SANDWICH Material Balance Approach for PM$_{2.5}$ Data Analysis

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Outline

• What is “SANDWICH”, why it is good way to describe PM2.5 composition

• How it can help with PM2.5 data QC

• Examples using STN data
Introduction

• What is the SANDWICH Approach?
  – Sulfate, Adjusted Nitrate, Derived Water, Inferred Carbon Hybrid material balance approach
    • for estimating PM2.5 mass composition produced by the PM2.5 FRM.
  – The approach uses a combination of speciation measurements and modeled speciation estimates to represent FRM PM2.5.
Introduction (cont.)

• Why is it needed?
  – The FRM defines the regulatory indicator of PM2.5.
  – FRM mass may not retain all nitrate, and includes particle bound water and other components not estimated directly with STN measurements.
  – To estimate FRM PM$_{2.5}$ composition including FRM carbonaceous mass without “fudge” factors.
  – To help QC speciation measurements

• SANDWICH is the default method in EPA modeling guidance to define baseline PM2.5
  – for SMAT (speciation modeled attainment test)
Old Practice: Use STN measurements to directly characterize PM2.5

<table>
<thead>
<tr>
<th>FRM and STN measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM2.5 mass</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
</tr>
<tr>
<td>NH$_4^+$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
</tr>
<tr>
<td>{Al SI Ca Fe Ti}</td>
</tr>
<tr>
<td>OC</td>
</tr>
<tr>
<td>EC</td>
</tr>
</tbody>
</table>

*These represent a subset of STN speciation measurements*
Old Practice: Use STN measurements to directly characterize PM2.5
Old Practice: Use STN measurements to directly characterize PM2.5

FRM and STN measurements

PM2.5 mass  SO4  NH4  NO3  {Al, Si, Ca, Fe, Ti}  OC  EC

| FRM Sampler | (Teflon filter) | (Nylon following denuder) | (Teflon) | (Quartz) |

Various Speciation Samplers*

FRM and speciation samplers have different flow rates, face velocity and monitoring protocols.

* Various STN speciation samplers, with different design and flow rates compared to FRM:
  MetOne (SASS), Anderson (RASS), URG (MASS), R&P
Old Practice: Use STN measurements to directly characterize PM2.5 with limited consideration of the different monitoring protocols.

FRM and STN measurements

PM2.5 mass  SO4  NH4  NO3  {Al SI Ca Fe Ti}  OC  EC

Create estimates of major components

Constructed Mass using STN measurements

Sulfate  Nitrate  {Crustal}  OCM  EC
Old Practice: Use STN measurements to directly characterize PM2.5

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Create estimates of major components

- Constructed Mass using STN measurements (RCFM)
  - Sulfate + Nitrate + {Crustal} + OCM + EC

Typical formulas to estimate major components

<table>
<thead>
<tr>
<th>Ammonium Sulfate*</th>
<th>Ammonium Nitrate*</th>
<th>Cr = 2.2<em>Al + 2.49</em>Si + 1.63<em>Ca + 2.42</em>Fe + 1.94*Ti</th>
<th>OCM = 1.4*(OC-b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH4)2SO4</td>
<td>NH4NO3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Typical formulas to estimate major components
Old Practice: Use STN measurements to directly characterize PM2.5

FRM and STN measurements

PM2.5 mass  SO$_4$  NH$_4$  NO$_3$  {Al Si Ca Fe Ti}  OC  EC

Create estimates of major components

Constructed Mass using STN measurements

Sulfate + Nitrate + {Crustal} + OCM + EC

Ammonium Sulfate* (NH$_4$)$_2$SO$_4$
Ammonium Nitrate* NH$_4$NO$_3$

Cr = 2.2*Al + 2.49*Si + 1.63*Ca + 2.42*Fe + 1.94*Ti

OCM=1.4*(OC-b)

