



PM_{2.5} Carbon Measurements in EPA Region 10

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June, 2011**



Motivation for this presentation:

2007-2009 EPA changed the urban (STN network) PM_{2.5} carbon sampling and analysis protocols to bring them in line with those used by the IMPROVE monitoring network.

After switching to the new sample and analysis protocols, we found a significant decrease in the observed % total carbon (TC=OC+EC).

2006 – 2010 Data for PM_{2.5} Samples > 25 ug/m³

Data for samples where PM _{2.5} > 25 ug/m ³							
		Before Change			After Change		
Location	Change Date	Mean %TC (of PM _{2.5})	stdev	N	Mean %TC (of PM _{2.5})	stdev	N
Fairbanks	10/2009	51.9	7.6	36	42.5	4.3	22
Tacoma	7/2007	57.9	2.6	6	47.3	3.7	9
Klamath Falls	7/2009	61.6	7.6	11	52.1	5.8	6

about 10% drop in TC at each site

Is this an issue with the measurement method or caused by an emissions change?

This presentation will show why we think it is primarily a measurement issue, and give some recommendations on how to deal with it.

More motivation for this presentation:

We also observed an increase in %EC at each site after switch
2006 – 2010 Data for PM2.5 Samples > 25 ug/m3

Data for samples where PM2.5 > 25 ug/m3		Before Change			After Change		
Location	Change Date	Mean %EC (TOT)	stdev	N	Mean %EC (TOR)	stdev	N
Fairbanks	10/2009	6.9	2.2	36	10.2	2.1	22
Tacoma	7/2007	8.1	2.9	6	9.7	1.9	9
Klamath Falls	7/2009	4.9	1.3	11	7.8	1.2	6


%EC increase at each site

and a decrease in %OC at each site

2006 – 2010 Data for PM2.5 Samples > 25 ug/m3

Data for samples where PM2.5 > 25 ug/m3		Before Change			After Change		
Location	Change Date	Mean %OC (TOT)	stdev	N	Mean %OC (TOR)	stdev	N
Fairbanks	10/2009	45.0	6.9	36	32.3	4.5	22
Tacoma	7/2007	49.7	1.0	6	37.6	4.8	9
Klamath Falls	7/2009	56.6	7.6	11	44.3	6.0	6


%OC decrease at each site

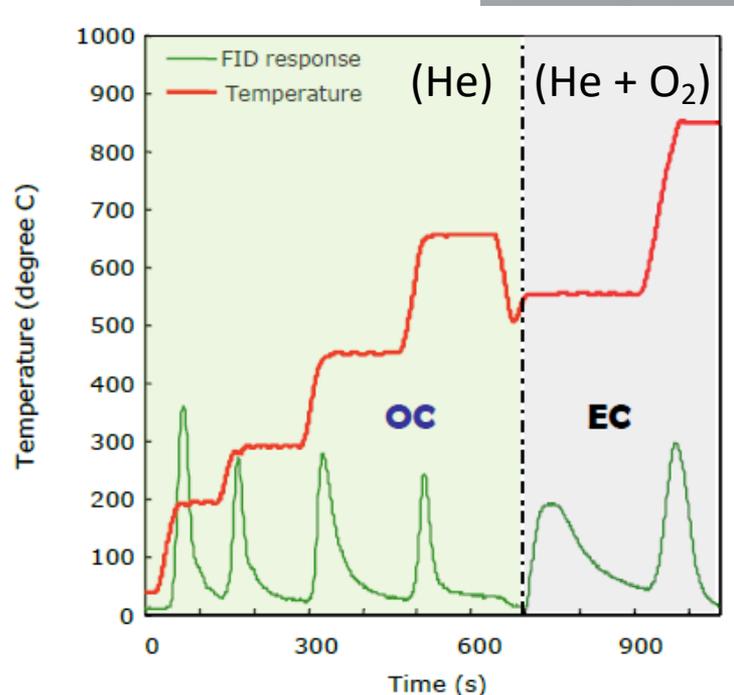
To get to the bottom of this – need to review some background on how OC & EC are defined:

OC and EC are ‘operationally’ defined based on a thermal and optical measurement protocol rather than objectively defined.

