The Biogenic VOC Contribution to Fine Particulate Matter: From the Laboratory to Policy Design

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PM_{2.5} US Standards





Daily Standard: Old 65 μ g m⁻³ New 35 μ g m⁻³ Annual Standard: 65 µg m⁻³

The New PM_{2.5} Standard



PM_{2.5} Concentrations During PAQS



Fine PM Composition



The Source-Receptor Challenge: Interactions between Fine PM and Their Precursors



PM_{2.5} Composition

PM and Health

- Health studies have failed to identify a safe fine PM concentration level
 - Health effects were present even at very low concentration levels
- What if ammonium sulfate or bisulfate is not the major problem?
 - Does not cause health problems on its own in laboratory animal studies
 - Organics from transportation and other combustion sources are the primary suspects

Organic Particulate Matter (PM) in the Atmosphere

Traditionally measured by combustion of the particles and measurement of the carbon as CO₂ or CH_{4.} Terms used:

- Organic Carbon (OC): thousands of organic compounds
- Elemental Carbon (EC) or Black Carbon (BC): graphite-like carbon that absorbs radiation
 - BC is probably the more appropriate term because it corresponds better to what is actually measured
- Carbonates (minor contribution to PM carbon)
- Soot contains both BC and OC

Organic PM Challenges

- Thousands and thousands of mostly unknown chemical compounds
 - Most of them appear to be quite complex big molecules
 - Complicated chemistry in both the gas and particulate phase
- A lot of them exist in both the gas and particulate phase
 - They appear to "move" from phase to phase
- A lot of different sources



The Sampling Challenge

- Traditional methods rely on the collection of particles on a filter (quartz, etc.)
- Sampling artifacts
 - Organic vapors adsorb on the filter
 - Organic vapors absorb (dissolve) on the particles that have been deposited on the filter
 - Organic particles evaporate from filters in periods where the atmosphere is cleaner or warmer
- Use of denuders to remove the vapors
 - It accelerates the evaporation
- Use of after-filters to collect the evaporated organic mass
- Even with a lot of effort it introduces uncertainty in the measurement
- Other methods that do not rely on filters have their own challenges (e.g, AMS the collection and ionization efficiencies, etc.)

Average OC and EC concentrations (PAQS, Summer 2001)



The Chemical Analysis Challenge

Thermal-Optical Transmittance OC/EC Analyzer



Elemental carbon measurements are operationally defined

Thermal-Optical Transmittance OC/EC Analysis



Conversion of OC to Organic PM

• Organic PM and OC:

Organic PM (μ g/m³) = a . OC (μ gC m⁻³)

a: Conversion Factor (μ g/ μ gC)

- Organic PM contains H, O, and N
 - Conversion factors of a=1.2-2.3 have been proposed or used
 - Introduces 30% uncertainty in the contribution of organic PM to PM concentration
- Aging of the organic PM increases the conversion factor
 - Turpin and Lim (AS&T, 2001) proposed 1.6±0.2 for urban and 2.1±0.2 for nonurban PM
 - A value of 1.8 was calculated for NE US
 - Lower values for fresh aerosol and higher for aged
- Additional information for a specific location can be provided by
 - AMS (but needs correction with the "Collection Efficiency")
 - Organic PM speciation (individual compounds)
 - FTIR measurements
 - Other measurement techniques (oxygen measurements ?)
 - Mass balance exercises



Policy and Biogenic VOCs

There have been two extreme approaches:

- DENIAL: Trees and their emissions are part of the natural background. We cannot do much them (EPA does not control trees). Their role in air quality is probably small. Let's worry about them later.
- THE REAGAN APPROACH: Trees are more important causes of pollution than automobiles

A MORE REALISTIC POLICY APPROACH

- What is the contribution of biogenic SOA to fine PM?
 - On average? During different seasons?
 - During the most polluted days?
- Is it going to change significantly when we control SO₂?
 - How much?
- Is it going to change when we control NOx?
 - How much?
- How about its response to controls of anthropogenic primary organic PM or SOA precursors (e.g., aromatics)?