From STN field blanks. Imperfect method
to account for O, H, N in C compounds
Carbonaceous Mass from measured C data is a very uncertain calculation
\[ k \times (\text{OC-b}) + \text{EC}, \text{ e.g. } k=1.4 \text{ or } 1.8 \]

Many Sources of error

- Analytical uncertainty
- Blank correction (avg value \( \sim 1-1.5 \text{ug/m}^3 \text{ OC, STN sites} \))
  - Varies among our 5 different EPA urban speciation samplers
  - We can’t do site or seasonal adjustments
  - NOTE: this is a minor issue with IMPROVE data

<table>
<thead>
<tr>
<th>STN sampler</th>
<th>24-hr sample Volume(m³)</th>
<th>Network Average Total Carbon on STN Blank Filters*</th>
<th>ug C/ filter</th>
<th>ug C/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetOne (SASS)</td>
<td>9.6</td>
<td>14.8</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Anderson (RAAS)</td>
<td>10.4</td>
<td>13.5</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>R&amp;P 2300</td>
<td>14.4</td>
<td>16.1</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>URG (MASS)</td>
<td>24</td>
<td>7.7</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

5th speciation sampler is the PM2.5 FRM
Uncertainty of k*(OC-b), continued

- Conversion of OC to OCM (± 33%), varies with aerosol type and mix
  - 1.4 < k < 1.8 ("typical" urban)
  - 2.0 < k < 2.4 ("typical" rural)
    - Weighted average for mixed urban/regional aerosol
  - Turpin's estimates based on limited speciation data
- OC- EC split (and unaccounted mass for “EC”)
- Retained carbon mass on FRM teflon vs STN quartz
  - Volatile or other OC may pass thru Teflon
    - FRM has higher face velocity than many STN samplers
  - Water [20-24% of measured PM2.5 water]
Old Practice: Use STN measurements to directly characterize PM2.5

Bottom line: Measurement data with standard adjustment does not add up to PM2.5
A better use of the STN speciation data to support the PM2.5 program is needed
Now, let's **modify** the STN measurements using **SANDWICH**

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Now, let's modify the STN measurements using SANDWICH

PM2.5 mass

SO4  NH4  NO3  {Al Si Ca Fe Ti}  OC  EC

PM2.5 = “Gravimetric” mass
- Teflon filters are equilibrated at ~21 deg C and 35% RH
- Net weight and sample volume are used to produce ug/m3

The SANDWICH approach considers sampling artifacts and idiosyncrasies of FRM’s gravimetric mass and STN’s monitoring protocols
Use SANDWICH to characterize PM2.5


SANDWICH does not directly use OC

Evaporation model described in my JAWMA paper

AIM (thermodynamic model) or with our response surface equation

Use SANDWICH to characterize PM2.5

FRM and STN measurements

PM2.5 mass

SO4 NH4

NO3 {Al SI Ca Fe Ti} EC

FRM Mass (incl. passive, Pa, based on blank=0.5μg/m3)

Est. H2O (with AIM)

SO4 NH4 as reported

Reduced NO3 (using hourly temp and RH from nearby met station)

Crustal (alternative formula which does not use Al)

For filter contamination (not affected by emissions)

For particle bound water which is part of gravimetric mass

For losses of semi-volatile nitrate on FRM filters during sampling

For detection problems with Al
Use SANDWICH to characterize PM2.5

\[
\text{OCM}_{mb} = \text{FRM} - (\text{SO4} + \text{NH4} + \text{NO3}_r + \text{H2O} + \text{EC} + \text{Cr} + \text{Pa})
\]

OCM_{mb} explicitly accounts for blank correction (sampling artifact), fudge factor to account for OC to OCM conversion, H2O & less (non-volatile) OC retained on Teflon.
FRM doesn’t retain all ambient nitrates
Monthly and Annual Average NO3, 2003

6 Nitrate Study Sites, 2003

FRM (calcualted)

RCFM (reflects ambient)