OC = the portion of total carbon that is not light absorbing and can be thermally volatilized in a non-oxidizing atmosphere

EC = the portion of total carbon that is light absorbing and can be thermally volatilized (combusted) in an oxidizing atmosphere

Idealized thermogram



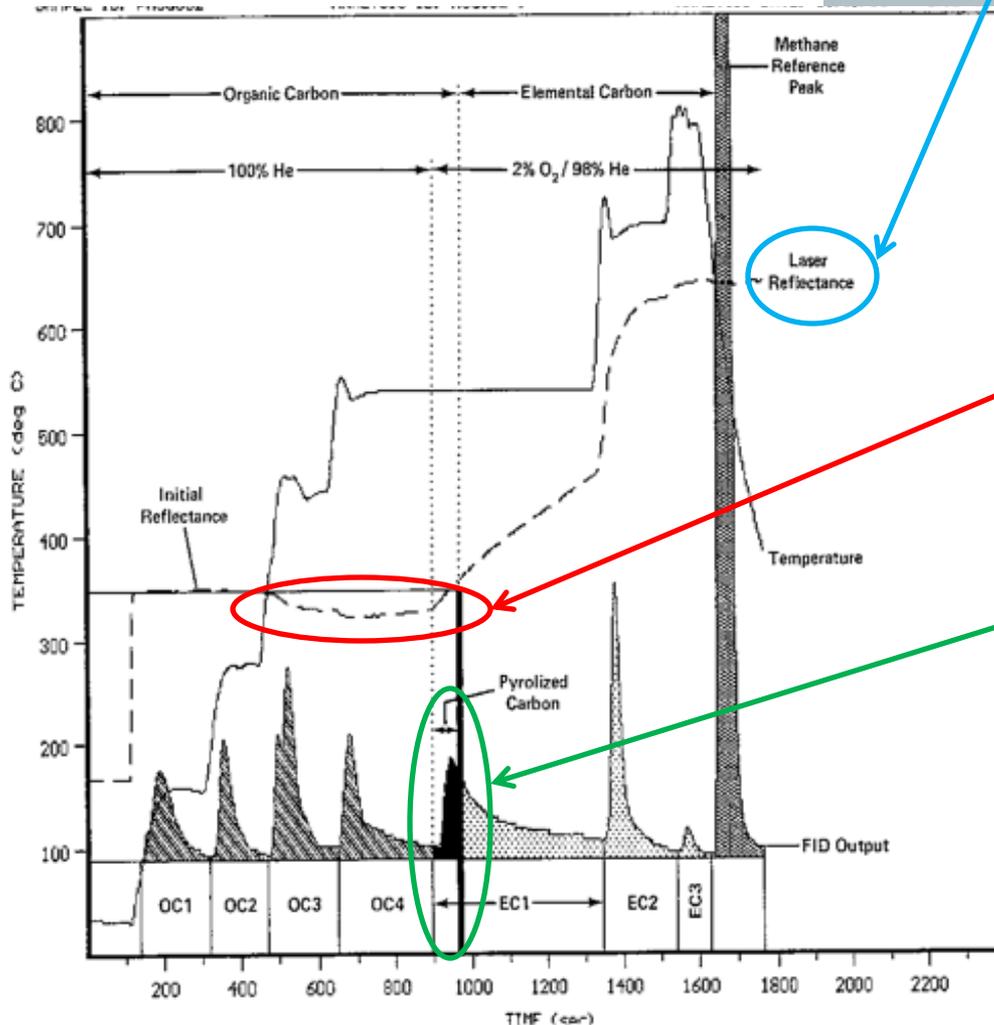
Idealized thermogram features:

- Temperature is ramped in stages under inert (He) atmosphere.
- Volatilized carbon is measured in each stage and total of the stages is = OC
- Temperature is further ramped in stages under oxidizing (He + 2% O₂) atmosphere.
- Volatilized carbon is measured in each stage and total of stages is = EC

That's the ideal ... BUT ... in reality some thermally unstable OC can pyrolyse in the He-mode to form EC.

Correcting for OC pyrolysis

Thermogram – IMPROVE (TOR) method



- OP (OC pyrolysis) is measured in one of two ways, looking at light reflectance off the quartz filter or looking at light transmittance through the filter.

