The absorption Angstrom exponent and the b_{abs}-EC relationship

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Background/Introduction

- Elemental carbon (EC) measurements are available at ~400 US chemical speciation sites (IMPROVE, CSN, SEARCH)
- Teflon filters are available from ~800 $PM_{2.5}$ NAAQS compliance sites (some collocated with chemical speciation locations measurements)
- Teflon filter light attenuation (b_{att}) correlates with EC concentrations, but the relationship σ (λ) varies with aerosol composition and size (Chow et al., 2010)
- Improved relationships might result from classifying data by those for which b_{att} varies by $\lambda^{-\sim 1}$ and $\lambda^{->1}$

Chow, J.C.; Watson, J.G.; and Green, M.C. (2010). Filter light attenuation as a surrogate for elemental carbon. In press, JAWMA.

Background/Introduction

- The absorption Angstrom exponent gives the change in light absorption as a function of wavelength and is calculated as:

$$AAE = -\ln(b_{abs\lambda 1}/b_{abs\lambda 2})/\ln(\lambda_1/\lambda_2)$$

Graphitic carbon has an AAE of ~1

AAE's of about 2 have been reported for biomass burning and AAE's of up to 6 have been reported for pure HULIS (humic-like substances)

Brown carbon (C_{BR}) typically considered as organic carbon compounds that absorb light in the UV and short visible wavelengths

C_{BR} may higher σ (λ) than graphitic carbon at λ<500 and lower σ (λ) than graphitic carbon at λ>600 nm

Methodology

- Calculate AAE from 7 λ Aethalometer data at Fresno (370, 470, 520, 590, 660, 880, 950 nm)
- Re-processed Aethalometer data to account for filter loading effects- Virkkula et al. (2007) as implemented in Washington University's data masher software. Correction for filter loading important for AAE calculation because shorter wavelengths saturate faster than longer wavelengths. Did not correct for scattering.
- Used Aethalometer default $b_{abs}(\lambda) = 14625 * BC/\lambda(nm)$ to get b_{abs} from Aethalometer BC
- Used Fresno IMPROVE sampler (2005-2006) and RAAS-100 and IMPROVE_A TOR and TOT EC
- Used hourly EC/OC from Sunset Laboratory TOT analyzer
- Used daily average filter light absorption measurements from HIPS for IMPROVE samples and photographic densitometer for RAAS-100 samples
- Consider brown carbon (C_{BR}) to be carbon that has AAE>1.3

Aethalometer not corrected for scattering, which may be important in some cases.