SANDWICH (reflects FRM PM2.5)

Ann Avg

* Note: Chicago has URG sampler whose data may underestimate ambient nitrates. URG has 2 filters to collect nitrates (Teflon followed by nylon). The teflon may loose nitrates when it is first used by XRF under vacuum prior to non-volatile nitrate determination.
PM2.5 Water Estimated with AIM, using SO4, NO3 and NH4

More water with higher % of Sulfates or More Acidic Aerosol

Monthly Average Water tracks Sulfate plus Total Ammonium for 6 study sites, 2003 data

Using Aerosol Inorganics Model (AIM) at 35% RH and 21° C (no solids are allowed to form).
http://www.hpc1.uea.ac.uk/~e770/aim.html
EQUATION TO ESTIMATE WATER  
(rePLICATES AIM AT FRM EQUILIBRATION CONDITIONS)

Let D = NH₄⁰ / SO₄, 0 < D < 0.375, where NH₄⁰ is the amount associated with SO₄.  
[The corresponding DON ('degree of neutralization', molar) varies from 0 to 2.]

Define relative amounts of SO₄, NO₃ (reduced) and NH₄:  
S = SO₄/(SO₄+NO₃+NH₄); N=NO₃/(SO₄+NO₃+NH₄); A=NH₄/(SO₄+NO₃+NH₄);  
Eliminate any excess NH₄ not needed to fully neutralize SO₄

High acidity:  DON < 1.2 (D < 0.225)

Water= [ 595.56 - 1440.58*S - 1126.49*N + 283.91*(S**1.5) - 13.38*(N**1.5)  
- 1486.71*(A**1.5) + 764.23*(S**2) + 1502.00*(N * S) + 451.87*(N**2)  
- 185.18*(S**2.5) - 375.98*(S**1.5) * N - 16.90*(S**3) - 65.81*(N**1.5) * S  
+ 96.83*(N**2.5) + 83.04*(N**1.5) * (S**1.5) - 4.42*(N**3)  
+ 1720.82*(A**1.5) * S + 1220.38*(A**1.5) * N - 311.50*(A**1.5) * (S**1.5)  
+ 148.77*(A**1.5) * (N**1.5) + 1151.65*(A**3)] * (SO₄+NO₃+NH₄)

Low acidity:  DON > 1.2 (D > 0.225)

Water= [ 202049.0 - 391494.6*S - 390912.1*N + 442.4*(S**1.5) - 155.3*(N**1.5)  
- 293406.8*(A**1.5)+189277.5*(S**2)+377992.6*N*S +188636.8*N**2  
- 447.1*S**2.5 -507.2*S**1.5*N -12.8*S**3 +146.2*N**1.5*S +217.2*N**2.5  
+ 30.0*N**1.5*S**1.5 - 18.6*N**3 + 216267.0*A**1.5*S +215419.9*A**1.5*N  
- 621.8*A**1.5*S**1.5 +239.1*A**1.5*N**1.5+95413.1*A**3] * (SO₄+NO₃+NH₄)
Use SANDWICH to characterize PM2.5

FRM and STN measurements

- PM2.5 mass
- SO4
- NH4
- NO3
- {Al, Si, Ca, Fe, Ti}
- OC
- EC

estimates of speciated FRM components

measurements and modeled estimates

- SO4
- NH4
- NO3r
- H2O
- Crustal
- OCMmb
- EC
- Pa
Use SANDWICH to characterize PM2.5

**FRM and STN measurements**

PM2.5 mass \[= \text{SO}_4 + \text{NH}_4 + \text{NO}_3 + \text{H}_2\text{O} + \text{Crustal} + \text{OCMmb} + \text{EC} + \text{Pa}\]

**By design, perfect mass balance**

Sulfate, Adjusted Nitrate, Derived Water, Inferred Carbon

Hybrid Material Balance Approach (SANDWICH)
Use SANDWICH to characterize PM2.5

FRM and STN measurements
PM2.5 mass = SO4 + NH4 + NO3 + {Al Si Ca Fe Ti} + OC + EC

