Speciation Analysis to Support State Implementation of PM NAAQS

Background

Material balance with FRM mass and comparisons with upwind rural values are needed for QA/QC, to understand local sources of PM2.5, to support modeling, to make comparisons to FDMS monitoring data, to develop control strategies and to track progress towards attainment. Using mathematical models together with STN and IMPROVE speciation measurements, we can provide estimates of the retained major components on FRM filters (carbon, sulfates and nitrates). These quantities are different than what's measured on STN or IMPROVE filters. Carbon accounts for most of the urban excess as well as most of the within-city variability in PM2.5 mass, but our ability to provide precise estimates is limited because of speciation and FRM sampling artifacts, differences between STN and IMPROVE carbon protocols, and lack of collocated speciation data at some design value sites. FRM filter contamination (i.e. passive sampling) has also been recognized as a contributor to PM2.5 mass (~0.3-0.5 ug/m3). All of these issues may be even more important with revised PM2.5 NAAQSs.

We have procedures (e.g. SANDWICH[1] and SMAT[2]) to account for some of the uncertainties and limitations in our speciation data and to make comparisons with reconstructed fine mass (RCFM). See Attachment A. Collocated STN and IMPROVE sampling (including several NA areas) was initiated to understand differences and to assist potential conversion of STN to IMPROVE protocols. However, data has not been fully analyzed, particularly with respect to relationship of speciation data and corresponding FRM retention with different filter face velocities and potential artifacts.

Therefore more refined data and analyses are needed to better understand

* Carbon sampling artifacts on quartz substrates in urban environments
* Retained carbonaceous mass on FRM Teflon filters
* Composition at DV sites currently without collocated speciation data (especially to quantify nitrates whose with-in city spatial variability is not well understood)
* Site, season and sampler specific FRM filter blank values which contribute a portion of PM2.5 mass unrelated to influencing emission sources.

Data Analysis Related Proposals

- Data analyses of carbon on 2001-2005 STN quartz field blanks (2002 RTI draft report is based on 2001 STN filters, see attachment B)
- Comparison of field and dynamic carbon blanks using existing IMPROVE sampling data, potentially coupled with new back-up filter field measurements on STN, IMPROVE and FRM samplers in a few urban areas. Explore need to modify IMPROVE blank correction protocol for urban sampling and develop carbon uncertainty estimates reflecting estimated sampling artifacts. (suggested source: DRI, in connection with the Fresno super site study)

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[1] **S**ulfate, **A**djusted **N**itrate, **D**erived **W**ater, **I**nferred **C**arbon mass balance approac**h**. (http://www.epa.gov/ttn/amtic/files/ambient/samwg/spring2004/frank.pdf)

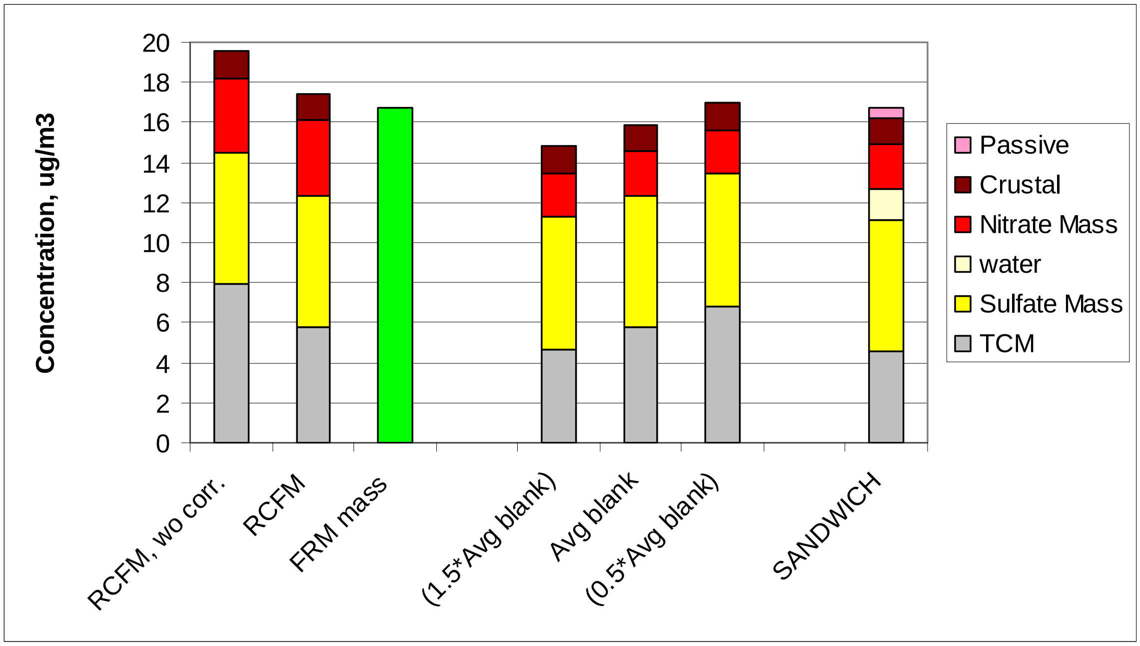
[2] **S**peciated **M**odeling **A**ttainment **T**est (http://www.epa.gov/air/interstateairquality/pdfs/Revised-SMAT.pdf)