M. Yang et al.: Attribution of aerosol light absorption to black carbon, brown carbon, and dust 2039

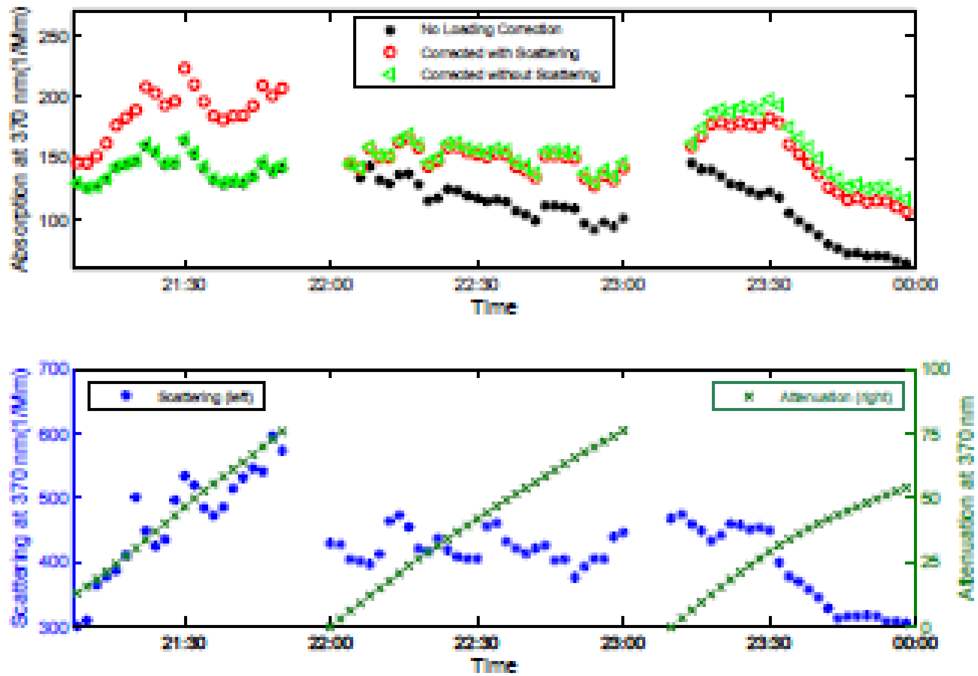
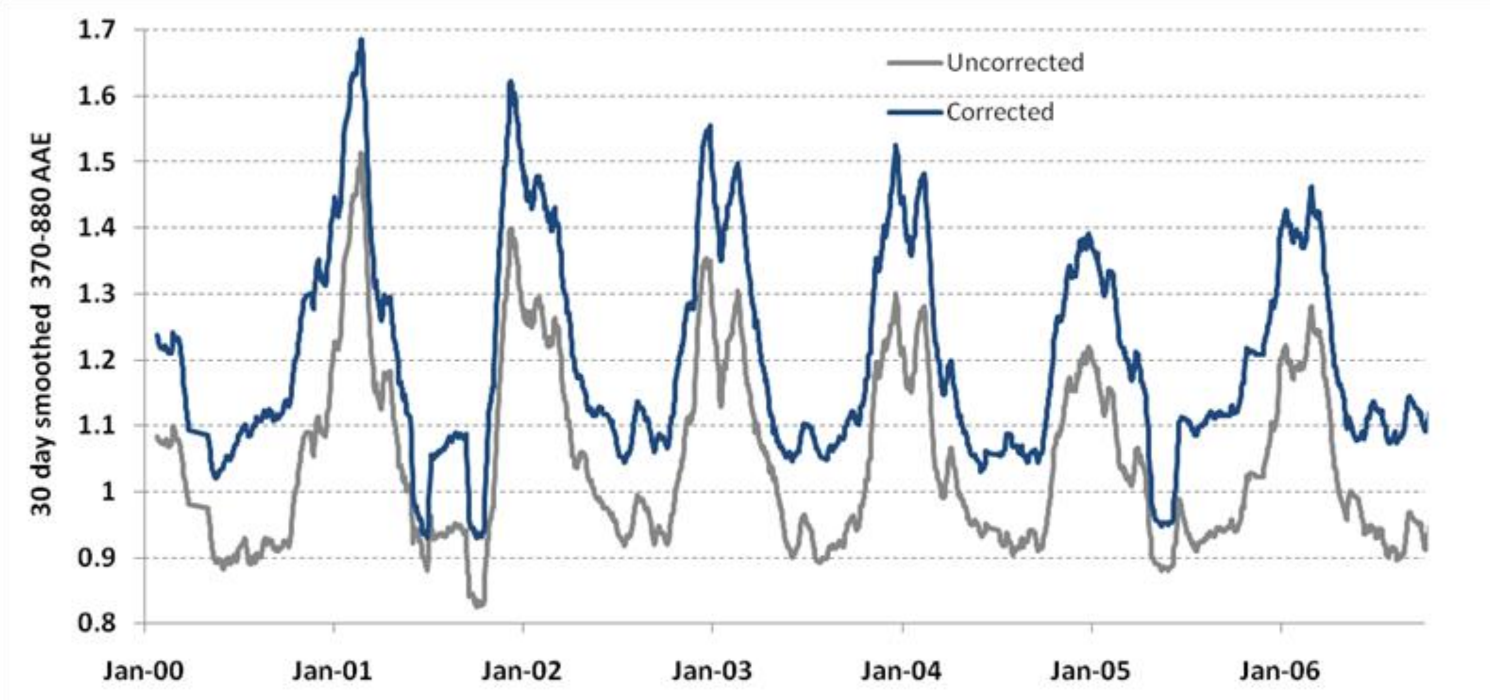


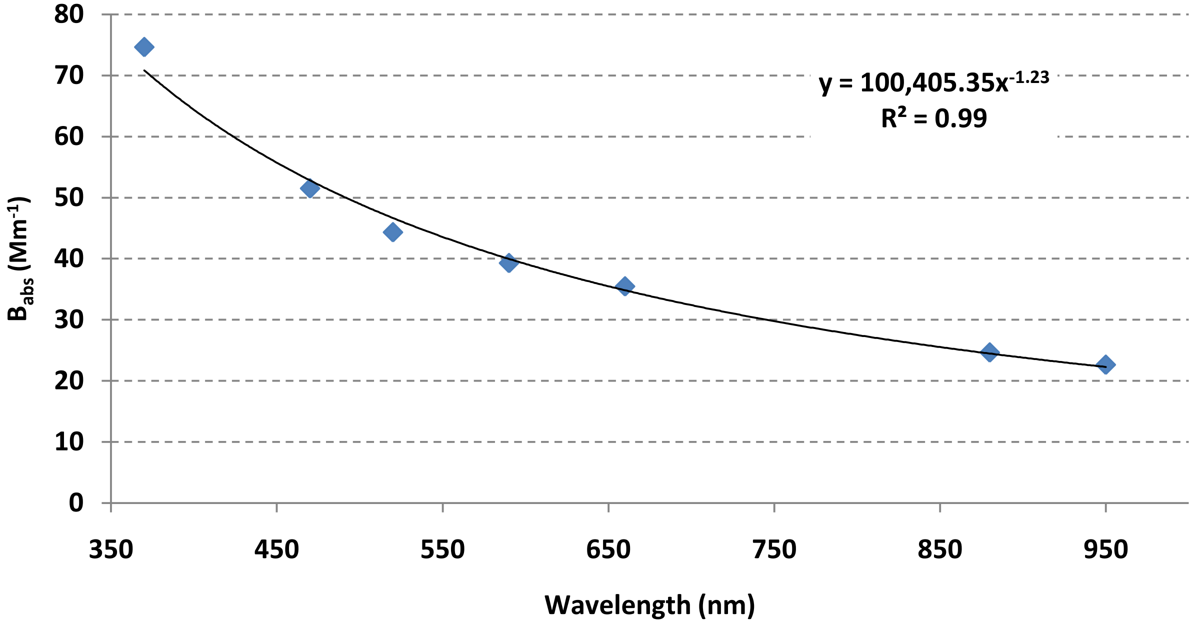
Fig. 1. Aethalometer loading correction: absorption coefficients not corrected, corrected with scattering, and corrected without scattering (top panel); scattering coefficient from the nephelometer and attenuation from the aethalometer (bottom panel). The aethalometer filter tape advances when attenuation at 370 nm exceeds 75. During the filter advancement at ~22:00 UTC, the aerosol concentration dropped rapidly, as indicated by concurrent scattering; this is reflected in the aethalometer absorption corrected with scattering, but not in the absorption corrected without scattering, where absorption before and after the filter change were forced to be equal. The aerosol concentration was relatively steady during the filter advancement just after 23:00, so corrections with and without scattering led to similar results.