By design, perfect mass balance

SANDWICH and STN measurements
PM2.5 mass = SO4 + NH4 + NO3r + H2O + Crustal + OCMmb + EC + Pa

Simpler representation of major components

SANDWICH and STN measurements
PM2.5 mass = Sulfate + Nitrate + Crustal + TCMmb + Pa
Use SANDWICH to characterize PM2.5

For Data Presentation Purposes:

Simplify components of PM2.5 into Sulfate and Nitrate portions, the NH4 and estimated H2O must be partitioned. Carbon can be represented as Total Carbonaceous Mass.

\[
\text{SANDWICH and STN measurements} \\
\text{PM2.5 mass} = \text{SO4 + NH4 + NO3r + H2O + Crustal + OCMmb + EC + Pa}
\]

Partition \text{NH4 and H2O} \quad \text{Combine OCM and EC}

\[
\text{SANDWICH and STN measurements} \\
\text{PM2.5 mass} = \text{Sulfate + Nitrate + Crustal + TCMmb + Pa}
\]

For further data details, See: [http://www.epa.gov/airexplorer/](http://www.epa.gov/airexplorer/)
(1) Approach using measurements and calculated values

Distribute unknown (or scale all down) equally

(2) SANDWICH
(a) W. Reduced Nitrates

(b) With added water

Sulfate mass increases

(c) Plus passive PM2.5 (= FRM blank)

(d) Remaining unknown mass is assigned to carbon

* Default SANDWICH can be modified to consider other components, like salt. This reduces estimate of TCM.
Uncertainties, Caveats and Data Use

• Assumptions:
  – Reduced nitrate and enhanced sulfate are more reflective of what might be measured by the FRM
  – OCM is the most uncertain mass component
• TCMmb is upper estimate and subject to errors in the non-C components
  • Inclusion of all “known” components is good
    – E.g. Salt for coastal areas or urban wintertime
• Sometimes, TCMmb can be negative
  – But, so can measurement derived “OC-b”
  – So, modified SANDWICH uses measurement data as an “OCM floor” (See discussion on Air Explorer)
• TCMmb can be used to ground truth k*(OC-b) + EC
Application of SANDWICH to STN Data

and

Some examples of SANDWICH for QC
Annual Average Composition (2002-04) in East NA areas
Less nitrate and more sulfate mass with SANDWICH

NA area without STN data (02-04)

<table>
<thead>
<tr>
<th>area</th>
<th>area_annual_dv</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA area: Johnstown, PA</td>
<td>15.3</td>
</tr>
<tr>
<td>NA area: Martinsburg, WV-Hagerstown, MD</td>
<td>16.1</td>
</tr>
<tr>
<td>NA area: Parkersburg-Marietta, WV-OH</td>
<td>15.2</td>
</tr>
<tr>
<td>NA area: Reading, PA</td>
<td>16.1</td>
</tr>
<tr>
<td>NA area: Steubenville-Weirton, OH-WV</td>
<td>17</td>
</tr>
<tr>
<td>NA area: Wheeling, WV-OH</td>
<td>15.1</td>
</tr>
</tbody>
</table>

Black outlined pies have collocated FRM and speciation
Annual Average Composition (2002-04) in West NA areas

Less nitrate and more carbon mass with SANDWICH

Black outlined pies have collocated FRM and speciation
Quarterly PM2.5 Composition in Eastern NA areas, 2002-04
Seattle
(More OCM)

(More sulfate mass, less nitrate, more OCM)

Rubidoux, CA
(Less nitrate, more sulfate mass and OCM)

Birmingham

(More sulfate mass and OCM)
Rubidoux, CA (2005)