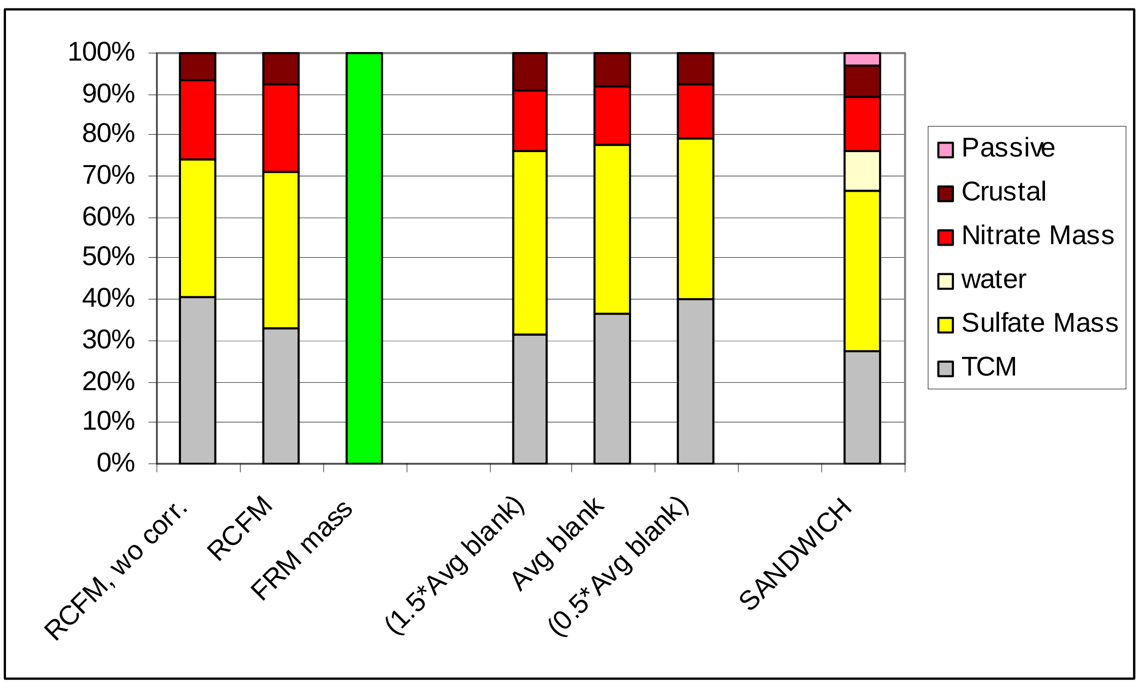
- Nitrate measurements from archived FRM filters in a few pilot urban areas to develop an analytical protocol (perhaps using composited filters to save resources) to understand spatial variability and assist with SIP development.
- Analyze site differences and trends in FRM filter blanks, for PEP and State network data. This can involve a survey or voluntary reporting of existing FRM blanks. Requiring FRM data reporting is also suggested for the new NAAQS to both support the FRM QA program and to help with PM implementation.

Attachment A.

Material Balances of Cleveland annual average PM2.5 to show uncertainty and effect of estimated carbonaceous mass (based on 2003 FRM and speciation data).

