## SANDWICH Material Balance Approach for PM2.5 Data Analysis

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- 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 PM2.5 composition including FRM carbonaceous mass <u>without</u> "fudge" factors.
  - To help QC speciation measurements
- SANDWICH is the default method in EPA modeling guidance to define baseline PM2.5
  - for SMAT (<u>speciation modeled attainment test</u>)

Old Practice: Use STN measurements to directly characterize PM2.5



### These represent a subset of STN speciation measurements

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





**Typical formulas to estimate major components** 



## <u>Carbonaceous Mass</u> from measured C data is a very uncertain calculation k\*(OC-b)+EC, e.g. k=1.4 or 1.8

Many Sources of error

- Analytical uncertainty
- Blank correction (avg value ~1-1.5ug/m3 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

	24-hr	Network Average Total Carbon on STN Blank		
	sample	Filters*		
STN sampler	Volume(m <sup>3</sup> )	ug C/ filter	ug C/m <sup>3</sup>	
MetOne (SASS)	9.6	14.8	1.5	
Anderson (RAAS)	10.4	13.5	1.3	
R&P 2300	14.4	16.1	1.1	
URG (MASS)	24	7.7	0.3	

5<sup>th</sup> speciation sampler is the PM<sub>2.5</sub> FRM

## Uncertainty of k\*(OC-b), continued

- Conversion of OC to OCM (<u>+</u> 33%), varies with aerosol type and mix
  - 1.4 < k < 1.8 ("typical" urban)
  - 2.0 < k < 2.4 ("typical" rural)</p>
    - Weighted average for mixed urban/regional aerosol
  - Turpin's estimates based on limited speciation data
- OC- EC split (and unaccounted mass for "EC")
- <u>Retained</u> 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]





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, lets modify the STN measurements using SANDWICH



### Now, lets modify the STN measurements using SANDWICH



The SANDWICH approach considers sampling artifacts and idiosyncrasies of FRM's gravimetric mass and STN's monitoring protocols



Frank, N. Retained Nitrate, Hydrated Sulfates, and Carbonaceous Mass in Federal Reference Method Fine Particulate Matter for Six Eastern U.S. Cities, *J. Air & Waste Manage. Assoc.* **56** :500–511

### Use SANDWICH to characterize PM2.5



### Use SANDWICH to characterize PM2.5



OCMmb 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



PM2.5 Water Estimated with AIM, using SO4, NO3 and NH4



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 New Development (included in Draft Modeling Guidance)

### EQUATION TO ESTIMATE WATER (replicates AIM at FRM equilibration conditions)

Let D = NH4<sup>s</sup> / SO4, 0<D<0.375, where NH4<sup>s</sup> 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)

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

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 For Data Presention 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.



## **Conceptual Overview of Mass Balance Approaches**



\* 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

### **RCFM**

### SANDWICH



## 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







#### Rubidoux, CA (2005) Riverside-San Bernardino, CA site= 060658001 (2005) **SANDWICH RCFM Over-estimates FRM mass** Less nitrate mass FRM PM2.5 mass More sulfate and carbon Sulfate\_mass OCMmb EC Passive Chem Nitrate\_mass Crustal

Gray line shows {OCMmb - OCM14}

PM2.5 and Components, ug/m3

### Birmingham, AL (2005)



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 CFM=[SO4]+[NO3]+[NH4]+ [TCM14]+[Cr]
 Use CFM=[SO4]+[NO3r]+[NH4]+[H2O] [TCM14]+[Cr]

- Examine TCMmb vs. [k\*(OC-b)+EC]
  - Negative numbers and large deviations can be informative.
  - Three examples
    - Use time series and scatter plots
    - Preliminary QC findings are presented









### TCMmb vs TCM1.4 for 3 sites in Seattle (2002-05)



rCMmb, ug/m3

FCMmb, ug/m3

-10

PLOT

10

20

tcm14

30

TCMplus

tcm14

50

TCMminus

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

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## A Few Summary Points

- Adjustments to STN speciation measurements are needed to represent FRM PM2.5 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"