Anthropogenic SOA Precursors Aromatic Hydrocarbons



m-ethyltoluene

o-ethyltoluene

p-ethyltoluene

1,2,3,5-tetramethylbenzene



Formation of Secondary Organic Aerosol 1. Gas Phase Chemistry



Some Identified Products

TABLE 2. Compounds Identified in Secondary Organic Aerosol from Aromatic Photooxidation^a

compound	toluene	<i>m</i> -xylene	<i>p</i> -xylene	1,2,4-trimethylbenzene	ethylbenzene	m-ethyltoluene	<i>p</i> -ethyltoluene
2'-hydroxy-5'-methylacetophenone						0.11 ± 0.06	
2,3,5-trimethyl-1,4-benzoquinoneb				0.04 ± 0.07			
2,4-dimethylbenzaldehyde				0.76 ± 0.82			
2,4-dimethylphenol		0.24 ± 0.27		0.03 ± 0.04			. a
2,5-dimethyl-1,4-benzoquinone ^c			0.46 ± 0.73				
2,5-dimethylbenzaldehyde				0.46 ± 0.57			
2,5-dimethylphenol			1.9 ± 2.7	1.2 ± 1.0			
2,5-furandione	9.6 ± 1.1	5.2 ± 4.2	1.7 ± 1.3	7.0 ± 1.0	16 ± 2.1	7.4 ± 3.4	4.9 ± 0.60
2,5-heptadione							1.0 ± 1.0
2,5-hexanedione			5.6 ± 3.0			1.6 ± 0.18	1.6 ± 0.89
2,6-dimethyl-1,4-benzoquinone ^b		0.44 ± 0.40					
2,6-dimethyl-4-nitrophenol		3.3 ± 0.86					
2,6-dimethylphenol		+					
2-acetyl-5-methylfuran		4.1 ± 3.0	2.0 ± 0.99	0.26 ± 0.11	0.48 ± 0.42	0.12 ± 0.02	0.42 ± 0.24
2-ethyl-1,4-benzoquinoneb					1.5 ± 0.42		
2-furaldehyde	0.15 ± 0.02		0.05 ± 0.06				
2-hydroxy-5-nitrobenzaldehyde	1.6 ± 1.2						
2-methyl-1,4-benzoquinonec	0.46 ± 0.35						
2-methyl-4,6-dinitrophenol	3.5 ± 4.0	0.39 ± 0.31					
3,4,5-trimethyl-2(3H)-furanoned				2.0 ± 2.2			
3,4-dimethylbenzaldehyde				0.83 ± 0.98			
3,4-dimethylbenzoic acid				12 ± 2.2			
3,4-dimethylfurandione		0.41 ± 0.36	0.19 ± 0.27	3.1 ± 1.5	0.12 ± 0.16		
3,4-dimethylphenol							+
3,4/4,5-dimethyl-2(3H)-furanone ^d				0.78 ± 0.25			
3,5-dimethyl-2(3H)-furanoned		0.49 ± 0.29					
3,5-dimethyl-2H-pyran-2-one		2.7 ± 2.1					
3-acetyl-2,5-dimethylfuran			0.32 ± 0.34	0.09 ± 0.05		1.1 ± 0.85	
3-ethyl-2(5H)-furanone ^e						0.42 ± 0.25	0.16 ± 0.10
3-ethyl-2,5-furandione ⁴					7.4 ± 3.8	24 ± 12	35 ± 5.0
3-ethyl-5-methyl-2(3H)-furanone ⁹						0.07 ± 0.06	
3-ethylbenzaldehyde						1.9 ± 0.81	
3-ethylbenzoic acid		6				6.6 ± 2.2	
3-hydroxybenzaldehyde	0.04 ± 0.05						
3'-methylacetophenone						12 ± 5.9	
3-methyl-2(5H)-furanone	1.4 ± 0.39	0.89 ± 0.49	1.9 ± 2.1				1.0 ± 0.35
3-methyl-2,5-furandione	26 ± 3.6	61 ± 14	53 ± 27	27 ± 0	17 ± 5.5	18 ± 6.4	16 ± 7.2
3-methyl-2,5-hexanedione ^h				9.9 ± 2.0			2
3-methyl-4-nitrophenol	6.8 ± 0.80	2.1 ± 1.9					
3-methyl-5-ethyl-2(3H)-furanone ⁷						1.3 ± 0.59	
3-methylbenzyl alcohol		0.38 ± 0.66					
3'-nitroacetophenone					1.6 ± 0.56		
3-nitrotoluene	0.18 ± 0.02		0.04 ± 0.05				
4'-hydroxy-3'-nitroacetophenone					1.5 ± 1.5		0.34 ± 0.10
4'-hydroxyacetophenone						0.52 ± 0.27	0.41 ± 0.05
4-ethylbenzaldehyde							4.0 ± 1.6
4-ethylbenzoic acid						•	4.7 ± 0.64
4-ethylnitrobenzene					1.8 ± 0.53		
4-hydroxy-3-methylbenzaldehyde		0.03 ± 0.06					



