Semi-Continuous Measurements of PM$_{2.5}$ Carbon at the South Bronx, New York: Comparison with Filter Measurements

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PM$_{2.5}$ Carbon

- Constitutes ~30-50% of PM2.5 mass in New York City.
- Elemental Carbon (EC)-(Black carbon, BC);
  - Direct emission from fuel combustion (pyrolysis of organic carbon). 10-20% of TC.
- Organic Carbon (OC)- Major fraction.
  - Primary-direct emission from combustion processes, cooking, industrial processes, biogenic sources
  - Secondary-(SOA), VOC photo-oxidation products
- Inorganic Carbon- carbonates, CaCO$_3$. (limestone, dust) - not observed in New York City.
South Bronx, IS52- (681 Kelly St.).
Inlets for Semi-Continuous Analyzers

IMPROVE Sampler

STN Sampler (R&P)
SUNSET Labs EC/OC Carbon Analyzer

- SUNSET Carbon
- PM2.5 cyclone
- SS Inlet
- Denuder (activated carbon strips)
- Quartz filter collects sample
- Hourly OC, EC
- Thermal conversion to CO₂
- NDIR Detection
Filter Measurements

• 24 hr, 1 in 3 Day Schedule, Quartz filter
• R&P 2300 Partisol (end 1/11/06), 10LPM, 14.4 m³
• Met-One SASS (beg. 1/14/06), 6.7LPM, 9.6 m³

Silicon greased impactor

sharp cut cyclone
Flow Characteristics of Sunset Analyzer

• Sunset Labs ECOC, 47 min samples, 8 li/min, ~0.4 m³ per sample

Comparison of Filter Face Velocities

• Sunset: ~ 80 cm/s
• R&P Partisol 2300 (24-hr filter): ~9.6 cm/s
• MetOne SASS (24-hr filter): ~6.4 cm/s
Measurement of “blank” or positive artifact for Sunset
Organic Carbon Blank, Jan 25-27, 2006

OC = 0.54 µg/m³, sd 0.29
Mean and Std Dev. SUNSET Hourly OC Blanks, South Bronx

total hourly average = 0.68
Elemental Carbon Blank, Jan 25-27, 2006

EC = -0.004 µg/m³, sd 0.003
Comparison of Semi-Continuous Sunset to STN Filter Measurements of EC & OC

Blank or positive artifact corrections are applied to the STN data based on averages of field and trip blanks at the South Bronx site. (Averages are done separately for R&P and MetOne samplers.)
24Hr SUNSET vs STN Filter Elemental Carbon

Partisol
\[ y = 0.87x + 0.03 \]
\[ R^2 = 0.59 \]

Met One
\[ y = 0.86x - 0.14 \]
\[ R^2 = 0.96 \]
24 hr SUNSET vs STN Filter Organic Carbon

Partisol

\[ y = 0.66x + 0.45 \]

\[ R^2 = 0.69 \]

Met-One

\[ y = 0.67x - 0.17 \]

\[ R^2 = 0.86 \]
24 hr SUNSET vs STN Filter Total Carbon

Partisol
\[ y = 0.73x + 0.43 \]
\[ R^2 = 0.65 \]

Met-One
\[ y = 0.73x - 0.35 \]
\[ R^2 = 0.92 \]
Seasonal and Day-of-Week Patterns from Sunset Data
Seasonal Variation

Monthly SUNSET Total Carbon, South Bronx, 2005-2006

whiskers indicate 5 and 95 percentiles

µg/m³, mean - median
Seasonal Variation

Monthly SUNSET OC, South Bronx, 2005-2006

whiskers indicate 5 and 95 percentiles

µg/m³,
Seasonal Variation

Monthly SUNSET EC, South Bronx, 2005-2006

whiskers indicate 5 and 95 percentiles

[Graph showing seasonal variation with months on the x-axis and concentration in µg/m³ on the y-axis, with bars indicating mean and median values]
Day-of-Week Variation

Organic Carbon, 2005-2006, South Bronx

µg/m³, weekday/weekend

July, August, September, October, November, December, January, February, March, April, May, June
Day-of-Week Variation

Elemental Carbon, 2005-2006, South Bronx
Example of the Power of Continuous Measurements for PM$_{2.5}$ Mass Reconstruction

• PM$_{2.5}$: TEOM - 50º C “standard”
• Sulfate: Thermo 5020 - Values x 1.375 to account for ammonium
• Nitrate: R&P/Thermo 8400N - Values x 1.29 to account for ammonium
• OM: OC x 1.5
• EC: used as measured
SO₄ = (NH₄)₂SO₄
NO₃ = NH₄NO₃
TC = OC * 1.5 + EC
PM2.5 = 50°C TEOM
Method Issues - Sunset

- Stable measurement of positive artifact ("blank") requires ~24 hours
- Variability of OC positive artifact - use annual, seasonal, or monthly values?
- Collection of SVOC - front oven cool down time, and ~30°C Filter Temp.
- Carbon paper denuder - are activated carbon monoliths more appropriate?
- Should we use Optical or Thermal EC? What do we do with the other?
Conclusions - Artifacts

• Artifacts (blanks) are an issue
• No clear solution:
  - Improve “correction” scheme
  - Improve method (i.e., eliminate issue)
  - ???
Conclusions – Filter Comparisons

• Mixed results
  - EC okay (<15% difference)
  - OC less good (>30% difference)

• How do we know which is right? (i.e., STN or Sunset)
  - STN - no denuder
  - Sunset - SVOC loss?
  - Need calibration “standards”

• Is there a “monitoring” method that can quantitatively collect SVOC?
Conclusions - Observations

• OC concentrations are highest from June to August
• EC appears to be a little higher in winter (as expected)
• Day-of-week dependence is weaker than expected. EC shows greater contrast for most months.
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