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#### 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 single 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 vary 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

Analytical uncertainty
 Blank correction to account for positive sampling artifact
 With STN field blanks, no dynamic back up filters.
 Differs among urban STN speciation samplers

	24-hr sample	Network Average Total Carbon on STN Blank Filters*		*Network-wide values	
STN sampler	Volume(m <sup>3</sup> )	ug C/ filter	ug C/m <sup>3</sup>	from 2001-02 data as	
MetOne (SASS)	9.6	14.8	1.5	reported by RTI and	
Anderson (RAAS)	10.4	13.5	1.3	previously used by	
R&P 2300	14.4	16.1	1.1	EBA to adjust OC	
URG (MASS)	24	77	0.3	LI A to aujust OC	

#### Conversion of OC to OC mass (OCM) (<u>+</u> 33%) 1.4 < k < 1.8 ("tvoical" urban) ref: Turpin (2001)</li>

- 1.4 < k < 1.8 ("typical" urban)</li>
  2.0 < k < 2.4 ("typical" rural)</li>
- Weighted average needed for mixed urban/regional aerosol
- Turpin's revised estimates based on limited speciation data
- OC- EC split (and unaccounted mass for "EC")
- <u>Retained</u> carbon mass on FRM Teflon vs STN quartz
   Less volatile OC may be retained on Teflon \*\*
- Water [= ~10-24% of PM2.5 water]
- \*\* Volatile OC can vary by location and sampling day. Retained particulate OC depends on filter face velocity.

#### "SANDWICH" Approach

- <u>Sulfate</u>, <u>Adjusted Nitrate</u>, <u>Derived Water</u>, <u>Inferred Carbonaceous</u> mass Hybrid material balance approach
- TCMmb = PM2.5 { [SO4] + [NO3FRM] + [NH4] + [water] + [Crustal] + [FRM blank]}
- OCMmb = [TCMmb] [EC]
- · Water and reduced FRM NO3 are estimated by models.
- Other PM2.5 constituents eg. salt, could also be considered
- TCMmb explicitly accounts for positive and negative sampling artifacts, OC hydration, and mass multipliers for carbonaceous material retained on FRM Teflon.
- material retained on FRM Teflon.
   TCMmb is upper estimate for TCM and is subject to error in non-C
- components.

Reference: Frank, N. Retained Nitrate, Hydrated Sulfates, and Carbonaceous Mass in Federal Reference Method Fine Particulate Matter for Six Eastern U.S. Cities, J. Air & Waster Manage. Assoc. 56: 500–511 (2006) Nov 1, 2006 Email: frank.neil@epa.qov

#### Trends in STN TC field blanks



#### Site Specific Differences in STN Field Blanks

No apparent consistent difference in TC field blank values among sites. Most site average values for Met-One SASS (2004-5) range from 0.75-1.5 ug/m3 as shown.



Similarly, no apparent pattern was observed among TC field blank values by calendar quarter (preliminary analysis). Due to large within-site and between year variability and few samples, multiyear network-wide values seem reasonable to use.

#### Regional Trends in TCM, 2002-2005



Regional average values of TCM agree well with k\*(OC-b) using k=1.4 and year specific b values. For some US Regions and sites, the old b values seem better. The successful choice of k to represent retained FRM mass (on Teflon) appears to depend on the selected value for "b". The value for "k" may also depend on the particular thermal analytical technique and OC-EC split. Distribution of site-quarterly averages of TCM are shown.



#### Example Site-Specific TCM Trends, 2002-2005



#### Monthly Average TCM (TCMmb nicely tracks k\*(QC-b))



#### Summary and Next Steps

#### Inferred carbon by mass balance (TCMmb, 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/season-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 TCMmb 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, TCMmb 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 field 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