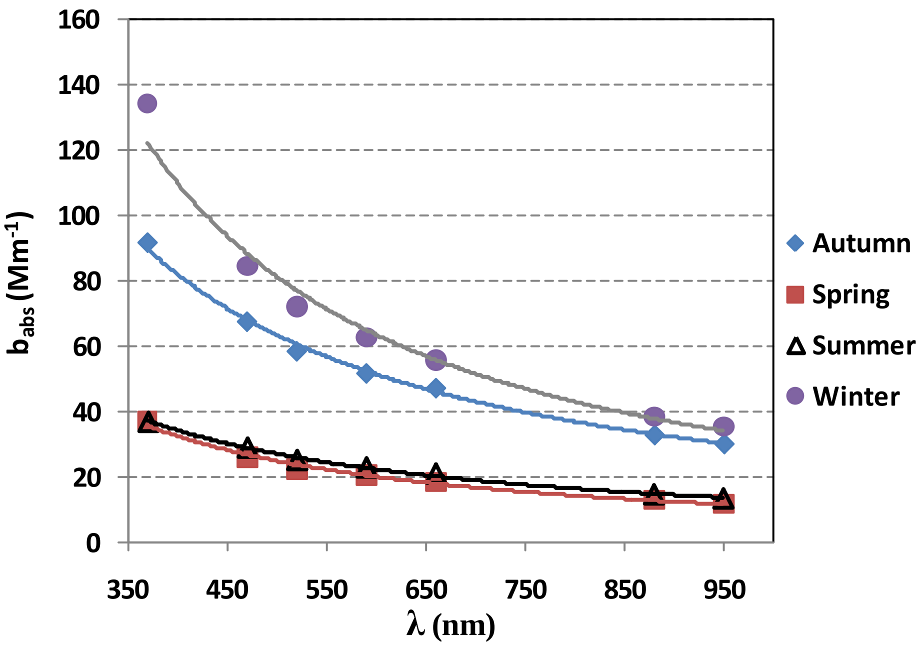
Yang, M.; Howell, S.G.; Zhuang, J.; Huebert, B.J. (2009). Attribution of aerosol light absorption to black carbon, brown carbon, and dust in China - interpretations of atmospheric measurements during EAST-AIRE. Atmos. Chem. Phys., 9(6): 2035-2050.

Importance of correcting Aethalometer data for filter saturation effects when computing AAE