Some More Identified Products

						15 + 5.1
			28 ± 5.3			
4.4 ± 1.4		6.0 ± 7.6				41 + 12
		1.8 ± 1.9				
10 ± 0.12			1			
				0.17 ± 0.24	1.4 ± 1.5	
				3.6 ± 2.0	0.29 ± 0.51	
2.9 ± 1.6	3.1 ± 1.6		0.15 ± 0.13	0.62 ± 0.41	0.56 ± 0.22	0.31 ± 0.27
1.6 ± 0.23		2.1 ± 2.0	1.8 ± 0.34	2.1 ± 3.0		0.91 ± 0.19
	0.84 ± 0.60					
				19 ± 7.8	$0.19 \pm +$	+
					0.03 ± 0.06	
3.0 ± 0.46	1.4 ± 1.4	0.75 ± 0.67	3.8 ± 0.71	7.8 ± 3.7	2.6 ± 1.7	1.8 ± 0.39
5.4 ± 1.2					2.8 ± 4.9	
0.72 ± 0.46						
22 ± 0.09		4.2 ± 4.7		2.5 ± 3.5	6.3 ± 5.6	
				9.1 ± 4.7	3.0 ± 3.1	
				7.0 ± 1.7		
0.15 ± 0.03						
	3.9 ± 3.0				6.31 ± 3.82	
	9.2 ± 4.6				1.2 ± 1.0	
0.02 ± 0.02						
		0.33 ± 0.35				0.29 ± 0.02
		14 ± 16				7.1 ± 2.6
		3.3 ± 4.0				0.86 ± 0.38
0.09 ± 0.01				$0.19 \pm +$	0.04 ± 0.01	0.02 ± 0.01
				1.3 ± 0.24		
						0.33 ± 0.08
	$\begin{array}{c} 4.4 \pm 1.4 \\ 10 \pm 0.12 \\ 2.9 \pm 1.6 \\ 1.6 \pm 0.23 \\ \end{array}$ $\begin{array}{c} 3.0 \pm 0.46 \\ 5.4 \pm 1.2 \\ 0.72 \pm 0.46 \\ 22 \pm 0.09 \\ \end{array}$ $\begin{array}{c} 0.15 \pm 0.03 \\ 0.02 \pm 0.02 \\ \end{array}$	$\begin{array}{c} 4.4 \pm 1.4 \\ 10 \pm 0.12 \\ \hline 2.9 \pm 1.6 \\ 1.6 \pm 0.23 \\ \hline 0.84 \pm 0.60 \\ \hline 3.0 \pm 0.46 \\ 1.4 \pm 1.4 \\ 0.72 \pm 0.46 \\ 22 \pm 0.09 \\ \hline 0.15 \pm 0.03 \\ \hline 0.02 \pm 0.02 \\ \hline 0.09 \pm 0.01 \end{array}$	$\begin{array}{c} 4.4 \pm 1.4 \\ 6.0 \pm 7.6 \\ 1.8 \pm 1.9 \end{array}$ $\begin{array}{c} 2.9 \pm 1.6 \\ 1.6 \pm 0.23 \end{array} \qquad 3.1 \pm 1.6 \\ 0.84 \pm 0.60 \end{array}$ $\begin{array}{c} 2.1 \pm 2.0 \\ 0.84 \pm 0.60 \end{array}$ $\begin{array}{c} 3.0 \pm 0.46 \\ 5.4 \pm 1.2 \\ 0.72 \pm 0.46 \\ 22 \pm 0.09 \end{array} \qquad 4.2 \pm 4.7 \end{array}$ $\begin{array}{c} 0.15 \pm 0.03 \\ 9.2 \pm 4.6 \\ 0.02 \pm 0.02 \end{array}$ $\begin{array}{c} 0.33 \pm 0.35 \\ 14 \pm 16 \\ 3.3 \pm 4.0 \end{array}$	$\begin{array}{c} 28 \pm 5.3 \\ 4.4 \pm 1.4 \\ 10 \pm 0.12 \\ \hline \\ 2.9 \pm 1.6 \\ 1.6 \pm 0.23 \\ \hline \\ 3.0 \pm 0.46 \\ 2.1 \pm 2.0 \\ \hline \\ 0.84 \pm 0.60 \\ \hline \\ 3.0 \pm 0.46 \\ 2.1 \pm 2.0 \\ \hline \\ 1.8 \pm 0.34 \\ \hline \\ 0.75 \pm 0.67 \\ 3.8 \pm 0.71 \\ \hline \\ 3.8 \pm 0.71 \\ \hline \\ 4.2 \pm 4.7 \\ \hline \\ 0.15 \pm 0.03 \\ 9.2 \pm 4.6 \\ \hline \\ 0.02 \pm 0.02 \\ \hline \\ 0.33 \pm 0.35 \\ 14 \pm 16 \\ 3.3 \pm 4.0 \\ \hline \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

