$ | Isoprene | OH |
| $SOA_5$ | Aromatics (benzene, toluene, xylene) | OH followed by $HO_2$ or NO |
| **Traditional GEOS-Chem primary organic aerosol:** | | |
| POA | Nonvolatile primary organic aerosol | none |

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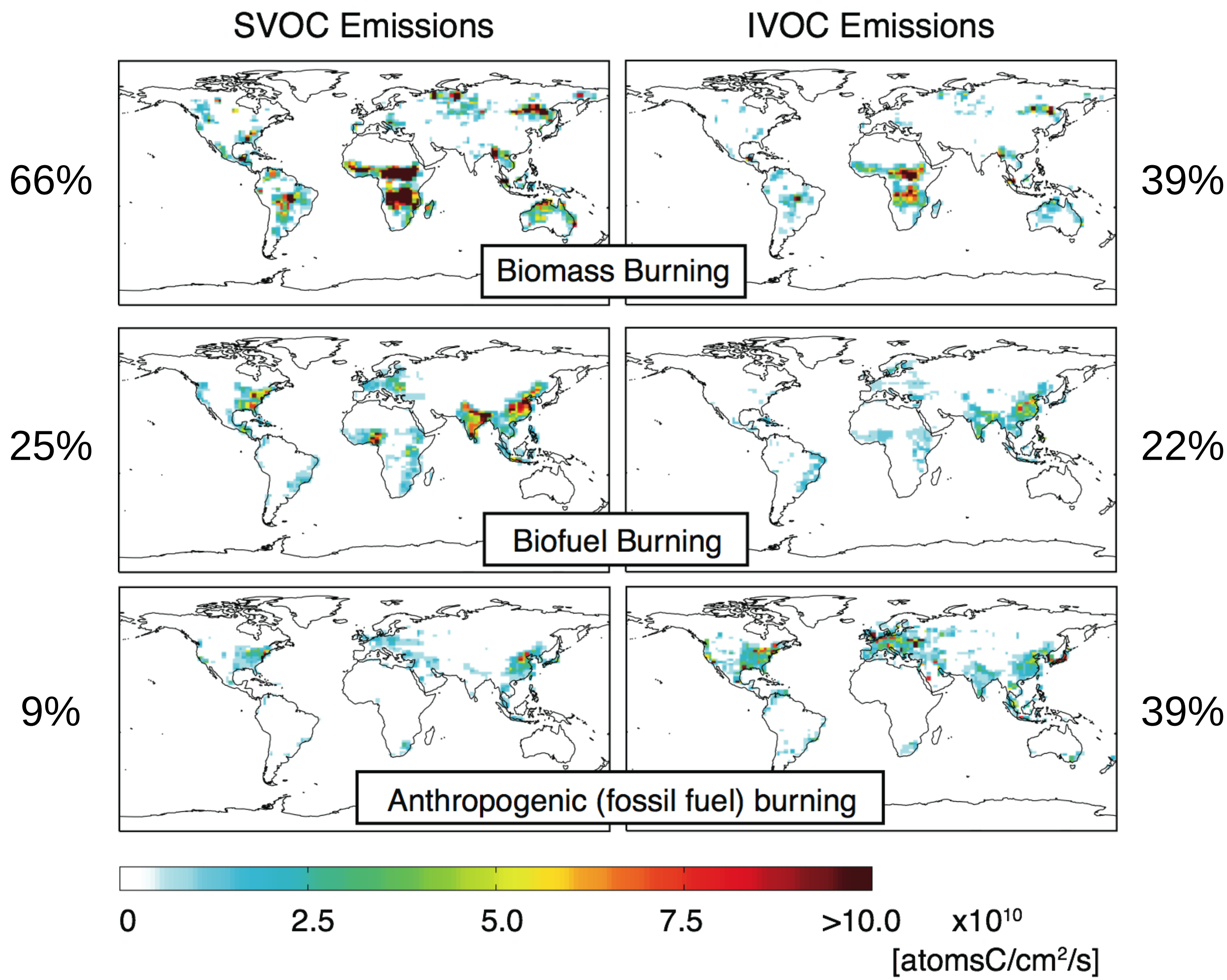
| **New aerosol from low volatility organic compounds (this work):** | | |
| **POA** | Emissions of SVOCs that partition to the aerosol phase | none |
| **$SOA_{SVOC}$** | SOA formed from SVOC emissions oxidized in the gas phase | OH |
| **$SOA_{IVOC}$** | SOA from IVOCs (naphthalene-like) | OH followed by $HO_2$ or NO |

# What are the SVOC & IVOC emissions?

| Region | SVOC emissions | IVOC emissions | Works |
|---|---|---|---|
| Global | 1.27 x POA (1st estimate)<br>~2 x POA (best estimate) | ~0.5 x POA (averaged) | This work: Pye and Seinfeld, ACPD (2010) |
| US Regional | 1 x POA | 1.5 x POA | Robinson et al., Science (2007)<br>Shrivastava et al., JGR (2008) |
| Mexico City | 3 x POA | 4.5 x POA | Tsimpidi et al., ACP (2010)<br>Hodzic et al., ACPD (2010) |

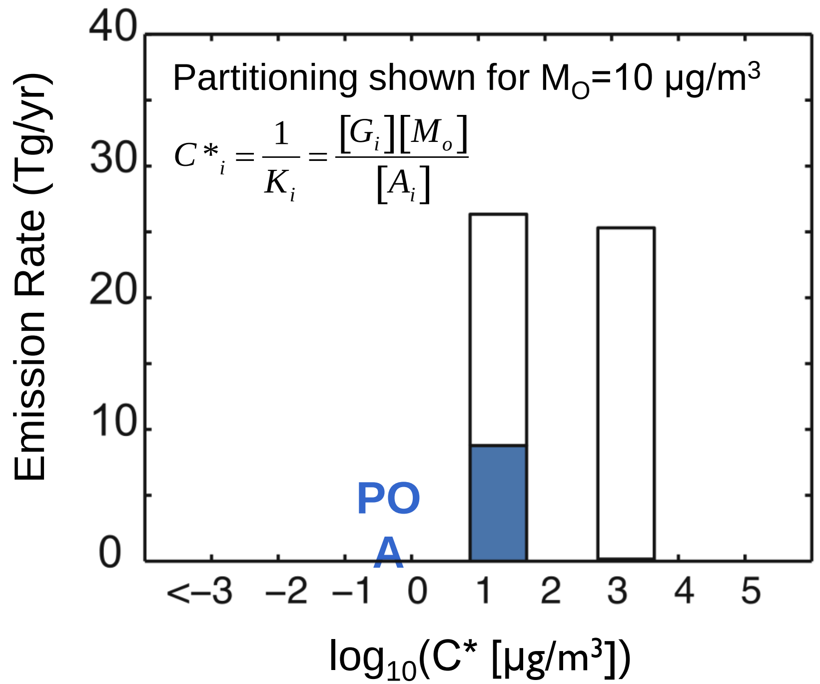
- Results indicate current POA inventories may be missing 50% or more of the SVOC emissions.
- Fossil fuel combustion sources are estimated to produce relatively more IVOCs than wood burning leading to large regional IVOC:POA ratios in the US and Mexico City but low IVOC:POA ratios globally.