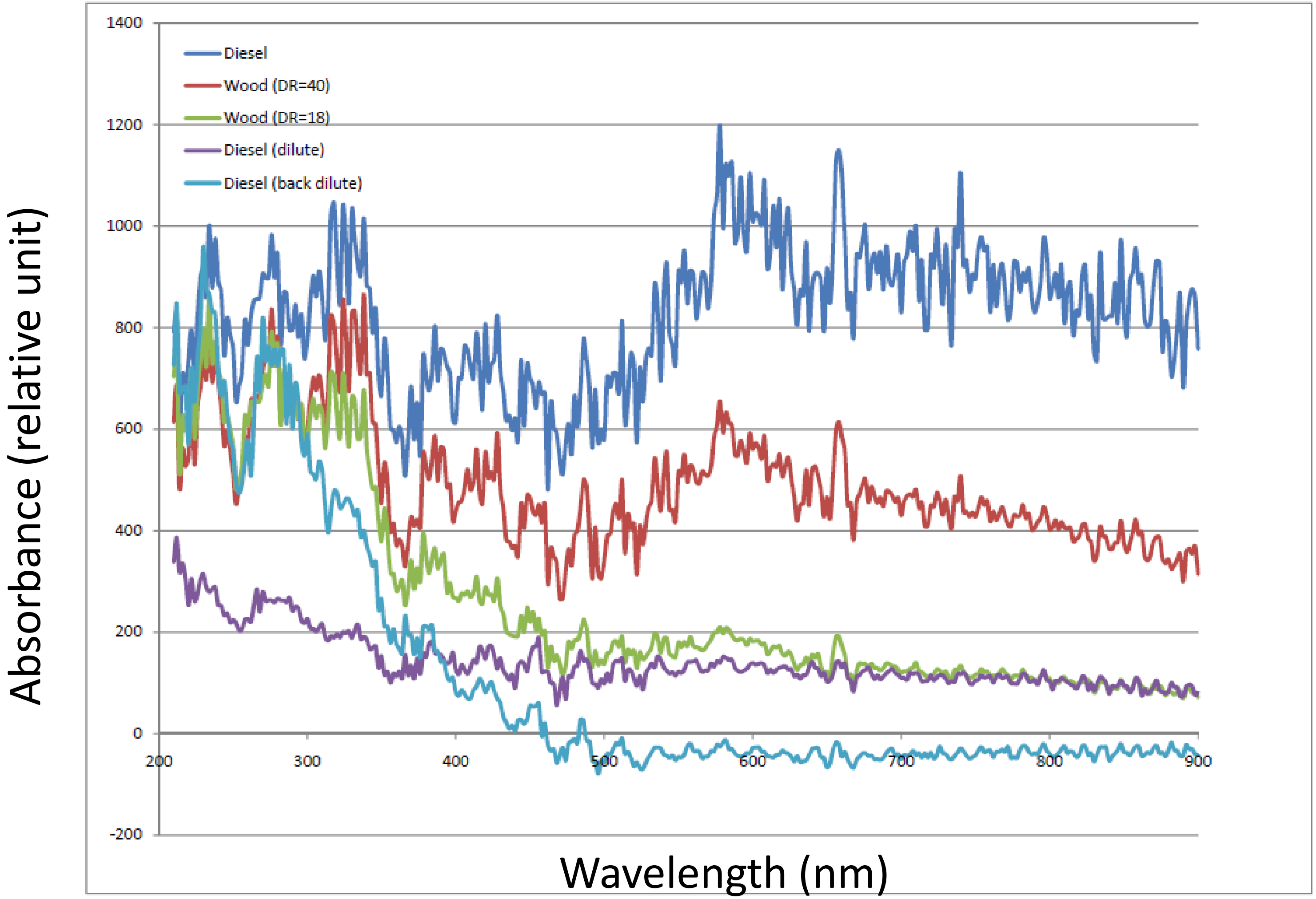
Thirty-day running mean 370-880 nm AAE computed from Aethalometer data uncorrected for and corrected for filter saturation effects