- Reflectance method is called TOR (Thermal optical reflectance). Transmittance method is called TOT (Thermal optical transmittance)

- OC pyrolysis is observed when reflectance or transmittance decreases in the non-oxidizing atmosphere from its starting point.

- Pyrolyzed OC (OP) is quantified when reflectance or transmittance reaches its initial level after O₂ is added.

- Final OC and EC determined as:
OC = OC1+OC2+OC3+OC4+OP
EC = EC1+EC2+EC3-OP

To understand what's causing the shift in TC, EC, and OC in the change in STN measurement method, we also need to know what biases the measurements are subject to.

- Mass can be added to the quartz filter by gaseous VOC adsorbing onto the filter
 - > **Positive bias (adds mass to OC & TC)**
 - > influenced by monitor flow rate
- Mass can be removed from the filter by particle OC volatilization
 - > **Negative bias (loses mass from OC & TC)**
 - > influenced by flow rate, pressure drop across filter
- Mass can be shifted between OC and EC based on the OP method used
 - > OP (TOT method) > OP (TOR method) [usually]
 - > **TOT shifts more mass to OC, from EC (but same TC)**
 - > possibly due to adsorbed VOC and SVOC charring in filter interior.
- Also, OC and EC can be more uncertain under high filter loading
 - > **TOT and TOR more uncertain for highly loaded filters**
 - > Highly loaded filters may have a starting transmittance and reflectance near zero (if OP is difference of two small numbers, more uncertain)

When the STN method changed, what was different?

- New STN was set to mimic the IMPROVE method, so
 - OC temperatures were lowered in new STN
 - TOR replaced TOT as default OP method in new STN
 - EC temperatures are a little lowered in new STN
 - New STN has a smaller filter size, higher flow rates, higher face velocity
- How are these changes expected to effect biases?

Method Comparison

			Temp and optical protocol										
Method	Use	Status	OC1 (°C)	OC2 (°C)	OC3 (°C)	OC4 (°C)	OP	EC1 (°C)	EC2 (°C)	EC3 (°C)	Filter size (mm)	Flow rate (L/min)	Face velocity (cm/sec)
OLD STN (Met One SASS)	Urban	Phased out 2007-2009	310	475	615	900	TOT	600	750	920	47	6.7	9.8
NEW STN (URG 3000N)	Urban	Phased in 2007-2009	140	280	480	580	TOR (& TOT)	580	740	840	25	22	? (> 100)
IMPROVE_A	Rural	In use	140	280	480	580	TOR	580	740	840	25	22.8	107.7
Changes for new STN			Lower OC T's				TOR now default	Lower EC T's		smaller	larger	>> larger	

OC and EC measurements

... expected effect on biases due to STN shift

Method	Use	Status	Temp and optical protocol									Filter size (mm)	Flow rate (L/min)	Face velocity (cm/sec)
			OC1 (°C)	OC2 (°C)	OC3 (°C)	OC4 (°C)	OP	EC1 (°C)	EC2 (°C)	EC3 (°C)				
OLD STN (Met One SASS)	Urban	Phased out 2007-2009	310	475	615	900	TOT	600	750	920	47	6.7	9.8	
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Changes for new STN			Lower OC T's				TOR now default	Lower EC T's			smaller	larger	>> larger	

Change

Higher flow rate and face vel. for new STN

Expected biases

- Less VOC adsorption (smaller positive bias to OC, TC)
- More OC volatilization (larger negative bias to OC, TC)

Both effects expected to cause lower %TC and %OC

OC and EC measurements

... expected effect on biases due to STN shift

Method	Use	Status	Temp and optical protocol							Filter size (mm)	Flow rate (L/min)	Face velocity (cm/sec)	
			OC1 (°C)	OC2 (°C)	OC3 (°C)	OC4 (°C)	OP	EC1 (°C)	EC2 (°C)				EC3 (°C)
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Change

TOR now default OP method

Expected biases - we know that TOT is usually > TOR for same temp
- but also Chow et al. (2004) have found that TOT method is sensitive to temperature, with higher temps causing higher OP(TOT)
- Hence, both lower OC temps and shift to TOR will result in a **significant shift in OC/EC ratio in favor of EC (but same TC)**