# SVOC and IVOC Emissions



# SVOC Emissions

SVOC emission $\rightarrow$ 0.51 $SVOC_1$ + 0.49 $SVOC_2$




$C^*_1$ = 20 μg/m$^3$

$C^*_2$ = 1646 μg/m$^3$

- Parameters for wood smoke POA from Shrivastava et al., ES&T (2006)

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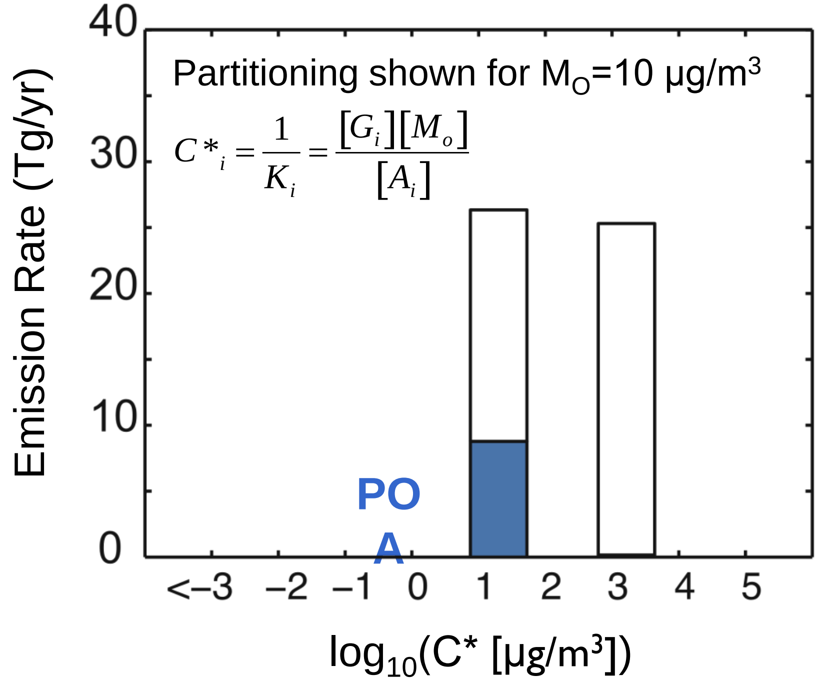


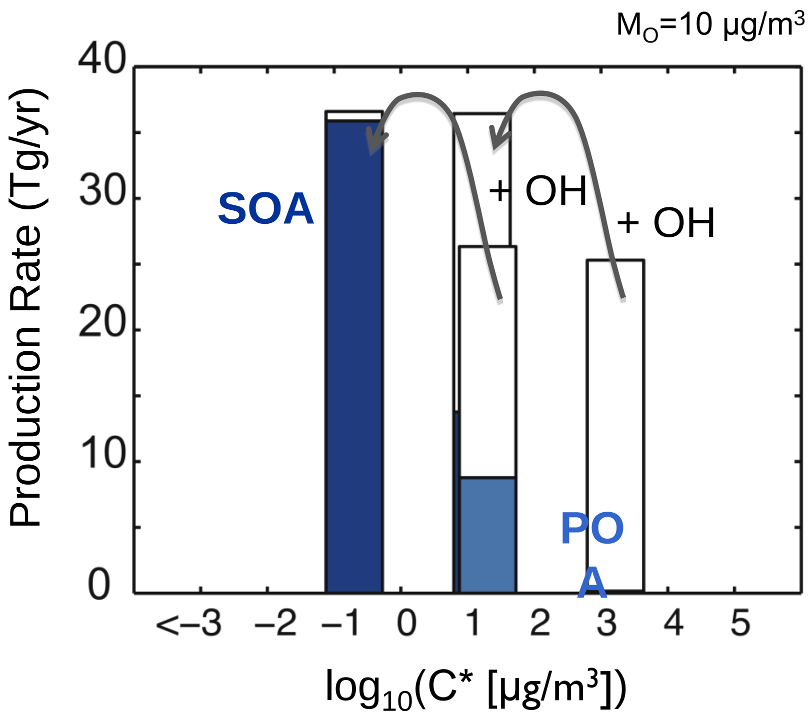

$C^*_1$ = 20 μg/m$^3$

$C^*_2$ = 1646 μg/m$^3$

- Parameters for wood smoke POA from Shrivastava et al., ES&T (2006)
- Non-volatile POA emission inventory scaled (up 27%) to represent all SVOCs according to Schauer et al., ES&T (2001)

$$\frac{Gas-phase\ SVOC\ surrogate}{Aerosol\ phase\ emission} = 0.27$$

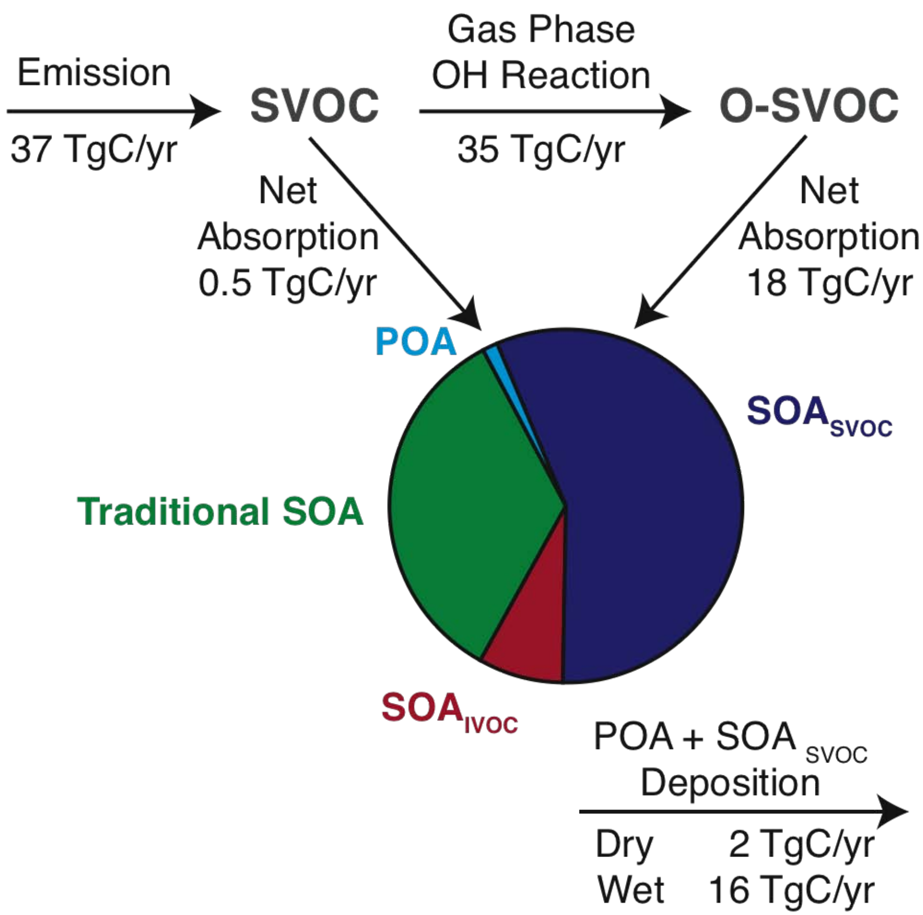
# SVOC Oxidation




| Parameter | Value |
|---|---|
| Reduction in volatility | 100x |
| Increase in mass | 50% |
| $k_{OH}$ ($cm^3$ $molec^{-1}$ $s^{-1}$) | $2x10^{-11}$ |
| Number of oxidations | 1 |

Oxidation in gas phase based on Grieshop et al., ACP (2009) and Robinson et al., Science (2007) with some adjustment