^a Numbers given are percentages of the total identified mass for the particular precursor aromatic. ^b Organic tentatively identified from its mass spectra. Contribution estimated using response of 1,4-benzoquinone. ^c Organic identified by match in Wiley mass spectral library. Contribution estimated using response of 1,4-benzoquinone. ^d Organic tentatively identified from its mass spectra. Contribution estimated using response of 2,2-dimethyl-3(2/H)-furanone. ^e Organic identified by match in Wiley mass spectral library. Contribution estimated using response of 5-ethyl-2(3/H)-furanone. ^e Organic identified by match in Wiley mass spectral library. Contribution estimated using response of 3-methyl-2(5/H)-furanone. ^e Organic tentatively identified from its mass spectra. This organic could also be 5-ethyl-3-methyl-2(3/H)-furanone. Contribution estimated using 3-methyl-2(5/H)-furanone. ^h Organic tentatively identified from its mass spectra. This organic could also be 5-ethyl-3-methyl-2(3/H)-furanone. ^c Organic matched using 2,5-hexanedione. ^e Organic tentatively identified from its mass spectra. This organic could also be 3-ethyl-2(3/H)-furanone. ^f Organic matched using 5-methyl-2(5/H)-furanone. ^f Organic tentatively identified from its mass spectra. This organic could also be 3-ethyl-2(3/H)-furanone. ^f Organic matched using 5-methyl-2(5/H)-furanone. ^f Organic identified from its mass spectra. This organic could also be 3-ethyl-2(3/H)-furanone. ^f Organic matched using 5-methyl-2(5/H)-furanone. ^f Organic identified from its mass spectra. This organic could also be 3-ethyl-12(H)-furanone. ^f Organic matched reference in NIST mass spectral library. Contribution estimated using 5-methyl-2(3/H)-furanone. ^f Organic identified by match in Wiley mass spectral library. Any isomer could be possible. Contribution estimated using 2,6-dimethyl-4-nitrophenol.