OC and EC measurements

... expected effect on biases due to STN shift

Method	Use	Status	Temp and optical protocol							Filter size (mm)	Flow rate (L/min)	Face velocity (cm/sec)	
			OC1 (°C)	OC2 (°C)	OC3 (°C)	OC4 (°C)	OP	EC1 (°C)	EC2 (°C)				EC3 (°C)
OLD STN (Met One SASS)	Urban	Phased out 2007-2009	310	475	615	900	TOT	600	750	920	47	6.7	9.8
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Change

Smaller filter and higher flow rate

Expected biases

- New STN filters will have higher loadings
- TOR and TOT reflectance and transmittance will start more saturated, therefore less sensitive to quantifying OP char.
- TOT and TOR will have higher uncertainty

Shift makes OC/EC uncertainty higher for high concentration samples

We are not the only ones to discover this:

Inter-comparison studies:

Others have studied this issue and developed correlations of OC and EC between methods (by analysis of co-located monitors) and corroborated our observed decrease in %TC & %OC and increase in %EC.

Rattigan et al. 2011, Atmospheric Environment 45 (2011) 3228-3236.

Compared co-located data at an urban and rural location in New York state.

EPA Speciation Network Newsletter, 2009.

(<http://www.epa.gov/ttnamti1/files/ambient/pm25/spec/spnews6.pdf>)

Compared co-located data in Birmingham, Alabama.

Schichtel et al., 2010. IMPROVE Carbon meeting.

http://vista.cira.colostate.edu/improve/Publications/Workshops/Carbon_Oct2010/CarbonMeeting2010.htm

Compared co-located data between 2007-2009 from all co-located sites.

So in summary:

Data for samples where PM2.5 > 25 ug/m3							
		Before Change			After Change		
Location	Change Date	Mean %TC (of PM2.5)	stdev	N	Mean %TC (of PM2.5)	stdev	N
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about 10% drop in TC at each site

- The decrease in %TC and %OC after the change in STN carbon method is mainly caused by increased OC volatilization from the quartz filter with higher flow rates and face velocities.
- The increase in %EC after the change in STN carbon method is mainly caused by changing OP methods to TOR (from TOT) and lower temperatures in the OC temperature protocol.

Recommendations:

For PM2.5 attainment demonstrations, should we use older STN carbon method or new?

Benefits of old STN carbon method:

- Less negative bias from OC volatilization
- In some cases, may be the majority of data you have (e.g., Fairbanks)

Benefits of new STN carbon method:

- TOR may have less bias/uncertainty than TOT
- May be the majority of data you have
- All future measurements will use new carbon method as default

The recommendation here is to collaborate with EPA to determine what is the best choice for each nonattainment area.

Recommendations:

TOR vs. TOT OP measurement method

Benefits of TOR:

- TOR is insensitive to changes in OC temp protocols
- TOR is possibly less susceptible to saturation at high loadings
- TOR has less bias from adsorbed VOC char
- TOR is also used in IMPROVE network, so comparable.

Benefits of TOT:

- Several recent papers from Georgia Tech. (Cheng et al., 2011a; Cheng et al., 2011b) suggest TOT method gives a better quantification of OC from biomass burning

Reasons for recommending TOR:

- May be less susceptible to bias and uncertainty than TOT
- Is EPA default and directly comparable to IMPROVE
- Not enough evidence (1 research group) behind TOT/biomass burning link

References:

- Cheng et al. 2011a, Atmospheric Environment 45 (2011) 1913-1918.
- Cheng et al. 2011b, Atmospheric Environment 45 (2011) 2060-2066.
- Chow et al. 2001, Aerosol Science and Technology 34: 23–34 (2001).
- Chow et al. 2004, Environ. Sci. Technol. 2004, 38, 4414-4422.
- Chow et al. 2010, Atmos. Chem. Phys., 10, 5223–5239, 2010.
- Rattigan et al. 2011, Atmospheric Environment 45 (2011) 3228-3236.
- Schauer et al. 2003, Environ. Sci. Technol. 2003, 37, 993-1001.

Thank you!