All estimates of total carbonaceous mass below use a 1.4 organic carbon to mass multiplier. RCFM (left) uses observed speciation measurements is presented with and without carbon blank correction. In the middle three composition bars, TCM is estimated using three carbon blank corrections (STN avg. network blanks ±50%). Nitrates are adjusted to reflect 40% lower FRM nitrates at this site. The right most bar shows SANDWICH estimates which include adjusted nitrates, particle bound water, passive mass (0.5ug/m3) and carbon by mass balance. Carbon mass estimates among the various presented alternatives range from 4.6 to 7.9 ug/m3 (27 - 40 % of PM2.5). Note: TCM using a 1.8 multiplier would be 29% higher. SANDWICH carbon is comparable to use of 1.4 multiplier and a 1.5*Avg Carbon blank.





Attachment B

Selected Figures from: ***Analysis of Speciation Network Carbon Blank Data***, DRAFT REPORT prepared by James B. Flanagan, Max R. Peterson RTI International, August 30, 2002

Figure and Tables show that Carbon blanks are variable and represent a large portion of measured carbon for many samplers (Figure 3-1 shows URG sampler data, but is illustrative of other samplers)

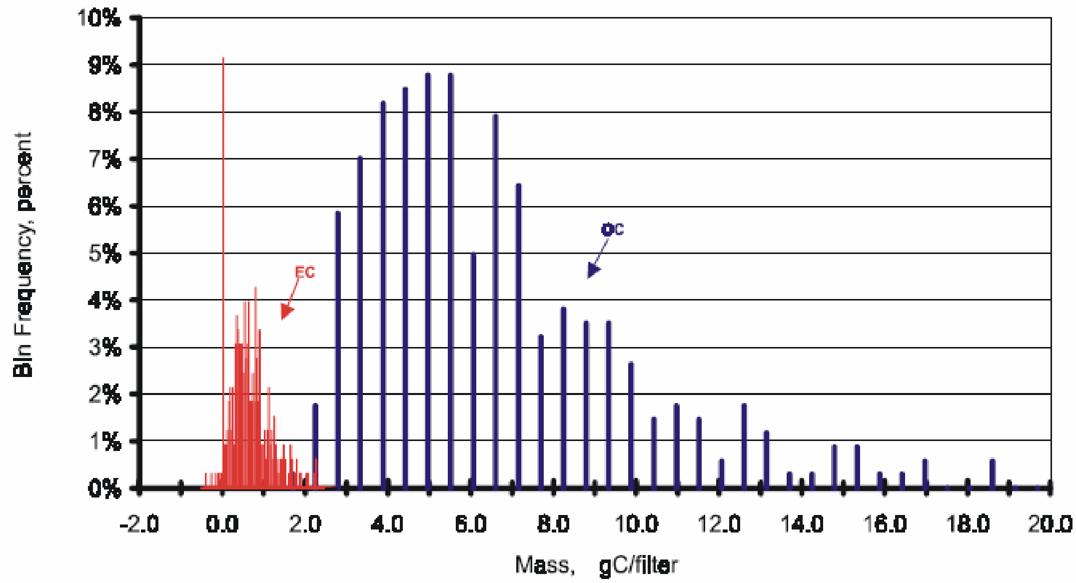


Figure 3-1. Typical Data Distributions for OC and EC Blanks (Trip and Field Combined).

Table 3-2. Summary of Average Blank Levels.

Sampler Type	Mass on Filter, µgC/filter			Converted to Ambient Concentration, µgC/m^3		
	EC	OC	TC	EC	OC	TC
URG MASS	0.63	7.08	7.71	0.03	0.29	0.32
R and P 2300	3.21	12.93	16.13	0.22	0.90	1.12
Andersen RAAS	0.97	12.54	13.51	0.09	1.19	1.29
R&P 2025*	1.67	18.42	19.91	0.07	0.77	0.83
MetOne SASS	1.03	13.75	14.78	0.11	1.42	1.53

* Includes data from both "ions on quartz" and "ions on Teflon" configurations.

Table 3-5. Total Carbon: Comparison of Average Routine vs. Average Trip and Field Blanks.

Sampler Type	Average Routine Mass of OC, µgC/filter	Average Blank Mass of OC, µgC/filter	Avg Blank as a Percentage of Avg Routine
URG MASS	81.08	7.71	9.5%
R and P 2300	47.61	16.13	33.9%
Andersen RAAS	56.61	13.51	23.9%
R&P 2025	89.03	19.91	22.4%
MetOne SASS	52.60	14.78	28.1%