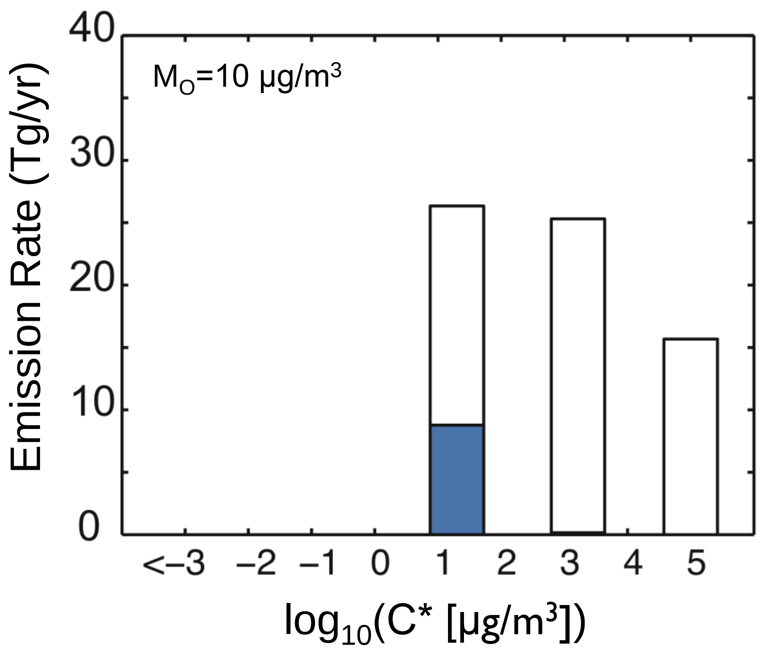
# SVOC Global Budget




Pie indicates annual net production in TgC (32 TgC total)
SVOC and O-SVOC are also wet and dry deposited in gas phase (not shown), all numbers for year 2000

# IVOC Emissions

IVOC emissions
- Distributed like naphthalene
- Scaled up to represent all IVOCs




Andreae and Merlet, GBC (2001); Schauer et al.,ES&T (2001); Zhang and Tao, Atm. Env.(2009)

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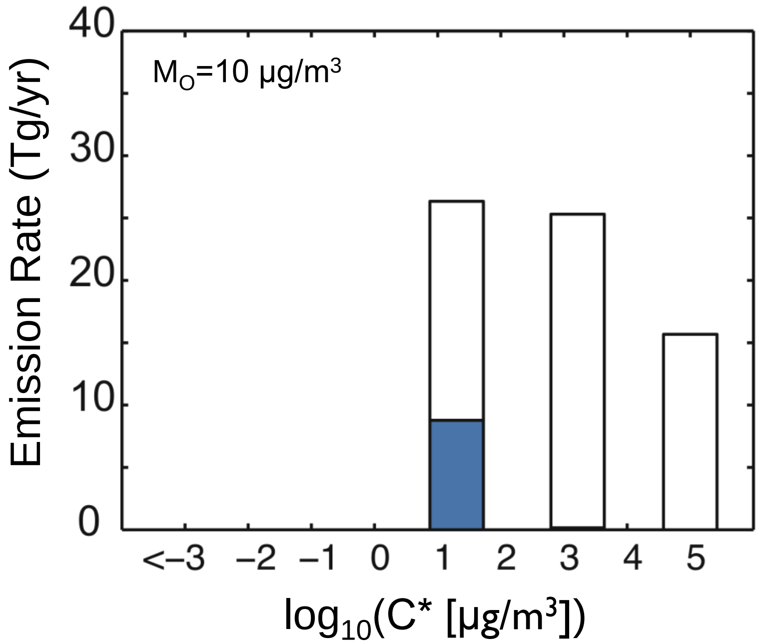
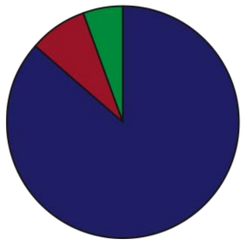
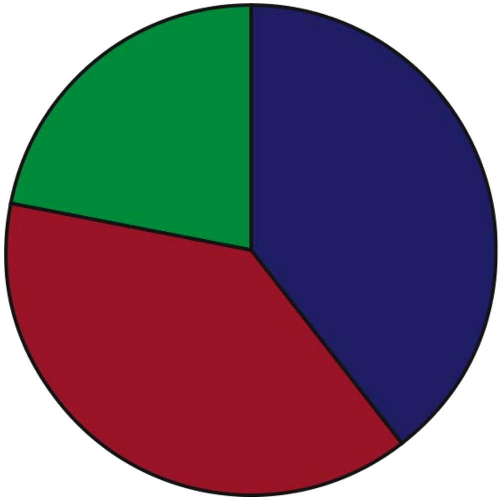



Andreae and Merlet, GBC (2001); Schauer et al., ES&T (2001); Zhang and Tao, Atm. Env. (2009)

Types of IVOCs:
**Anthropogenic**
**Biomass Burning**
**Biofuel Burning**

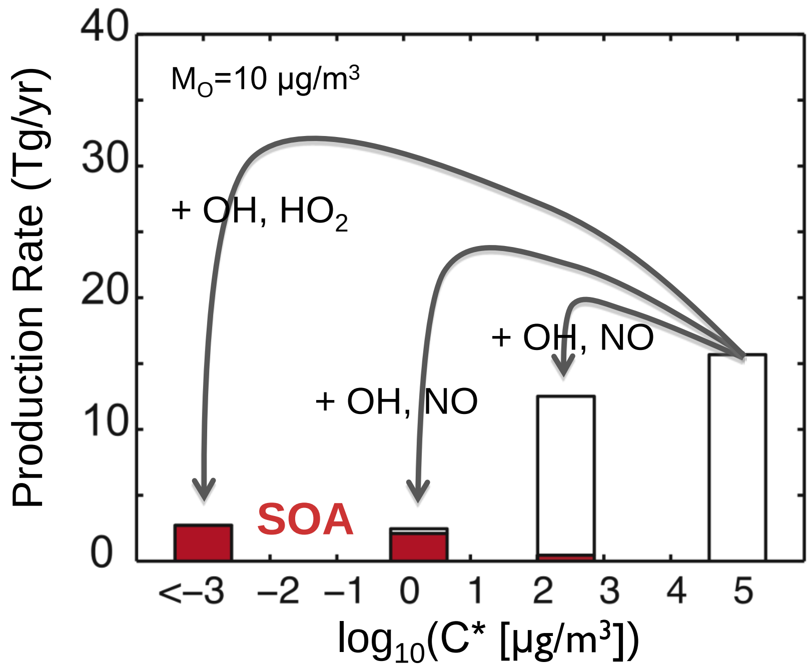


U.S. IVOC emissions: 1.5 TgC/yr



Global IVOC emissions: 15 TgC/yr

# IVOC Oxidation




Based on naphthalene:

$$IVOC + OH \rightarrow RO_2$$

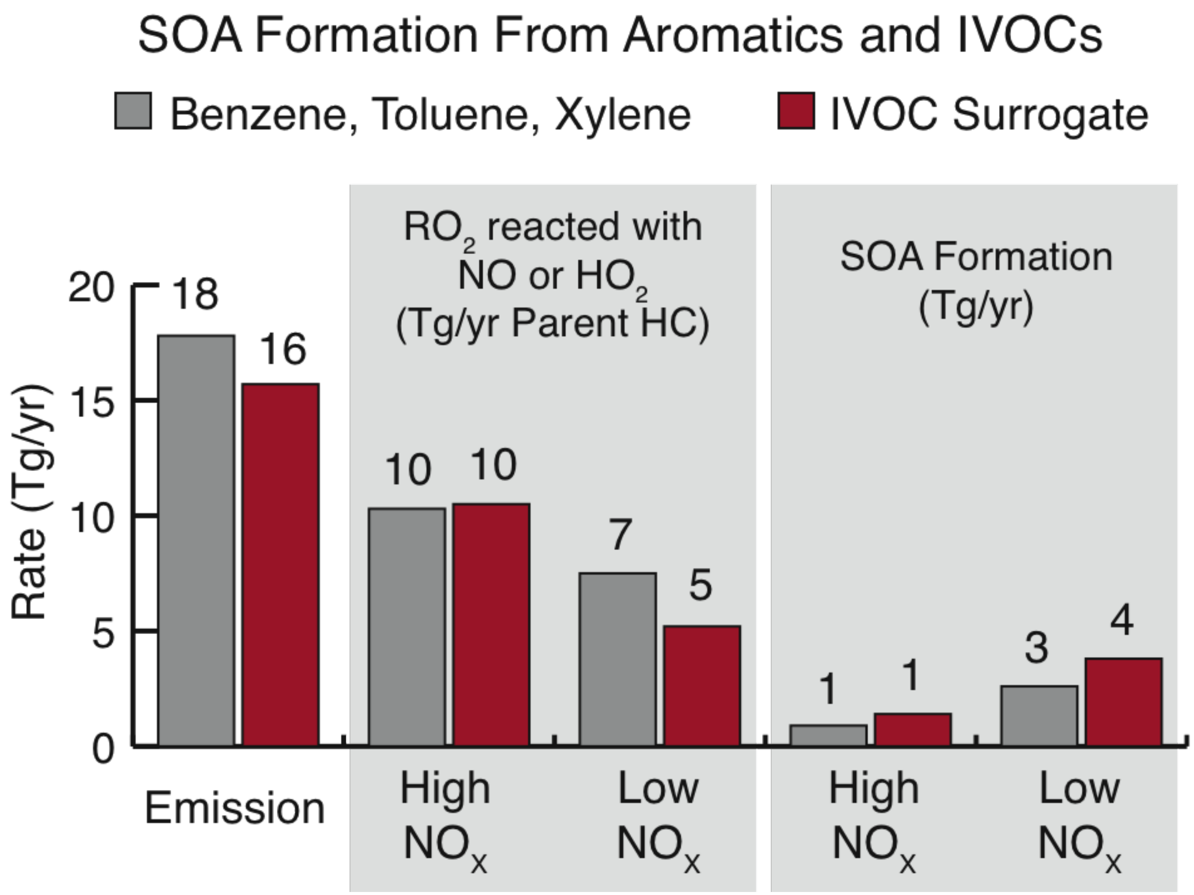
$$RO_2 + HO_2 \rightarrow \alpha_1 P_1$$

$$RO_2 + NO \rightarrow \alpha_2 P_2 + \alpha_3 P_3$$

| Product | Alpha | K ($m^3/\mu g$) | C* ($\mu g/m^3$) |
|---|---|---|---|
| 1 | 0.73 | -- | $<10^{-3}$ |
| 2 | 0.21 | 0.59 | 1.7 |
| 3 | 1.07 | 0.0037 | 270 |

Parameters for IVOC oxidation from Chan et al., ACP (2009); Henze et al., ACP (2008)

# SOA Production from IVOCs



# Global Estimate of OA Sources

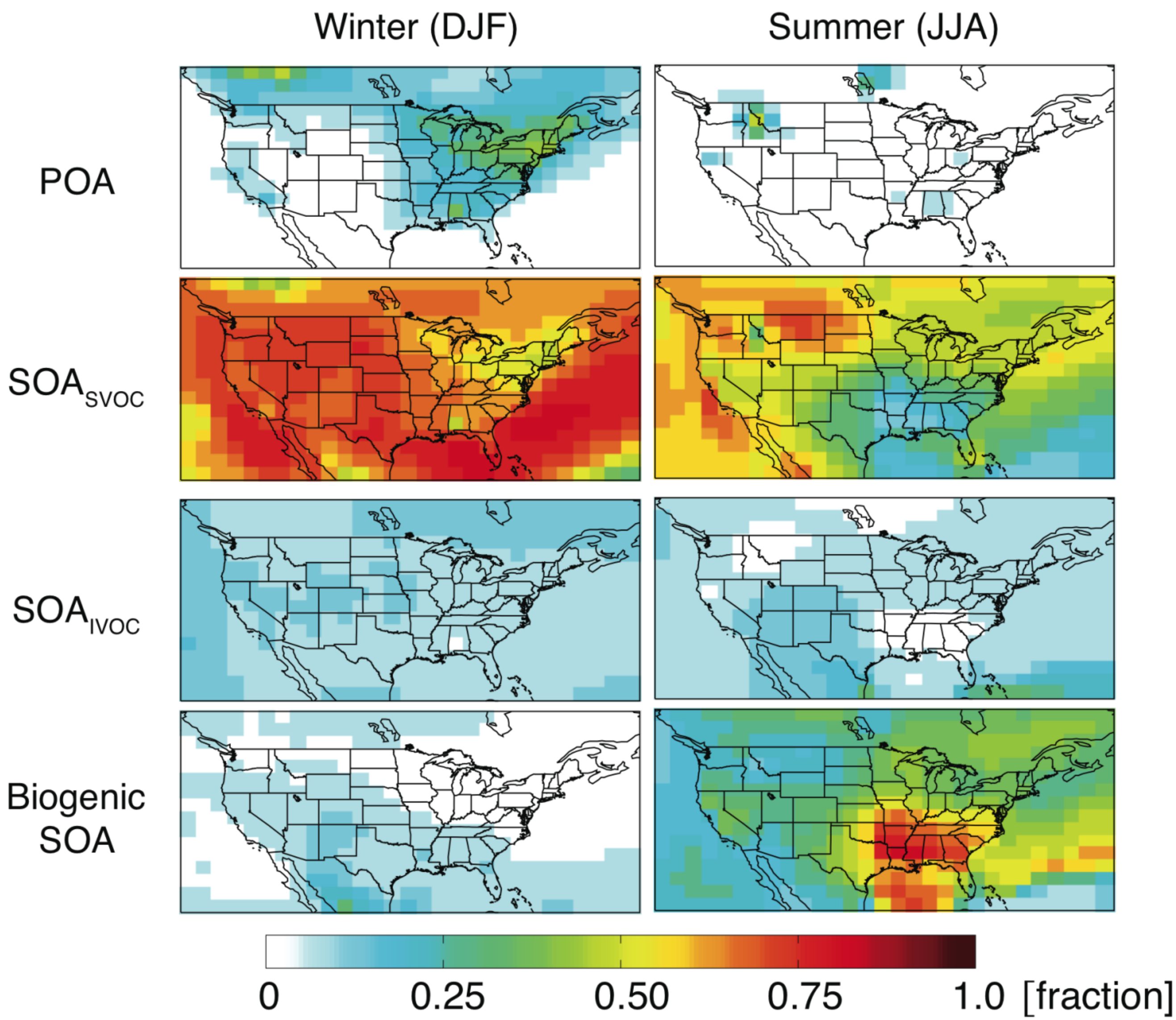
| SECONDARY SOURCES (Tg/yr) | |
|---|---|
| Terpenes* | 8 |
| Isoprene* | 11 |
| Aromatics | 3 |
| SVOCs (SOA) | 38 |
| IVOCs | 5 |
| **PRIMARY SOURCES (Tg/yr)** | |
| SVOCs (POA) | 1 |
| **TOTAL (Tg/yr)** | **67** |