31, NO. 5, 1997 / ENVIRONN

VOL

The above represent the composition of 10-20% of the produced aerosol. The rest of the compounds could not be identified.

Results from the Caltech smog chamber.

Formation of Secondary Organic Aerosol 2. Partitioning Between Gas and PM



Formation of Secondary Organic Aerosol 3. Further Reactions



Secondary Organic Aerosol Formation

 Zeroth-order approximation : One precursor produces one condensable species

 $VOC_i + Oxidant \rightarrow ... + y_i A_i$

- The condensable is species is transferred to the aerosol phase when its gas-phase concentration exceeds its saturation concentration c_i^o
- Two parameters (yield and vapor pressure) needed for each precursor
- Saturation concentration depends exponentially on temperature
 - ΔH_{evap} also needed
- Assumes no interactions among organic aerosol species or with inorganics.

Carnegie Mellon University Smog Chamber



chromatograph with flame ionization detector

Aerosol Fromation from a-pinene/Ozone







Example Experimental Time Series



SOA Formation

 Pankow/Odum et al. approach. Two condensable products formed from each precursor

 $VOC \rightarrow ... + y_1 A_1 + y_2 A_2$

A₁, A₂ form pseudo-ideal solution in the aerosol phase

 $c_i^{eq}(g) = x_i p_i^{o} / RT = x_i c_i^{o}$

where x_i : mole fraction of i in the organic aerosol phase

- Four parameters per precursor (two yields and two vapor pressures) estimated from smog chamber experiments
- Two more parameters are needed for the temperature dependence
- Experiments suggest that most organic species participate in this solution

Fitted Curve for Sabinene (Caltech Experiments)



$$Y = \sum_{i} Y_{i} = \Delta M_{o} \sum_{i} \left(\frac{\alpha_{i} K_{om,i}}{1 + K_{om,i} \Delta M_{o}} \right)$$

Implications of Organic Solution Formation

- Organics interact with each other because they co-exist in the same solution
- Transfer of a molecule of an organic from the gas to aerosol phase reduces the mole fraction of all other species => reduces their vapor pressure => transfers more organic molecules to the aerosol phase
- Increase (or decrease) of anthropogenic SOA can increase (or decrease) biogenic SOA
- All of these are based in assuming a pseudo-ideal solution (things can be more complicated)



- Fitting one monotonically increasing curve with 4 parameters is dangerous
- The highly parameterized SOA models are accurate close to the experimental conditions (concentrations, temperature, RH) used for their derivation
- The errors can increase significantly away from these conditions for such a nonlinear system
- First-principles representation of gas-phase chemistry and gas-particle mass transfer and equilibrium could be the solution
 - For the time being there are too many unknown parameters for this approach for most SOA precursors

SOA Studies at Ambient Concentration Levels (Presto et al., ES&T, 2006)



Rethinking our approach

- Organics in the atmosphere (both in primary and secondary PM) cover a wide range of volatilities
- Splitting of the volatility spectrum into bins
- Basis set: saturation concentrations (0.01, 0.1, 1, 10, 10², 10³, 10⁴, 10⁵)



SOA from β-pinene Ozonolysis



β-pinene SOA Formation Partitioning vs Gas-Phase Chemistry

 β -pinene = 40 ppb; Ozone = 750 ppb



SOA Yield from a-pinene/O₃ and NO_x (Presto et al., 2005)





Organic PM: PMCAMx Predictions vs Observations × STN × STN IMPROVE IMPROVE predicted predicted **OCTOBER** JULY measured measured × STN × STN IMPROVE IMPROVE JANUARY **APRIL** predicted predicted measured measured

