A Revised Framework for Treating Primary Organic Aerosol Emissions in Inventories and Models

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Fine Particulate Matter Composition

Pittsburgh July 2001, 20.1 ug/m$^3$
Sources of Organic Aerosol (OA)

Photochemistry
VOC + hν, O₃, OH, NO₃

Secondary Organic Aerosol

Condensed Phase Emissions

Primary

Secondary

Gas Phase Emissions

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What is primary organic aerosol?

Hildemann et al.

- Broad range of compounds
- ~10% Resolved
- ~90% Unresolved Complex Mixture (UCM)
  - branched compounds
  - cyclic compounds

Measure with dilution sampler

GC/FID of extracted filter sample
Gas-Particle Partitioning and the Volatility Distribution

Partitioning Theory:

- Raoult’s Law
  \[ P_i = \gamma_i P_{sat,i}(T) y_i \]
- C* or Partitioning Coefficient

\[
X_{p,i} = \left( 1 + \frac{C_i^*}{C_{OA}} \right)^{-1}
\]

\[ C_{OA} = \sum X_{p,i} C_i \]

Donahue et al. ES&T 2006

Pankow AE 1987 & 1994

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Volatility Distribution

Donahue et al. ES&T 2006
Volatility distribution of NEI 2002

C* (ug/m^3)

Mass (Ktons/Yr)
Comparing NEI and ambient data

LA data from Fraser et al. ES&T 1996, 1997
How do primary emissions evolve after leaving the tail pipe?

- Initial dilution of exhaust
- Continued mixing and photochemical processing
- Deposition

Spatial Scale:
- Near Source (~ m)
- CTM Grid Cell (~ 10 km)
- Regional (100+ km)
Gas-particle partitioning of primary emissions in near field

Hildeman et al. AST 1989
Lipsky and Robinson ES&T 2006

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Volutility distribution of diesel exhaust

Partitioning Plot

Volutility distribution and partitioning at $C_{OA} = 10 \ \mu g \ m^{-3}$

Shrivastava et al. ES&T 2006
Robinson et al. Science 2007

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\[ X_p = \sum_{i=1}^{n} f_i \left( 1 + \frac{C_{i}^*}{C_{OA}} \right)^{-1} \]
POA emission factors may be biased high

Shrivastava et al. EST 2006.
Cannot represent emissions with a single, static emission factor

Particulate fraction ($X_p$) vs. $C_{OA}$ ($\mu g m^{-3}$)

Atmospheric Plume-like

$25^\circ C$, $0^\circ C$, $40^\circ C$

(Shrivastava et al. EST 2006)
Simulating Organic Aerosols in Eastern US with a Chemical Transport Model

- **PMCAMx+**
  - 36x36 km grid
  - MM5
  - July 12-28, 2001

- **LADCO Base E Inventory**
  - NEI 1999 V2

- **Modifications**
  - Apply diesel volatility distribution to all primary emissions
  - Partitioning of primary emissions
Evaporation dramatically reduces regional POA

Volatility Distributions

Traditional Model

Allowing POA to partition

July 2001

Photochemical aging of diesel exhaust

CMU smog chamber

Diluted Diesel exhaust

T=22 ± 2 °C
RH= 7 ± 3%

Particle Measurements:
- SMPS
- Q-AMS

Gas Measurements:
- Ozone Monitor
- PTR-MS
Photo-oxidation creates significant amounts of SOA

What is contribution of known SOA precursors?

- SOAM II (Koo et al. 2003)
- 58 precursors
  - Measured Aromatics
  - Estimates for other species
- Assume ideal solution
- Wall losses

Aging of low volatility vapors source of unexplained SOA

Predicted Summertime Organic Aerosol

Traditional Model

Allowing POA to partition

Partitioning + Aging

July 2001

Revised model predicts a more regional aerosol

Ratio of Revised-to-Traditional Model Predicted OA levels

Model-Measurement Comparison

Dramatic shift in primary-secondary split

Predicted fractional contribution of SOA to total OA concentration

Traditional Model

Semivolatile Emissions + Aging

July 2001

Conclusions

- Revised conceptual model for treating primary emissions
  - Gas-particle partitioning of semivolatile organics
  - Photochemical aging of semivolatile emissions

- Implications for regional OA
  - Reduce POA
  - Increase SOA
  - Developing control strategies?

- Implications for emission inventory
  - Represent emissions using volatility distribution
  - Include all low-volatility organics
Acknowledgments

- Funding US EPA through the STAR Program
Evaporation dramatically reduces regional POA

Volatile Distributions

- Traditional Model
- Semivolatile POA

Traditional Model

Allowing POA to partition

PMCAMx July 2001

Gas-particle partitioning of semivolatile organics

Partitioning Theory:
- Raoult's Law
  \[ P_i = \gamma_i P_{\text{sat},i}(T) y_i \]
- C* or Partitioning Coefficient
  \[ X_{p,i} = \left( 1 + \frac{C_{i^*}}{C_{OA}} \right)^{-1} \]
  0.1 \( \text{ug/m}^3 \) < C* < 1000 \( \text{ug/m}^3 \)

(Pankow AE 1987, 1994)
Gases Dominate Organic Emissions

Anthropogenic VOC
~ 15,000 Kton/year

POC
~ 1,200 Kton/year

NEI 2002