* Depends on resolution, biogenic inventory, and meteorology
(these numbers: 2x2.5 GEOS4 only considering absorptive partitioning)

# Questions

- How much aerosol do SVOCs and IVOCs produce globally?
  - SVOCs are predicted to be the dominant global OA source
  - SVOCs + IVOCs lead to about 44 Tg/yr of net OA production

# Simulated Aerosol Composition



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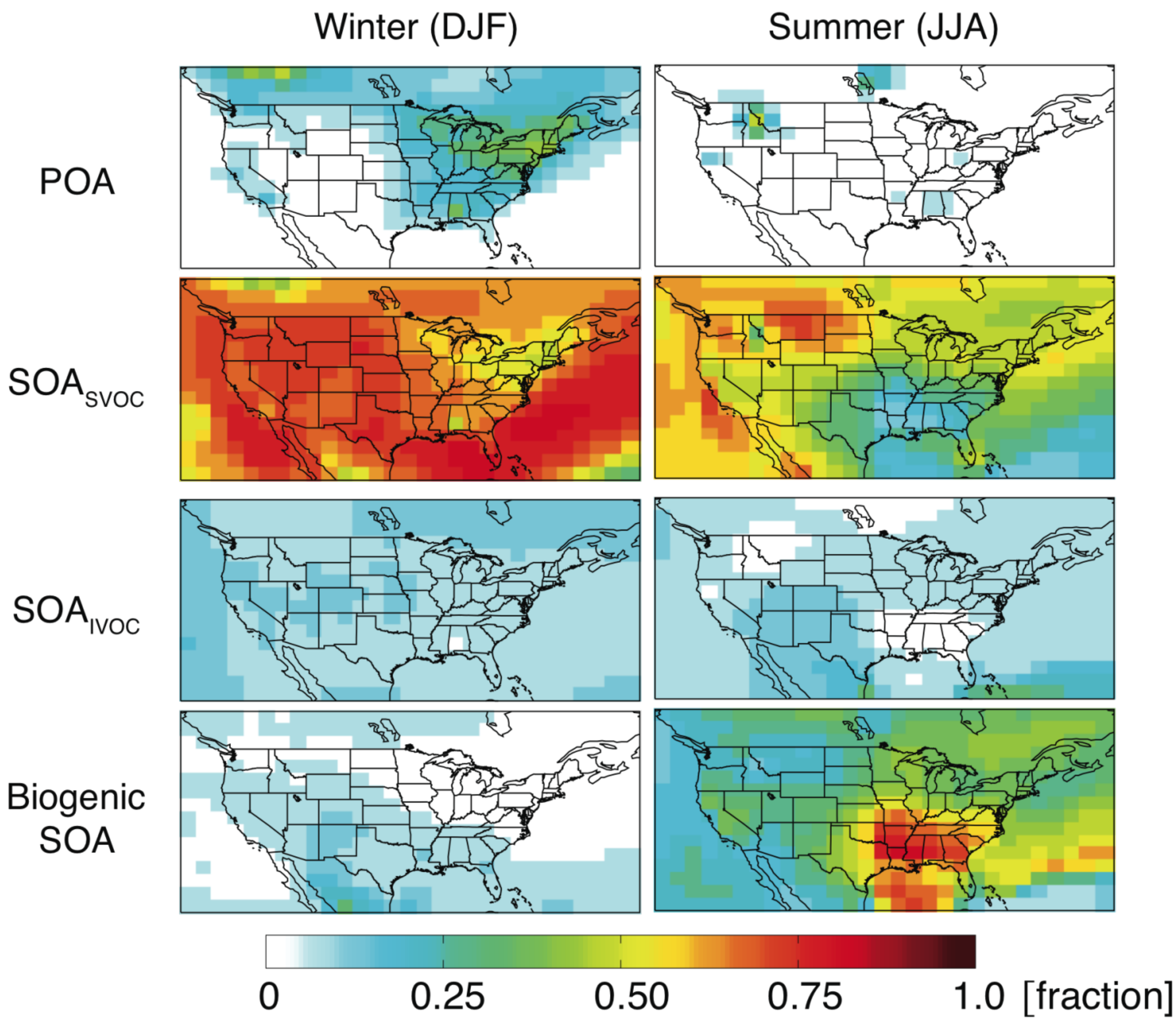



Aerosol from SVOCs dominates in winter

Aerosol from SVOCs significant in summer and winter

# Questions

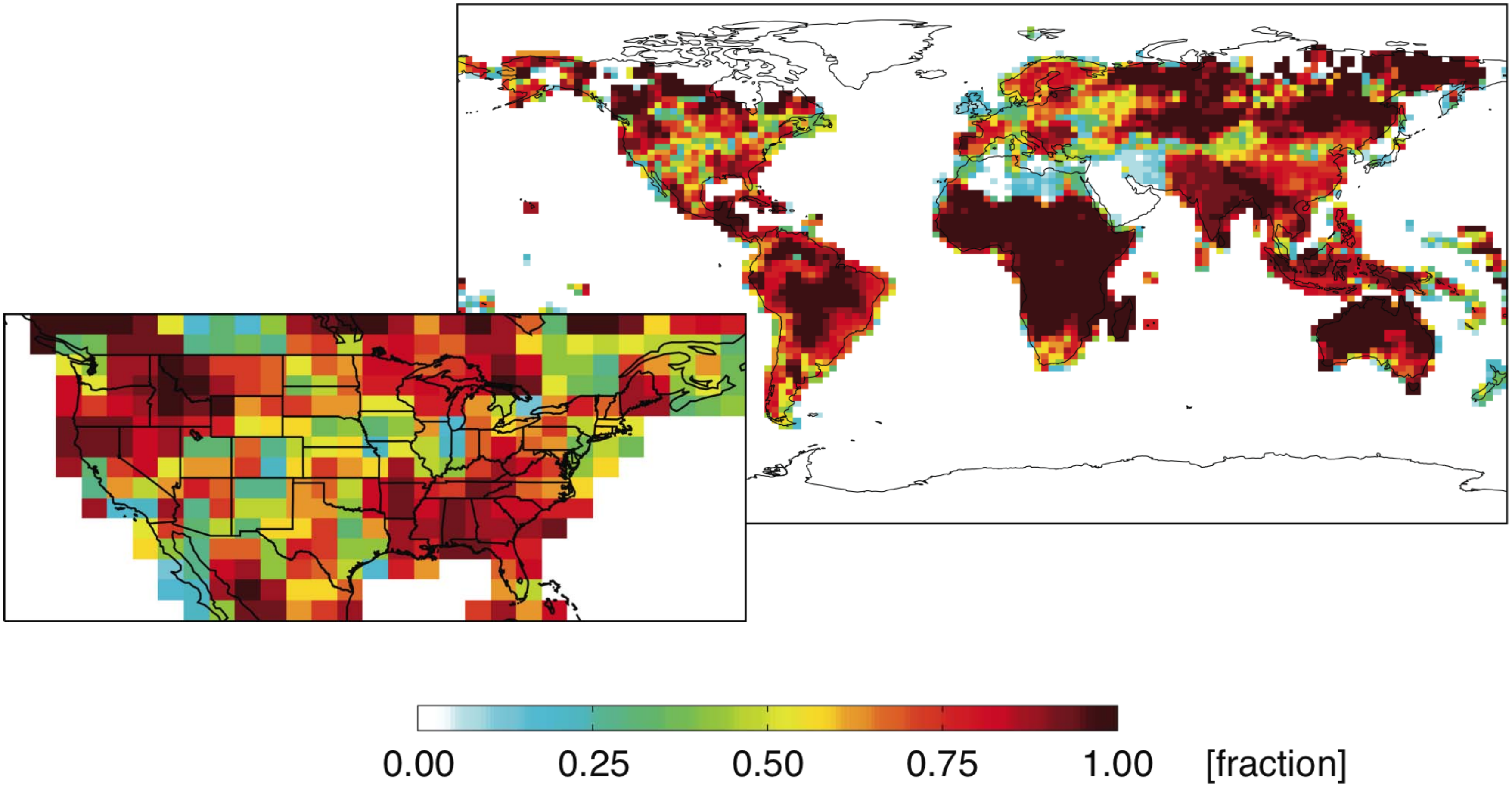
Can we simulate reasonable surface concentrations with semivolatile POA in a global model?