- **RCFM**
  - Over-estimates FRM mass

- **SANDWICH**
  - Less nitrate mass
  - More sulfate and carbon

Gray line shows \{OCMmb - OCM14\}
Birmingham, AL (2005)

- **RCFM**
  - Under-estimates FRM mass

- **SANDWICH**
  - Less nitrate mass
  - More sulfate and carbon

**FRM PM2.5 mass**

**PM2.5 and Components, ug/m3**

Chem
- Sulfate_mass
- Nitrate_mass
- Crustal
- EC
- Passive

Gray line shows {OCMmb - OCM14}
How to Use SANDWICH for QC

• Comparisons of Constructed Fine Mass with measured FRM mass
  – Using reduced nitrate and hydrated sulfate
    Instead of $\text{CFM} = [\text{SO}_4] + [\text{NO}_3] + [\text{NH}_4] + [\text{TCM14}] + [\text{Cr}]$
    Use $\text{CFM} = [\text{SO}_4] + [\text{NO}_3\text{r}] + [\text{NH}_4] + [\text{H}_2\text{O}] [\text{TCM14}] + [\text{Cr}]$

• Examine $\text{TCMmb}$ vs. $[k^*(\text{OC}-\text{b})+\text{EC}]$
  – Negative numbers and large deviations can be informative.
  – Three examples
    • Use time series and scatter plots
    • Preliminary QC findings are presented
Ashland KY, 2002-05
TCMmb vs TCM1.4

FRM PM2.5=4.3 (Too Low!)
SO4=5.9
TCM1.4= 3.8 ug/m3
TCM14=1.4(OC-1.5)+EC

TCMmb= -6.9 ug/m3

PLOT
- tcm
- cr
- sulfate
- nitrate
- tcm14
- mf2
PM2.5 and chemical component mass, ug/m³

PM2.5 = 40.1 ug/m³
TCMmb = 39.2 ug/m³
SO₄ = 0.1 ug/m³
Seattle, WA 2002

- PM$_{2.5}$ = 29.1 (Mar3)
- TCM$_{mb}$ = 25.1
- TCM$_{1.4}$ = 8.9

TCM$_{14}$ = $1.4(OC-1.3)+EC$
Measurement Program Implications:
TCM can be estimated from PM2.5, sulfate and nitrate.
TCM\textsubscript{mb} vs TCM\textsubscript{1.4} for 3 sites in Seattle (2002-05)

Site 024 RAAS

TCM\textsubscript{14}=1.4(OC-1.3)+EC

Site 057 RAAS

TCM\textsubscript{14}=1.4(OC-1.3)+EC

Site 080 MASS

TCM\textsubscript{14}=1.4(OC-0.3)+EC

MASS sampler appears to require different combination of “k” and “b” to attain consistency between TCM\textsubscript{mb} and k*(OC-b)

Higher “k” =1.8 more consistent with woodsmoke aerosol

→ suggests that SASS sampler may retain add'l artifact in proportion to particle OC (this is offset by “k=1.4”)

See TCM poster (for further discussion)
SANDWICH data are now available on Air Explorer
http://www.epa.gov/airexplorer/
See Mark Schmidt’s Demo, Wednesday 3:30pm
A Few Summary Points

• Adjustments to STN speciation measurements are needed to represent FRM PM$_{2.5}$ mass
• SANDWICH estimates composition as might have been measured by the FRM
• TCMmb
  – helps evaluate C fudge factors (k & b) and validate C measurements
  – Use it to estimate TCM without measured C
Questions?
Now or at Tomorrow's Poster Session

I hear they will be serving Frank Sandwiches!
Trends in Carbonaceous PM2.5 using Measured STN Carbon and “SANDWICH”

Neil Frank
Office of Air Quality Planning and Standards, USEPA Research Triangle Park NC 27711