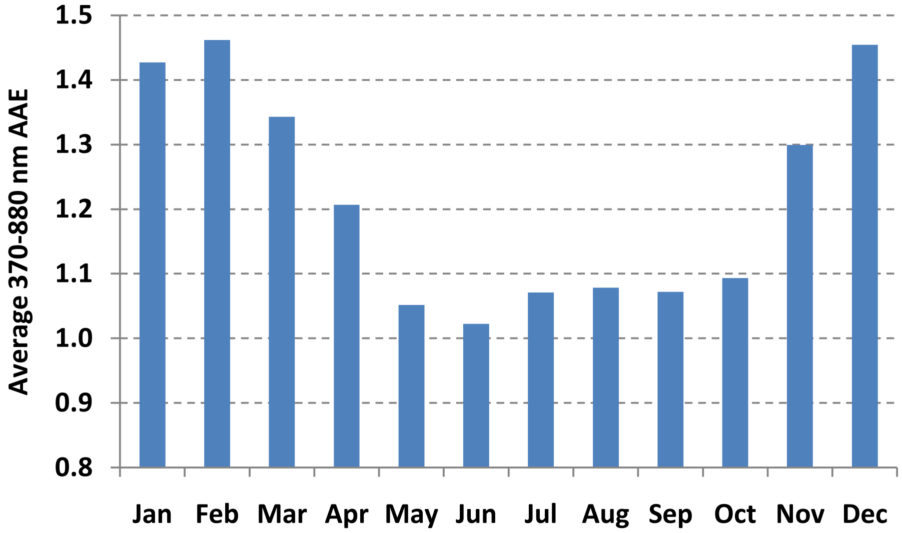


Power law coefficients: Autumn- 1.15; Spring- 1.10; Summer- 1.10; Winter-1.35

Actual absorbance spectra are more complex

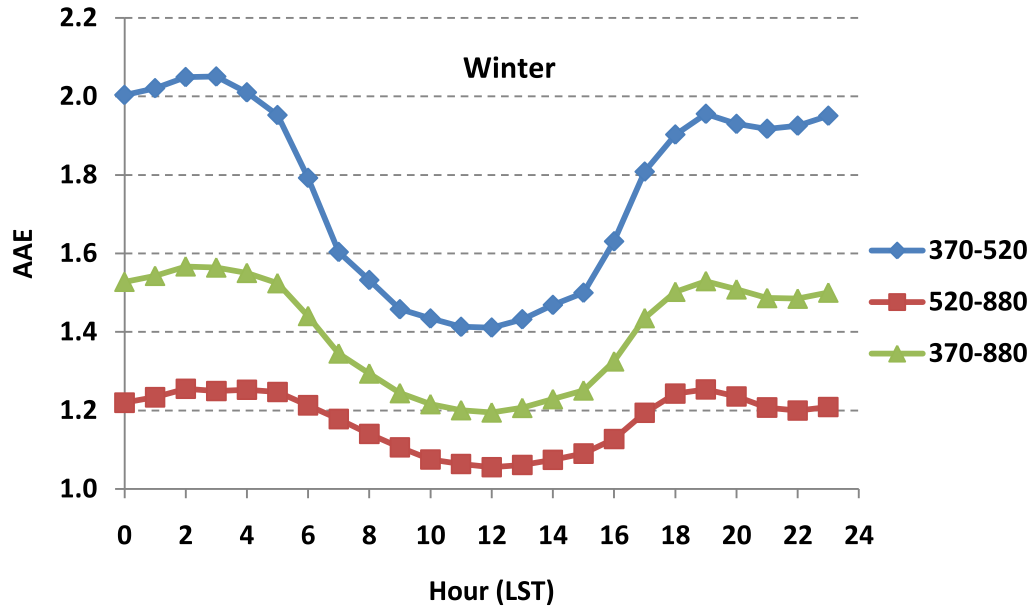


Absorbance spectra for laboratory generated particles collected on quartz fiber filters



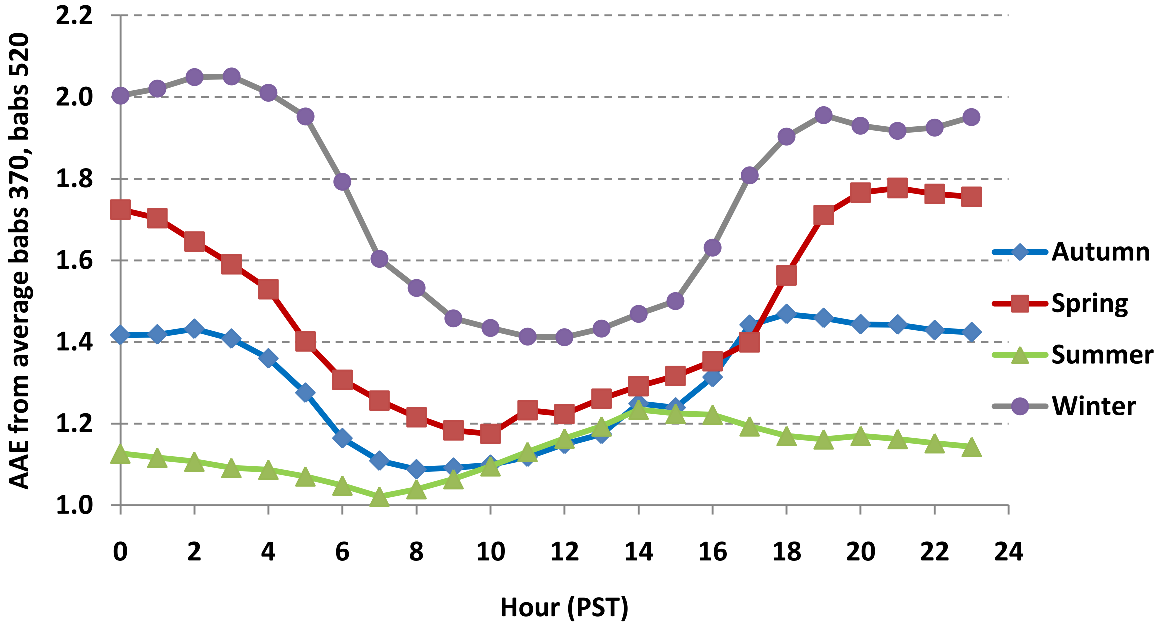
Average 370-880 nm AAE at Fresno by month January 2000-January 2007. Total number of days was 2269.

Strong seasonal variation in average AAE – near one in summer



Strong diurnal variation in AAE in winter- highest night & morning when wood smoke is expected to be greatest

Most of the departure from 1/λ (AAE=1) at λ less than 520 nm



370-520 nm AAE by time of day by season

Summer has different diurnal pattern than other seasons- smoke aloft mixing to ground in afternoon?

	N	TOR EC µg/m³	TOT EC µg/m³	BC µg/m³	b_{abs} Mm^{-1}	Fe µg/m³	AAE	AAE< 1.1	AAE 1.1-1.3	AAE> 1.3
Winter	46	1.73	0.98	1.56	12.22	0.09	1.43	0	12	34
Spring	49	0.71	0.38	0.73	6.91	0.09	1.22	15	15	19
Summer	57	0.75	0.50	0.82	8.91	0.15	1.09	38	17	2
Autumn	47	1.45	0.97	1.62	12.65	0.24	1.16	19	20	8