•Surface concentrations are substantially underestimated unless SVOC emissions are significantly scaled up or the volatility of the emissions is reduced

- There is a larger pool of organics to form aerosol
  - SVOC emissions are 27% higher than the traditional POA inventory
  - IVOCs represent a new source of aerosol
- However, surface concentrations are lower
  - Generally, 50% or more of the SVOC emissions evaporate
  - SOA from SVOCs is semivolatile as well
  - IVOCs have a relatively low yield of aerosol (~30%)

# Significant Amount of Modern OC

Fraction Modern C of SVOC Emissions



# Questions

What are the relative contributions of modern and fossil carbon to US organic aerosol?

- Total OA over the US is likely dominated by modern C
  - Summer aerosol contains significant amounts of modern carbon due to biogenic SOA formation.
  - SVOC aerosol (either POA or SOA) contributes significantly to surface concentrations in the winter and summer over the U.S.
    - SVOC aerosol over the US is likely dominated by modern C due to biomass and biofuel burning emissions

- Aerosol in remote global regions may have a larger fossil component due to low-$NO_x$ oxidation and formation of nonvolatile SOA from aromatics and IVOCs

# Conclusions

- Approximately 50% of the SVOC carbon is responsible for net aerosol production (SVOC aerosol source: 39 Tg/yr)

- The yield of aerosol from IVOCs is ~30% (IVOC aerosol source: 5 Tg/yr)

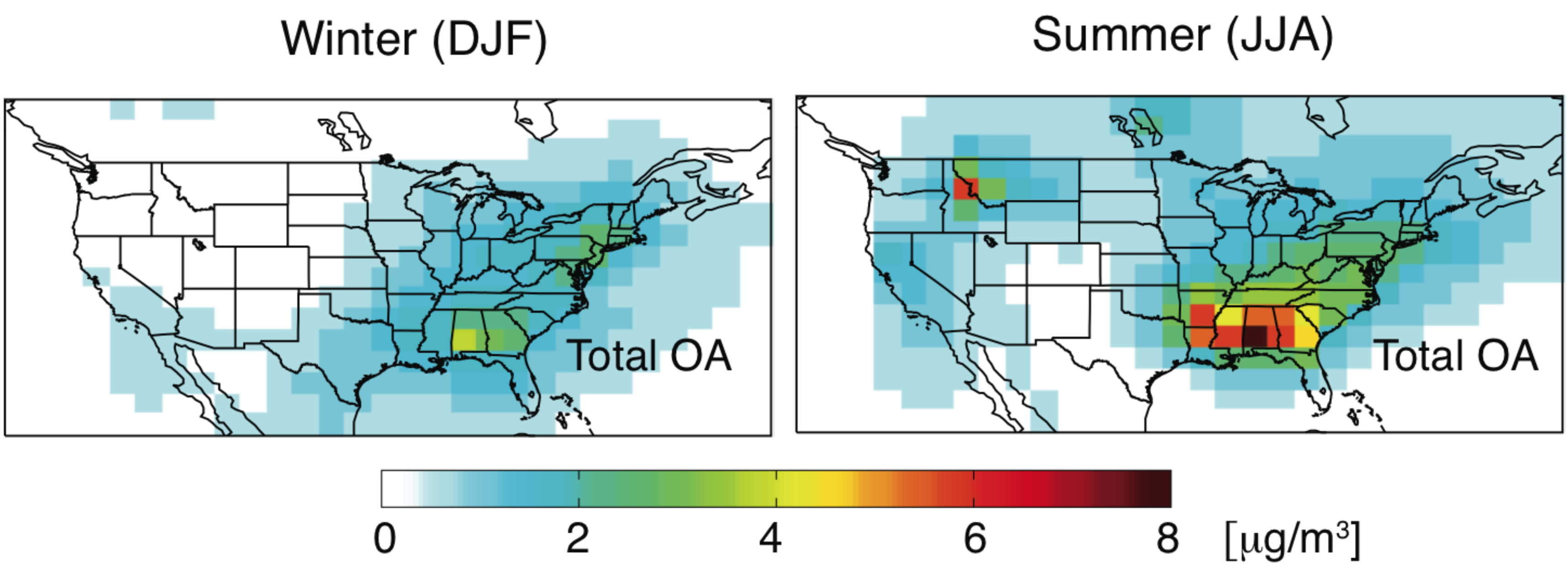
- Revised simulation does not provide better measurement/model agreement
  - Sensitivity simulations indicate that SVOC emissions may be significantly underestimated
  - Errors in the SVOC emission volatility could have an impact on estimated OA concentrations