Average Diurnal Organic PM Profiles in Pittsburgh



PREDICTED SOA FRACTION OF ORGANIC PM





April

0.1

PREDICTED BIOGENIC FRACTION OF SOA

0.9

8.0

0.7

0.6

0.5

0.4

0.3

0.2

0.1



July





October



Contributions of Biogenic SOA Precursors (July 2001)



OC and EC Measurements -OC-ECOC and EC (ug C/m³) July August •Use of 3 samplers (TQQQ, denuder-based, semi-continuous)

• Five sets of measurements for EC-OC

Ozone as indicator of SOA Production



Daily Averaged OC Composition (July 2001)







EC Tracer SOA vs. Secondary Biogenics



Secondary Biogenics = Sum(Nopinone, Norpinonic Acid, cis-Pinonic Acid)

SOA/OM Estimates from Different Source-Apportionment Techniques







PMF of Pittsburgh September 2002



Ulbrich, Zhang, Canagaratna, Worsnop, and Jimenez using the Baltensperger approach

Paul Scherrer Institut • 5232 Villigen PSI

Organic PM and Acidity June 25, 2002



Estimated OC increase due to inorganic acidity of around 1%.
Less than 5% based on Caltech lab studies (worst case scenario)

Carnegie Mellon

Effect of a 30% NOx Reduction on Biogenic SOA

Biogenic SOA Change (µg m⁻³) Ozone Change (ppb) -2 -0.005 -4 -0.01 -6 -0.015 -8 -0.02 -10 -12 -0.025 -14 -0.03 -16 -0.035 -18 -0.04 .20

The increase in SOA yield is offset by the decrease in ozone and the net predicted change is very small during the summer. During the winter NOx reductions are predicted to increase SOA.

Effect of Anthropogenic Organic PM on Biogenic SOA



Biogenic SOA was reduced by 10-20%

ASSUMING FORMATION OF A PSEUDO-IDEAL SOLUTION

Conclusions

For Pittsburgh and similar areas in the NE US:

- Sulfur dioxide emission controls:
 - Will help satisfy the existing fine PM standards
 - They will probably not change organic PM significantly
- Organic aerosol sources:
 - Roughly 30-60% of the organic PM is secondary during the summer (higher in the worst days) and around 10-30% during the winter.
 - The contribution is quite variable from day to day
 - Based on PMCAMx roughly half of it is biogenic in the summer
 - 80% is biogenic in Atlanta (in the summer)
 - These percentages drop to half of their summer values in the winter
 - Relatively consistent with the estimates based on the few ¹⁴C measurements
- NOx controls are predicted to leave biogenic SOA the same in the summer and to increase it a little during the winter
- Reductions in primary OM emissions are predicted to decrease moderately biogenic SOA
 - Need to investigate the thermodynamics of realistic organic mixtures

Conclusions (continued)

- PMCAMx does a surprisingly good job in reproducing observations given what we know that we do not know
 - May be it knows something more ?
 - Offsetting errors but there is probably some truth in there at least for groups of sources (e.g., primary versus secondary)
- Variety of new techniques are coming into play
 - PTR/MS, AMS, improved source receptor techniques, ¹⁴C analysis
- We still need to build a bridge between the lab and the field

Acknowledgments

CMU and UP Graduate Students

- Juan Cabada
- Vlassis Karydis
- Timothy Lane
- Albert Presto
- Charles Stanier
- R. Subramanian
- Satoshi Takahama
- Alexandra Tsimpidi

Post-docs

- Andrey Khlystov (now in Duke)
- Beth Wittig (now in CUNY)
- Ravi Pathak

Collaborators

- Barbara Turpin (Rutgers)
- Wolfgang Rogge (FIU)
- Jose Jimenez (Colorado)
- Doug Worsnop (Aerodyne)

CMU Colleagues

- Allen Robinson
- Neil Donahue

Funding by US EPA, US Department of Energy, and NSF