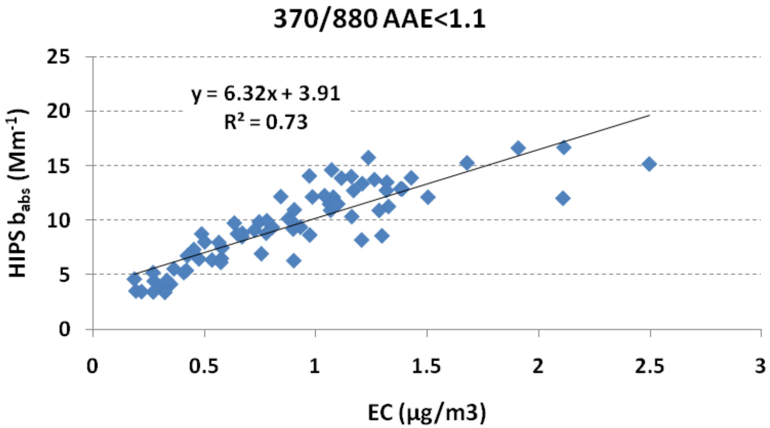
HIPS σ(633 nm)

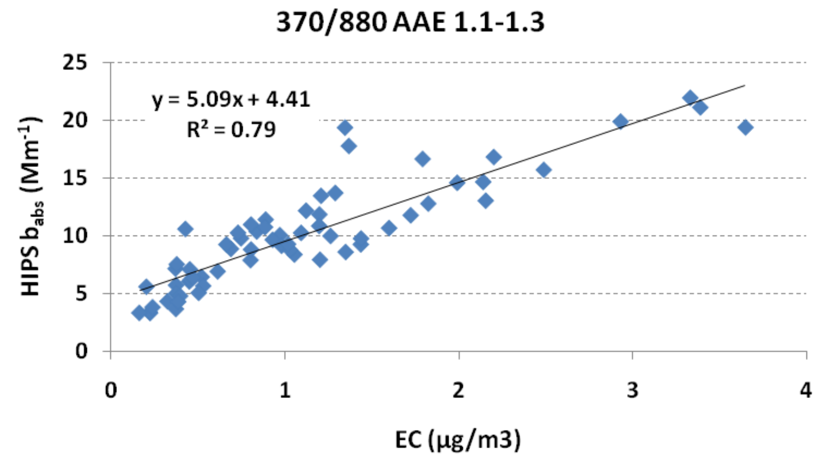
Aeth σ(633 nm)

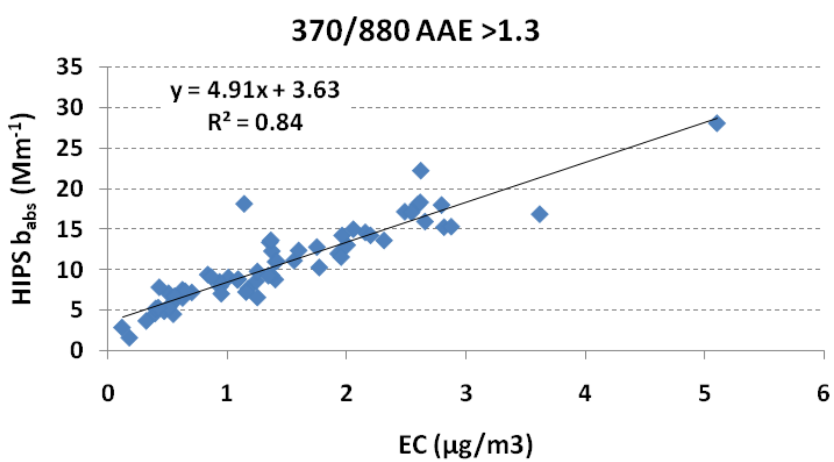
AAE range	**N**	**Avg b_{abs} (Mm^{-1})**	**Avg TOR EC (µg/m³)**	**Avg Fe (µg/m³)**	**Avg b_{abs}/ EC (m²/g)**	**R^2**	**Avg b_{abs}/ (Ec+Fe)**	**R^2**	**Avg b_{abs}/ BC (m²/g)**
<1.1	72	9.61	0.90	0.17	**10.65**	0.734	8.94	0.798	9.04
1.1-1.3	64	9.99	1.09	0.16	**9.13**	0.787	7.96	0.851	7.96
>1.3	63	10.68	1.44	0.09	**7.44**	0.842	7.01	0.850	8.00

σ(633 nm) decreases for higher AAEs for TOR EC

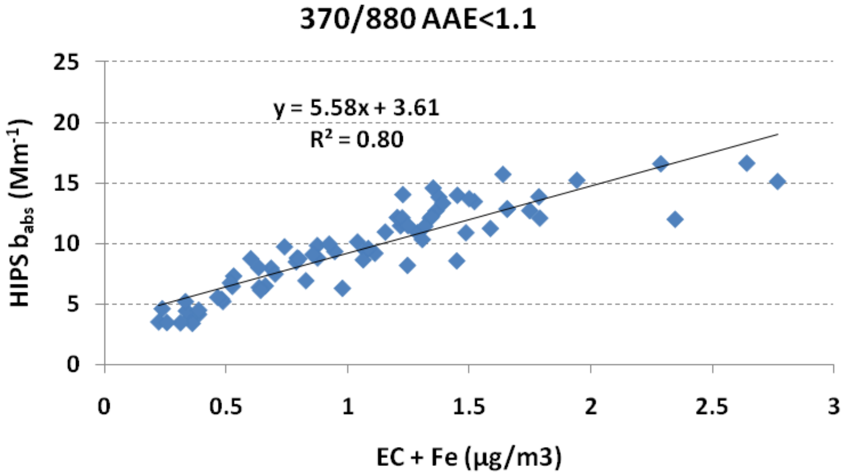
HIPS σ(633 nm) decreases for higher AAEs
(large positive intercept lowers slope)