- Organic aerosol over the US is likely dominated by modern carbon

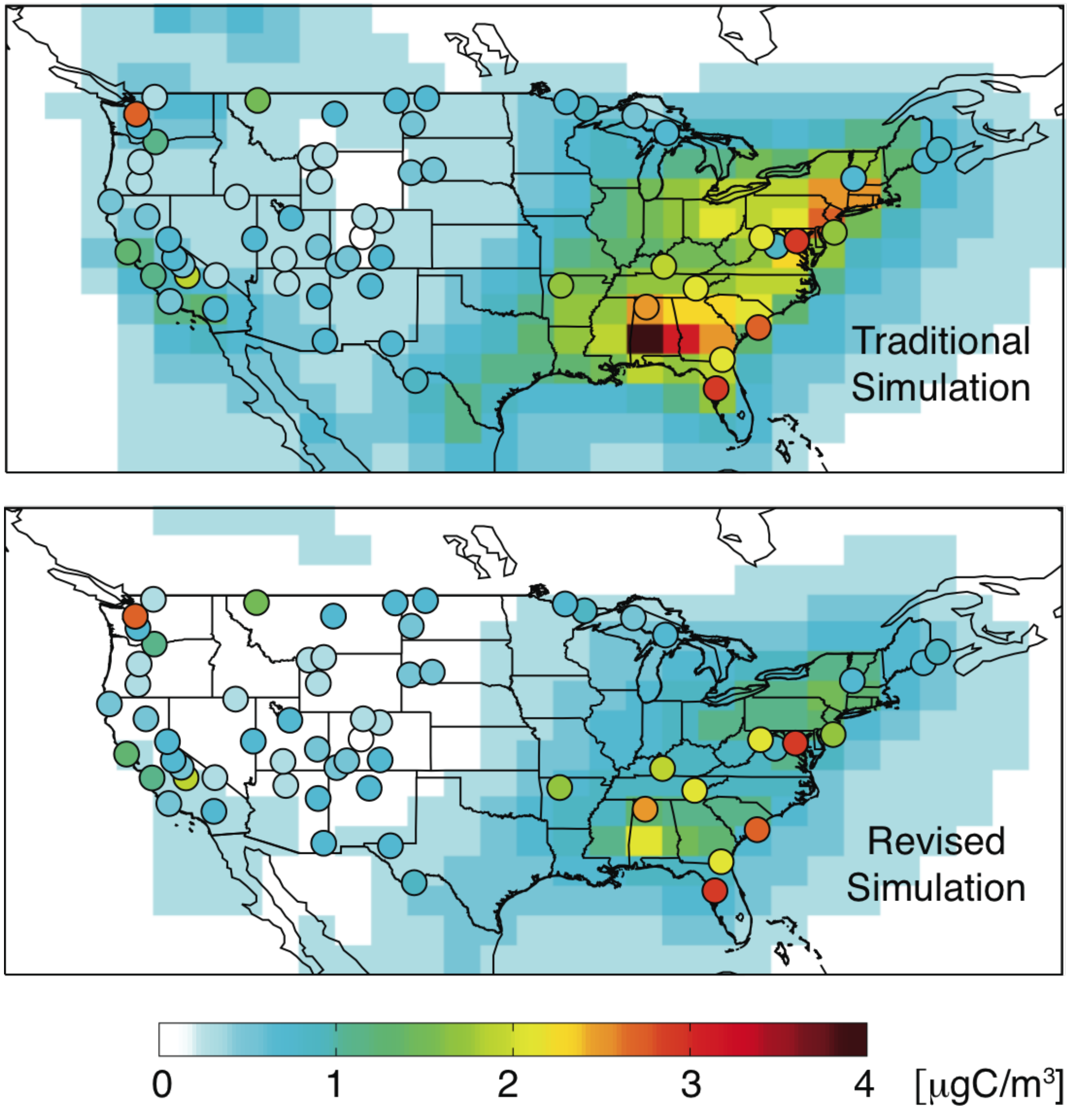
# Extra

# Aerosol Concentrations

Total Organic Aerosol During Winter and Summer 2000



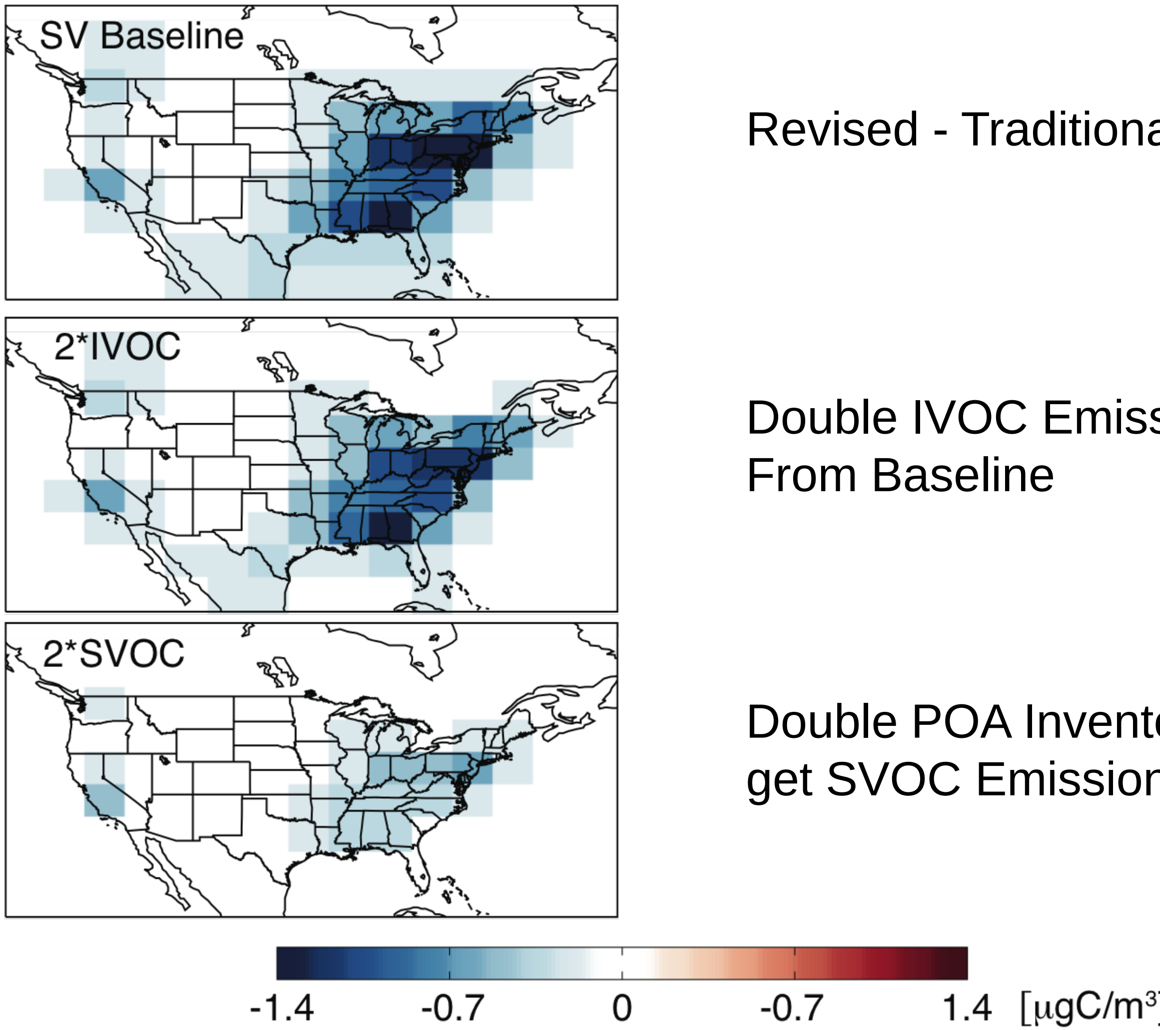
# Winter OC Concentration




- Simulated OC values shown on grid
- Observations from the IMPROVE network shown as circles
- Data from DJF 2000
- The traditional simulation provides a better estimate of surface OC concentrations than the revised simulation

