

# High-Time Resolution Measurement of Particulate Matter Mass and Chemical Speciation



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## Introduction

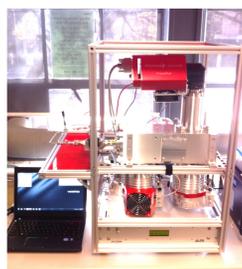
- Continuous high-time resolution measurements of particulate matter (PM) mass and chemical composition, collected over an extended time course are needed to provide important links between sources and exposure in rapidly changing environments.
- New instruments are facilitating such measurements but their capabilities and limitations need to be explored and understood so as to properly use the valuable data they can provide.
- In order to evaluate the performance of an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne), an equivalence study was performed by comparing ACSM chemical speciation data to collocated aerosol monitoring instruments.
- Positive matrix factorization (PMF) analysis with ACSM organics was performed to identify the sources of organics in an urban area.

## Methodology

### Sampling Site

- Downtown Toronto (~2.5 Million Population), Canada
- Near-roads site (~15m from the road, ~6m above ground level, and ~33 000 vehicles/weekday) at the Southern Ontario Centre for Atmospheric Aerosol Research (SOCAAR) of the University of Toronto
- December 2011 – June 2012

### Instrumentation



#### Aerodyne Aerosol Chemical Speciation Monitor (ACSM)

The same technology as Aerosol Mass Spectrometer (AMS) combining an aerodynamic particle focusing lens with high vacuum thermal particle vaporization and mass spectrometry.

Provides non-refractory chemical compositions (i.e., organics, nitrate, sulphate, ammonium, and chloride) of PM1 with 15 min resolution.

Uses naphthalene (Nap) as an internal source

Needs routine calibrations (i.e., Ionization Efficiency (IE) calibration) and post data corrections.

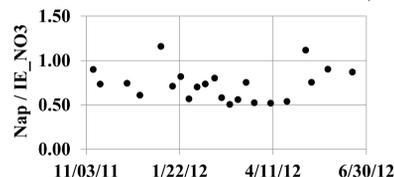


Fig. 1. The variation of the ratio of naphthalene to nitrate ionization efficiency.

Nap signal :  $1.98e-11 \pm 3.25e-12$  amp  
IE NO3 Slope :  $2.85e-11 \pm 7.73e-12$  amp  $\mu\text{g m}^{-3}$   
 $\frac{Nap}{IE_{NO_3}} = 0.73 \pm 0.18$

#### Size-segregated PM mass concentration

Fast Mobility Particle Spectrometer (FMPS, TSI) : 0.1 to 0.5  $\mu\text{m}$

Aerodynamic Particle Sizer (APS, TSI) : 0.5 to 2.5  $\mu\text{m}$

Integrated number and size distribution data, FMPS+APS

To convert mass concentrations from the size and number data the effective density was assumed to be 1.2.

#### Carbonaceous species and optical properties

Sunset Lab OCEC analyzer : Organic Carbon (OC), Elemental Carbon (EC)

Organic Matter (OM) = 1.8 OC

PM1 Mass = 0.85-PM2.5 mass

2-wavelength (780nm, 405nm) Photo Acoustic Soot Spectrometer (PASS, DMT): absorption coefficient ( $b_{\text{abs}}$ ), scattering coefficient ( $b_{\text{scat}}$ ), mass absorption coefficient (MAC)

$$\frac{b_{\text{abs},405\text{nm}}(M\text{m}^{-1})}{\text{Sunset Lab EC } (\mu\text{g m}^{-3})} = \text{MAC } (\text{m}^2 \text{g}^{-1}, 12.9 \text{ m}^2 \text{g}^{-1})$$

## Results

### Equivalence Study

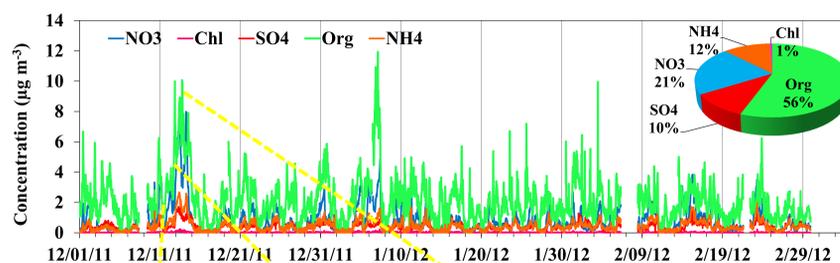


Fig. 2. Time series plots for organics (Org), sulphate (SO4), nitrate (NO3), ammonium (NH4), and chloride (Chl) measured by the ACSM in Toronto.