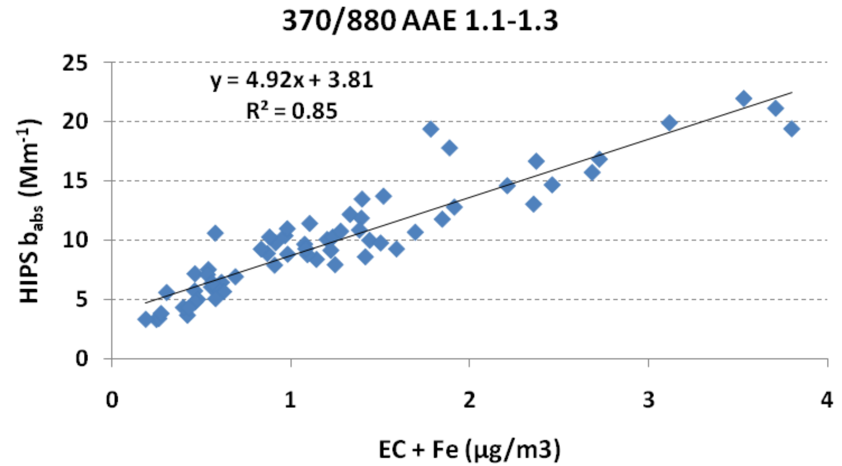


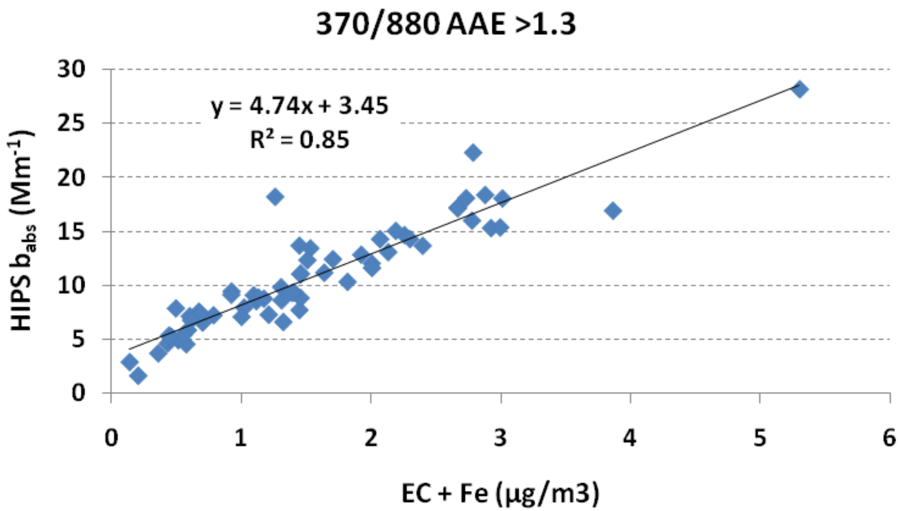




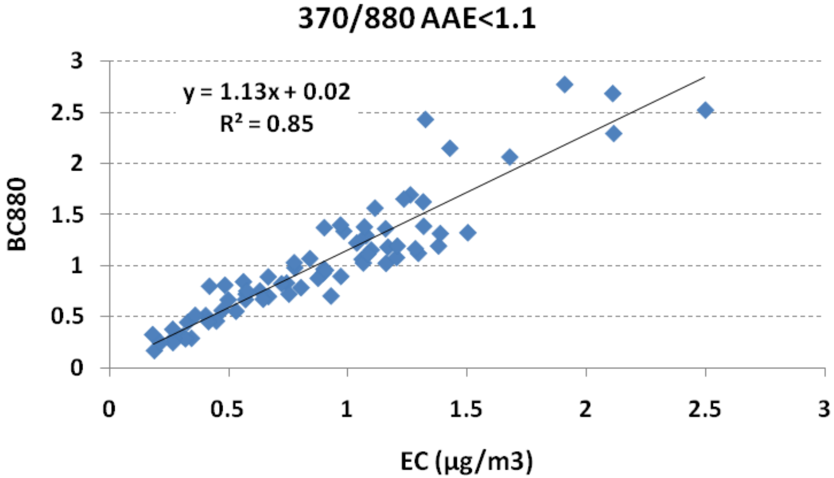
Iron oxides have a minor effect, but improve correlations
(large positive intercept lowers slope)