# Effect of Emission Parameters

Simulated DJF OC concentration relative to traditional simulation



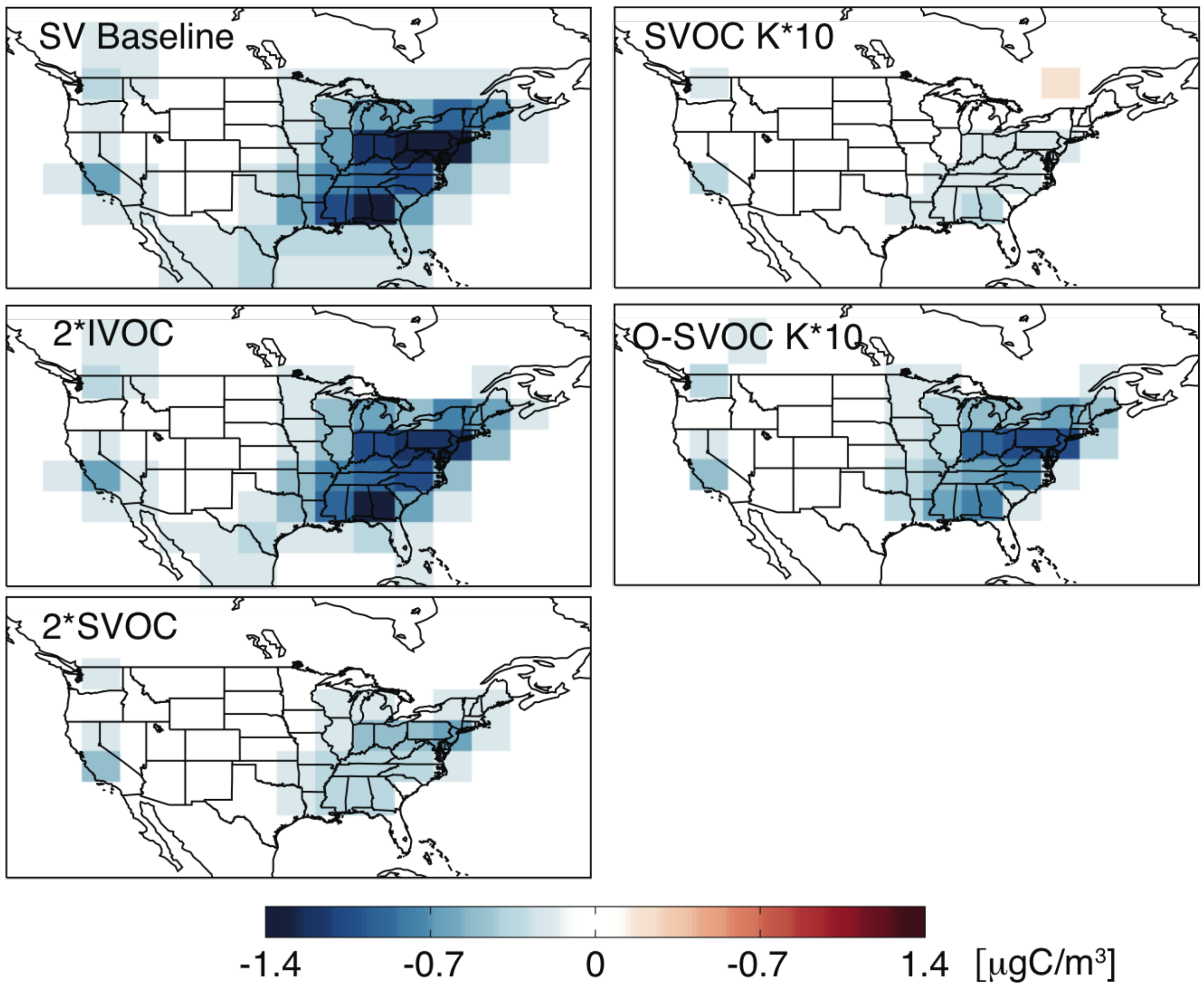

Revised - Traditional

Double IVOC Emissions From Baseline

Double POA Inventory to get SVOC Emissions

# Effect of Volatility Parameters

Simulated DJF OC concentration relative to traditional simulation

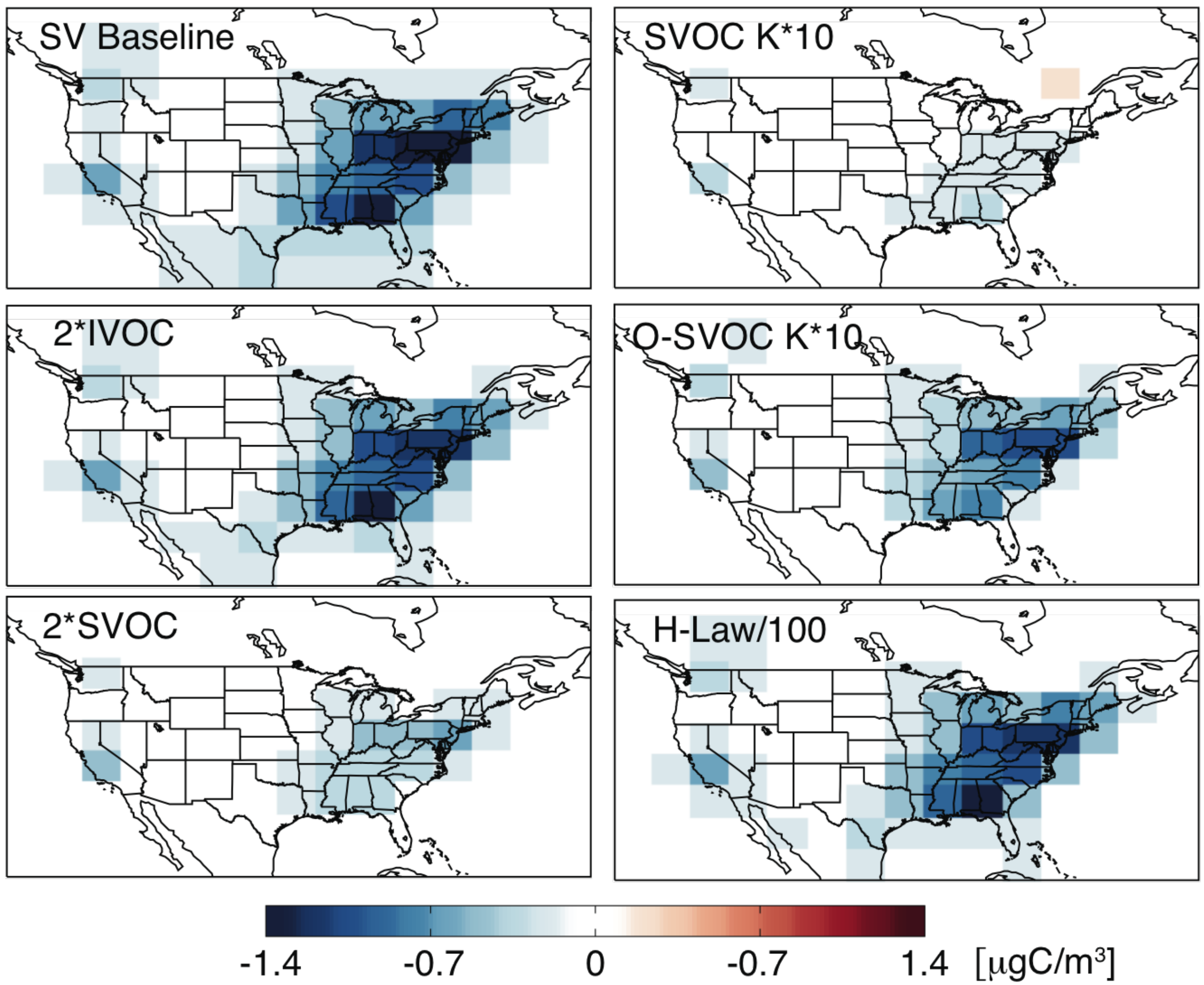



Make SVOC Emissions 10x Less Volatile

O-SVOC is 1000x Less Volatile than SVOC

# Effect of Henry's Law Parameters

Simulated DJF OC concentration relative to traditional simulation

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H-Law is $10^3$ M/atm