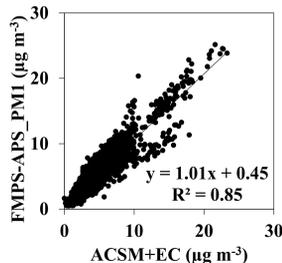
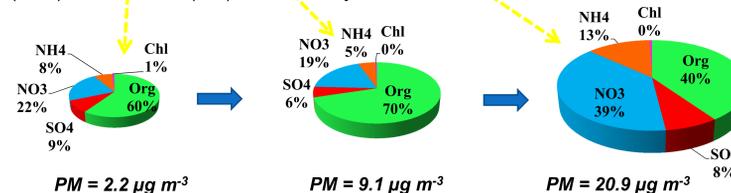


Fig. 3. Correlation between the reconstructed ACSM PM compositions with EC and the FMPS\_APS PM1 mass concentrations.

30-min average  
ACSM+EC =  $4.4 \pm 3.1 \mu\text{g m}^{-3}$   
FMPS\_APS PM1 =  $4.9 \pm 3.4 \mu\text{g m}^{-3}$

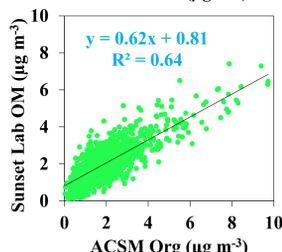
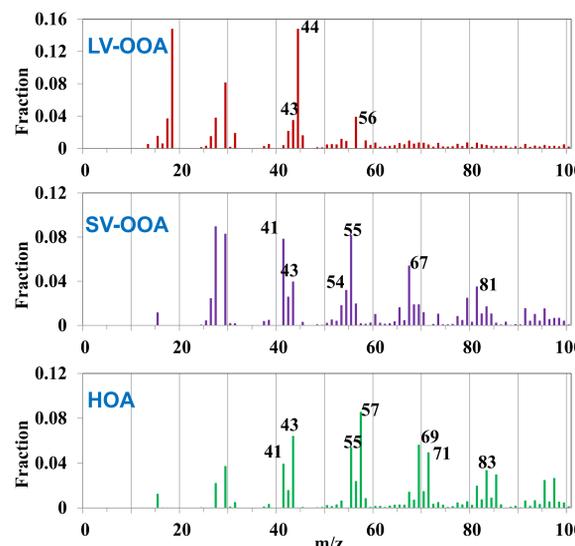


Fig. 4. Correlation between AMS organic and organic matter (OM) concentrations from the Sunset Lab OCEC analyzer. Sunset Lab OC concentration was converted to OM by multiplying a factor of 1.8.

Sunset OM accounted for ~54% of the FMPS\_APS PM1.  
Sunset OM < ACSM Org, at higher concentrations  
Higher OM/OC factor may need to be applied for photochemical processing and aged secondary OA.

### PMF Analysis



#### Low-volatility oxygenated organic aerosol (LV-OOA)

Aged, oxidized OM  
m/z 44 (COO+)

#### Semi-volatile oxygenated organic aerosol (SV-OOA)

m/z 41>43, m/z 55>57  
Possible influences of HOA

#### Hydrocarbon-like organic aerosol (HOA)

Diesel exhaust profile  
hydrocarbon-like fragments  
m/z 57>55, m/z 43>41

## Results

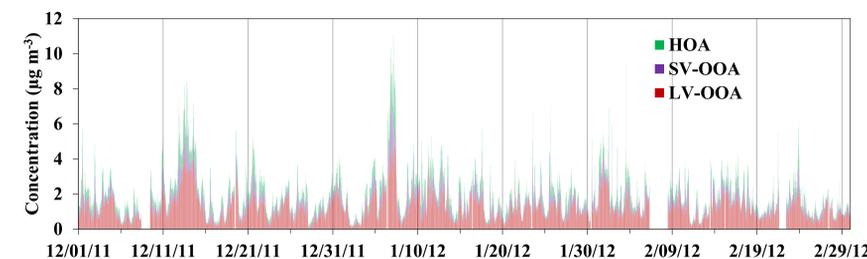


Fig. 5. Stacked areas of PMF factor contributions.