Background
Carbonaceous mass is one of the largest PM2.5 chemical components, but is the most challenging to estimate. The typical method to calculate total carbonaceous mass (TCM) involves correcting measured organic carbon (OC) for positive sampling artifact (blank correction), multiplying the result by a simple factor (e.g. 1.4) to account for oxygen, hydrogen and other elements in ambient carbon compounds and then adding measured EC. Neither of these OC adjustments can be accurately estimated from existing STN measurements or data. The STN program does not currently utilize backup filters; therefore, field and trip blanks together with sampler flow rate permit at best a crude estimate of the OC artifact. EPA has used a simple network wide value derived from 2001-02 STN data. For the multiplier to create OCM, generic values are usually taken from the literature; but in reality with the mix of particulate OC compounds and could therefore vary by location, season and even day. To estimate FRM PM2.5 (retained on Teflon with typically higher face velocity), different adjustments are probably needed. This poster provides estimates of TCM by material balance with FRM mass and its non-C components. These “SANDWICH” results are compared to measurement derived TCM. Trends in STN blank values are also considered.

Sources of error in TCM = k*(OC-b)+EC

- Analytical uncertainty
- Blank correction to account for positive sampling artifact
- Variation between sites
- Conversion of OC to OC mass (OCM) (33%)
- TCM is calculated as 1.4 x < 1.5 “typical” urban (Tafel 2003)
- Weighted average needed for mixed urban/regional aerosol
- Tafel's revised estimates based on limited speciation data
- OC-EC split (and unaccounted mass for “EC”)
- Retained carbon mass on FRM Teflon vs STN quartz
- Less Reactive OC may be retained on Teflon **
- Water (k=10-30% of PM2.5 water)
- OCM can vary by location and sampling day. Retained particulate OC depends on filter face velocity.

“SANDWICH” Approach
• Gullato, 2005b: Derived Water, Inferred Carbonaceous Mass, Hybrid material balance approach
• TCMme = PM2.5 - (SO4 + [NO3] + [NH4] + [water])
• OCMme = TCMme - [EC]
• Water and reduced FRM NO3 are estimated by models.
• Other PM2.5 constituents eg. salt, could also be considered
• TCMme explicitly accounts for positive and negative sampling artifacts, OC hydration, and mass multipliers for carbonaceous material retained on FRM Teflon.
• TCMme is upper estimate for TCM and is subject to error in non-C components.

Summary and Next Steps
Inferrer carbon by mass balance (TCMme, using SANDWICH)
• Directly accounts for
  • Adsorbed organic gases and carbon-particle water (positive artifacts)
  • Volatilized OC and other carbonaceous particles not retained on Teflon (negative artifacts).
  • Total FRM mass associated with carbon.
• Eliminates need for blank corrections or site-specific multipliers to account for non-carbon elements associated with measured organic or elemental carbon.
• Can be used to corroborate measurement derived carbon mass and visa versa.

Comparison of TCMme with k*(OC-b)+EC
• The correct combination of “k” and “b” is critical for calculating TCM from measurement data.
• With STN’s Met One (SASS) and Anderson (RAAS) data in urban sampling environments, TCMme generally agrees best with k=1.4 and year specific blank corrections. Assuming that k=1.8 would be more appropriate for a mixed urban-regional aerosol, then higher blank correction (b) would be needed to maintain mass balance. This suggests that backup filters behind Teflon might record higher values than quartz filter blanks.
• For sites with the URG MASS sampler, higher “k” appears to be needed. This is consistent with published values. Data from these higher flow rate samplers require smaller blank correction & are more sensitive to “k” for calculating mass.

Next Steps
• For national consistency in ambient carbon monitoring, EPA is switching the STN carbon protocol to the IMPROVE method. STN’s new IMPROVE like samplers (22 Lpm flow rate) to be phased in over three years will also likely have less carbon sampling artifact than current STN data from SASS and RAAS samplers.
• EPA has funded DRI to recommend procedures to estimate sampling artifact for the new urban samplers (using backup filters) and to develop appropriate factors for estimating...