Understanding the Components of FRM mass

Part 2: Carbonaceous Mass by Mass Balance

Neil Frank For Presentation to SAMWG May 13-15 2004 Point Clear, Alabama

> Draft Data -- Results are Preliminary

Background on Constructing Masser

- <u>Current Approach (use speciation measurements</u>)
 - PM2.5 Mass = SO4 + NH4 + NO3 + "Organic Carbon Mass]

+ EC + "crustal" + unknown

- The unknown (generally positive) is apportioned to all components
- How can we better assign the unknown?
- Do we have the PM2.5 chemical components correctly characterized?



Source: EPA Speciation Network, 200 From EPA Trends Report

Crustal

Better characterization of PM2.5 mass

Adjustments are needed to account for what is <u>actually on the filter</u>

- Retained NO3
- Particle bound water (sulfates and nitrates)
- <u>Retained</u> carbonaceous mass
- Other
 - Metallic oxides (crustal material)
 - Passively collected particles (FRM filter blank ~0.3-0.5ug/m3)
 - Salt and metal oxides can also be considered

PM2.5 = NO3FRM + SO4 + NH4 + Water + Crustal + TCM + Blank + Other What PM2.5 FRM mass components can we confidently characterize?

- Sulfates
- Nitrates \rightarrow FRM NO3
- Ammonium
- Water associated with inorganics
 - Thermodynamic model (AIM)
- Crustal Material
- Other (FRM filter blank)
- What about OC and EC <u>mass</u>?

Carbonaceous Mass from measured C data is a very uncertain calculation Commonly, as 1.4*OC+EC

Many Sources of error

✓ Blank correction (avg value ~1.5ug/m3 OC)

- Varies among our 5 different urban speciation samplers
- We cant do site or seasonal adjustments

✓ Conversion of OC to OCM (\pm 33%)

- 1.4 < k < 1.8 ("typical" urban)
- 2.0 < k < 2.4 ("typical" rural)
- Weighted average for mixed urban/regional aerosol
- Turpin's revised estimates based on limited speciation data
- ✓ OC- EC split (and unaccounted mass for "EC")
- Retained carbon mass on tellon vs quartz
 - Volatile OC [teflon OC =~0.8 * quartz OC in Pittsburgh]
 - Potentially more for predominantly urban aerosol
 - Water [10-24% of PM2.5 water]

How to Estimate FRM Carbon Mass

- Use **k*OC+EC** (despite all known uncertainties)
 - k =1.4 or k=1.8 or ???
 - What approach is best for blank correction??
- <u>Alternative approach:</u>
 - Use precise PM2.5 mass and other better characterized chemical measurements
 - With collocated speciation measurements or suitable estimates
 - Then, calculate TCM by difference
 - TCMmb = PM2.5 { [SO4] + [NO3_{FRM}] +[NH4] +[water] + [crustal] +[blank]}

 \rightarrow OCMmb = TCMmb - EC

- ✓ Advantages
 - "Unknown" mass is completely associated with TCMmb
 - No need to estimate blanks, retained carbon, water, etc.

A new fine particle chemical "SANDWICH"

 Sulfates, Adjusted Nitrates, Derived Water, Inferred Carbonaceous Mass and estimated aerosol acidity (H+
the greatest thing since sl bread!

The "Frank"SANDWICH







Fits the new Patriotic Theme

Comparison of TCMmb (red) with TCM1.4 (blue) -- Fits "Conceptual" Model



Estimated Carbonaceous Mass as TCMmb



cityname	TCM14	TCM _{mb}	%diff
Mayville	1.9	2.8	53%
Chicago	4.6	4.9	6%
Indianap	4.7	4.4	-5%
Clevelan	5.7	4.1	-29%
New York	4.4	4.2	-4%
Birmingh	8.0	7.3	-8%



Putting it all Together: Preliminary Results (Jan-Dec 2003)

Preliminary Summary

Expected IMPACT of SANDWICH in the East

- Ammonium Sulfate (AS) would be ~15-35% higher
- Ammonium Nitrate (AN) would be ~30-85% lower
- New mass associated with sulfates+nitrates is similar to old
- Changes in sulfates+nitrates (SAN) offset by carbon

cityname	delta AS	delta AN	delta SAN
Mayville	13%	-44%	-16%
Chicago	17%	-30%	-4%
Indianap	23%	-51%	-1%
Clevelan	33%	-39%	9%
New York	25%	-52%	-1%
Birmingh	21%	-85%	2%

Draft Jan-Dec 03 data

Applications of SANDWICH to Support NAAQS Implementation

- Better partition of major chemical components to guide control strategy development
- Estimate and track changes in TCMmb (major local contribution to PM2.5) at all PM2.5 design value sites without need for additional collocated speciation sampling (idea for review)
 - Quarterly composite sulfate, ammonium and nitrate (SAN) from FRM Teflon (cheap!)
 - Estimate carbon by difference (TCMmb) from PM2.5 and hydrated SAN
 - Assume average crustal is relatively constant and <10%
 - Don't throw away 2001-2003 filters

End of Presentation

Reconstructed Fine Mass (RCFM) is ~= PM2.5 Good Agreement because of Canceling errors!

cityname	PM2.5	RCFM	unknown	%,PM2.5
Mayville	10.0	8.7	1.3	13%
Chicago	14.1	13.0	1.1	8%
Indianap	14.9	14.6	0.3	2%
Clevelan	16.8	17.7	-0.8	-5%
New York	14.5	14.1	0.4	3%
Birmingh	17.0	16.8	0.2	1%

Estimate <u>Water</u> using a thermodynamic model (AIM)

Water is approximately 25% of the sulfate + ammonium concentration

Less during periods with high nitrates



Preliminary H20 predictions using monthly avg SO4, NH4, FRM NO3 and Calculated H+ from the 6 Study Sites

Monthly Particle Bound Water as % of PM2.5 Among 6 Study Sites



6% January(1ug/m3) and 12% August(4 ug/m3) reported by CMU researchers