LV-OOA (54%), SV-OOA (19%), and HOA (19%) of total ACSM Org mass (~2.1  $\mu\text{g m}^{-3}$ )

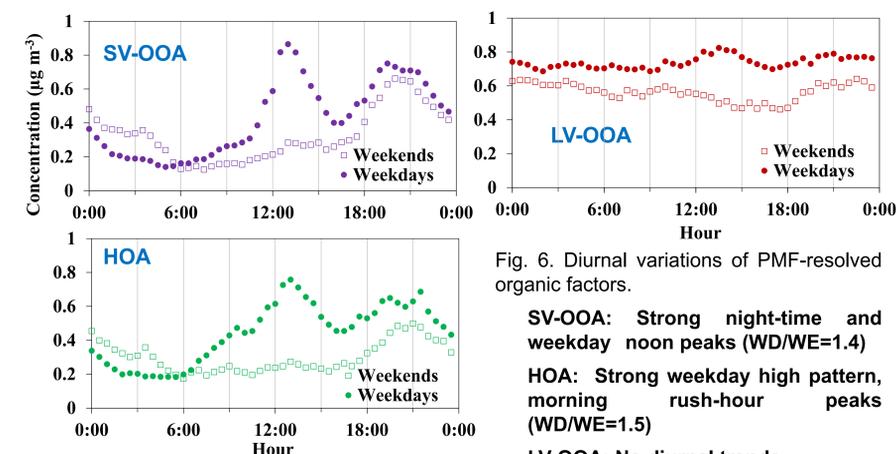


Fig. 6. Diurnal variations of PMF-resolved organic factors.

SV-OOA: Strong night-time and weekday noon peaks (WD/WE=1.4)

HOA: Strong weekday high pattern, morning rush-hour peaks (WD/WE=1.5)

LV-OOA: No diurnal trends

Pearson r	m/z 44	m/z 57	LV-OOA	SV-OOA	HOA
$b_{\text{abs},405\text{nm}}$	0.58	0.67	0.68	0.47	0.68
$b_{\text{abs},780\text{nm}}$	0.49	0.59	0.55	0.39	0.59
$b_{\text{scat},405\text{nm}}$	0.79	0.56	0.75	0.35	0.45
$b_{\text{scat},780\text{nm}}$	0.78	0.59	0.76	0.39	0.49
Sunset Lab EC	0.55	0.72	0.63	0.48	0.73

Table 1. Correlation analysis between PMF organic factors and particle optical property measurements as well as Sunset Lab EC.

HOA: Strong light absorption, high correlation with EC

LV-OOA: Strong light scattering

## Summary

- Organic matter (OM) was the largest PM contributor to PM (~50% of PM1 mass).
- Reconstructed mass concentrations from the ACSM and EC showed good agreement with the estimated PM1 by the FMPS\_APS system.
- Average Sunset OM concentrations were fairly well correlated with the ACSM organic concentration. The OM/OC ratios may vary by the oxidation state of organic aerosol.
- PMF data analysis tool was used to apportion organic matter measured by ACSM and a three factor solution was resolved (LV-OOA, SV-OOA, and HOA).
- The LV-OOA factor was highest and accounted for 54% of OM.
- Strong diurnal trends and weekdays-high patterns were observed for the HOA factor, indicating the direct contribution of diesel exhausts.
- SV-OOA was a slightly aged factor that is characteristic of indirect, secondary aerosol related to vehicle emissions.
- High correlations between the HOA factor and light absorbance ( $b_{\text{abs}}$  and EC) were found, while the LV-OOA factor was associated with high light scattering.

## Acknowledgement

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