Sources of Organic Aerosol: Semivolatile Emissions and Photochemical Aging

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A knowledge gap...
Complexity of Combustion Emissions

Diesel exhaust

87% of particle-phase & SVOC/IVOC emissions are UCM

Schauer et al., ES&T 2002
Old conceptual model

Primary Organic Aerosol
- Non-volatile
- Non-reactive

Secondary Organic Aerosol
- Very volatile precursors
- Semivolatile products

Primary Emissions
- Diesel exhaust
- Wood smoke

POA

SOA Precursor
- Monoterpenes
- Light aromatics

Volatile Products

C* (µg m⁻³)

- S₁
- S₂

α₁

α₂
Revised conceptual model

- Semivolatile
- Reactive

Primary Emissions

\[ C^* \, (\mu g \, m^{-3}) \]

\( f_1 \) \quad \( f_2 \) \quad \( f_3 \) \quad \( f_4 \) \quad \( f_5 \)

- \( P_1 \)
- \( P_2 \)
- \( P_3 \)
- \( P_4 \)
- \( P_5 \)

Volatile Products

\( S_1 \) \quad \( S_2 \)

\( \alpha_1 \) \quad \( \alpha_2 \)

SOA Precursor

(Robinson et al. Science 2007)
Traditional SOA

Non-Traditional SOA

Estimated Yield

Cummulative OA (Tg yr⁻¹)

Emissions (Tg yr⁻¹)

Biogenic

Anthropogenic

( Donahue et al. AE 2009)
Objectives of Research

- What is the volatility distribution of fresh emissions?
- What is the effect of aging on primary emissions?
- What are the implications for urban and regional organic aerosol concentrations?
Objective 1. Quantifying volatility distributions

- Change $T$ or $C_{OA}$
- Measure changes in partitioning
- Fit data to derive volatility distribution

Lipsky et al., ES&T, 2006
An et al., J. Aerosol Sci., 2007
Combining TD and Dilution Data

Grieshop et al. EST 2010
Partitioning and POA Emission Factors

Robinson et al. JAWMA 2010
Objective 2. Effects of aging

Experiments with increasingly complex mixtures

Single components
- $n$-alkanes
- branched alkanes
- aromatics
- simple mixtures

Emission Surrogates
- motor oil (new & used)
- diesel fuel
- mixtures of fuel & oil

Diluted exhaust
- diesel exhaust
- wood smoke
- aircraft exhaust
Aging of Wood Smoke Experimental Setup

- Woodstove
- Heated Dilution Air
- Isolation Valve
- Heated Inlet
- Bypass (for stove startup and shutdown)
- Teflon-lined chamber
- UV Lights
- Fuel: Laurel Oak and Yellow Pine
- Gas-phase Instruments: VOCs: PTR-MS, GC-MS, NDIR CO CO₂ O₃, Chemiluminescence NOₓ
- Aerosol Instruments: SMPS, Q-AMS
- Aerosol Instruments: SMPS, 8-channel Aethelometer (BC)

End of Experiment: OC/EC Filter Samples
Wood smoke Aging Rapidly Creates Lots of “SOA”

(Grieshop et al. ACP 2009)
Data from multiple wood smoke aging experiments

(Grieshop et al. ACP 2009)
Similarity of Aged Organic MS

Wood smoke versus lab diesel

Wood smoke versus ambient

Elapsed Time since UV (hrs)

R²

Wood smoke versus lab diesel

Wood smoke versus ambient

Elapsed Time since UV (hrs)

Ambient Factors courtesy of J. Jimenez CU Boulder

(Grieshop et al. ACP 2009)
$n$-alkane high NOx SOA yields

(Presto et al. EST 2010)
Yields are “high”
Parameterizing yields based on C*

(Presto et al. EST 2010)
SOA from IVOCs can be highly oxygenated

Composition C15 SOA

(Presto et al. EST 2009 & 2010)
Objective 3. Regional and global modeling to quantify organic aerosol

- **Modifications**
  - Update inventory
  - Added species
  - Aging

- **Critical inputs**
  - Volatility distribution
  - Aging mechanism
  - IVOC emissions
  - Activity coefficients
Aging mechanism

Aging Scheme

- Gas-phase Reactions with OH
- $k_{OH} = 4 \times 10^{-11} \text{ cm}^3 (\text{molec s})^{-1}$

C$^* @ 298K (\mu g/m^3)$

Concentration (\mu g/m$^3$)

Scheme #1

Data

Scheme #2

Primary

Time (hrs)

Aerosol Mass (\mu g/m$^3$)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

0 5 10 15 20 25

Particle Gas
Updating Emission Inventories

Redistributing Non-Volatile POA

Revised Inventory

NEI 2002

Emissions (Tg yr$^{-1}$)

$C^* \text{ (g m}^{-3}\text{)}$

Emissions (Tg yr$^{-1}$)

$C^* \text{ (ug m}^{-3}\text{)}$

Emissions (kton/yr)

$C^* \text{ (ug m}^{-3}\text{)}$
Are there missing emissions?

Emissions Data

(Schauer et al. EST 99, 00, 02)
Summertime OA Predictions

Traditional Non-volatile POA  Semivolatile POA  Revised Semivolatile + Aging

July 2001

OA  \( \mu g \text{ m}^{-3} \)

0  1  2  3  4

Shrivastava et al. JGR 2008
July 2001 OA

Ratio of Revised-to-Traditional Predicted OA levels

Shrivastava et al. JGR 2008
Wintertime OA Predictions

Traditional
Non-volatile POA

Semivolatile POA

Revised
Semivolatile + Aging

January 2002

Shrivastava et al. JGR 2008

OA
µg m⁻³

0 1 2 3 4
January 2002

Ratio of Revised-to-Traditional Predicted OA levels

Shrivastava et al. JGR 2008
Revised model predicts a more regional aerosol

Shrivastava et al. JGR 2008
Oxygenated Organics Dominate in Summer

Traditional Model
Non-Volatile POA

Revised model
Semivolatile + Aging

Traditional SOA
Total OA

Traditional SOA + Aged Primary
Total OA

July 2001

Carnegie Mellon
Revised Model and AMS OOA

Fractional contribution to total OA

AMS data Zhang et al. GRL 2007
Conclusions

- Primary emissions are semivolatile
- Aging of emissions create substantial SOA
- Accounting for aging and partitioning improves predictions of CTMs
- Important implications for developing control strategies


Journal Papers

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