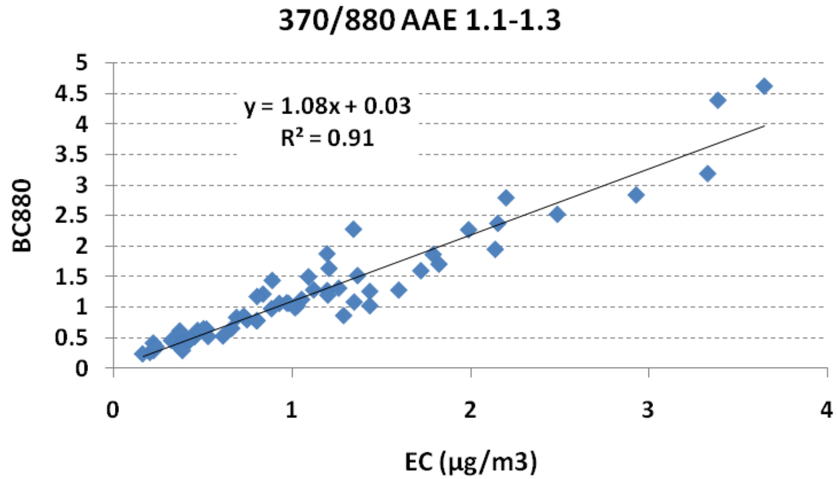


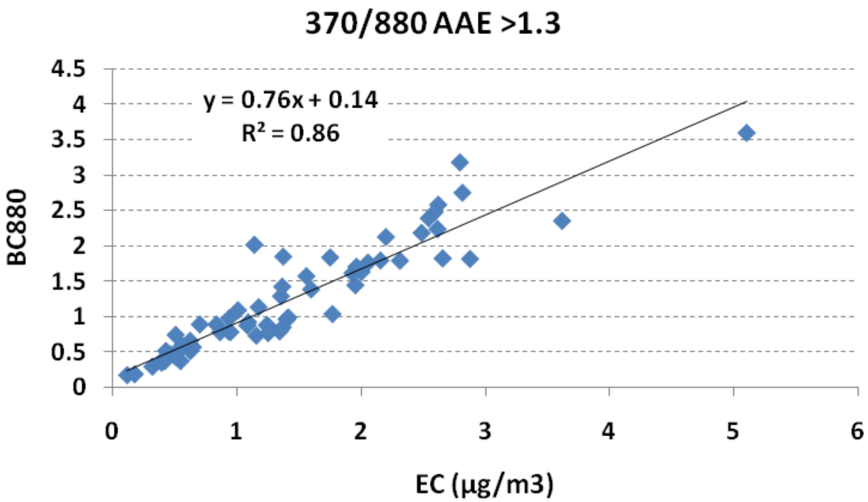




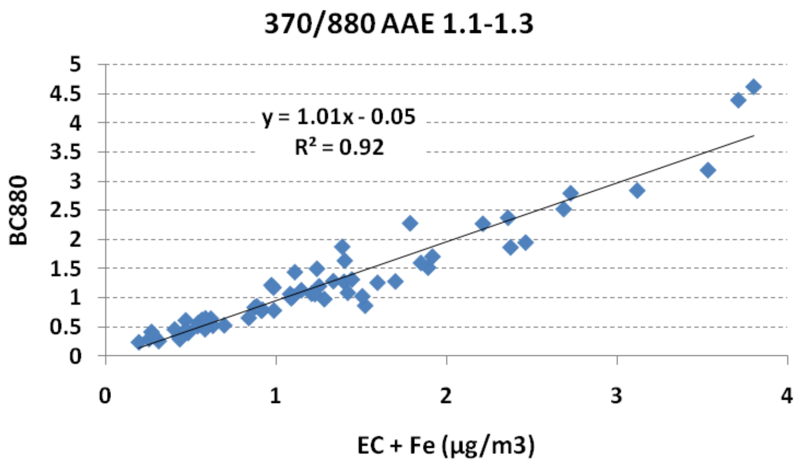
Aethalometer BC880 nm) decreases for higher AAEs
(smaller intercept gives more reasonable slopes)

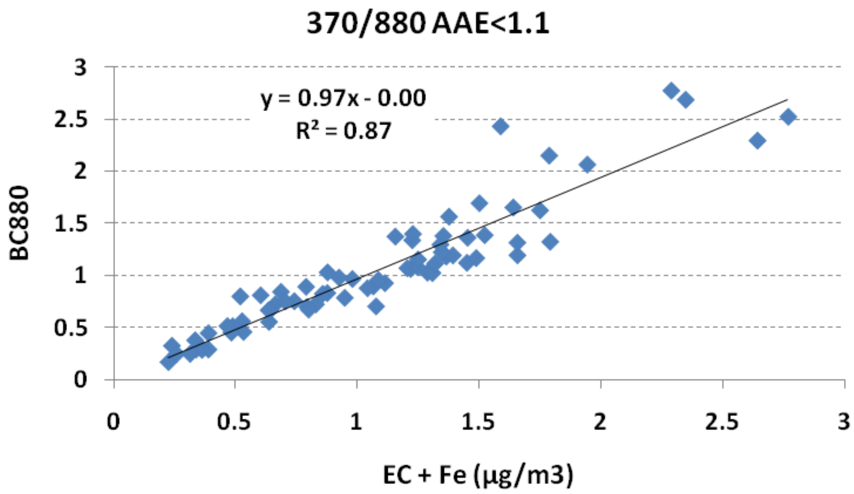


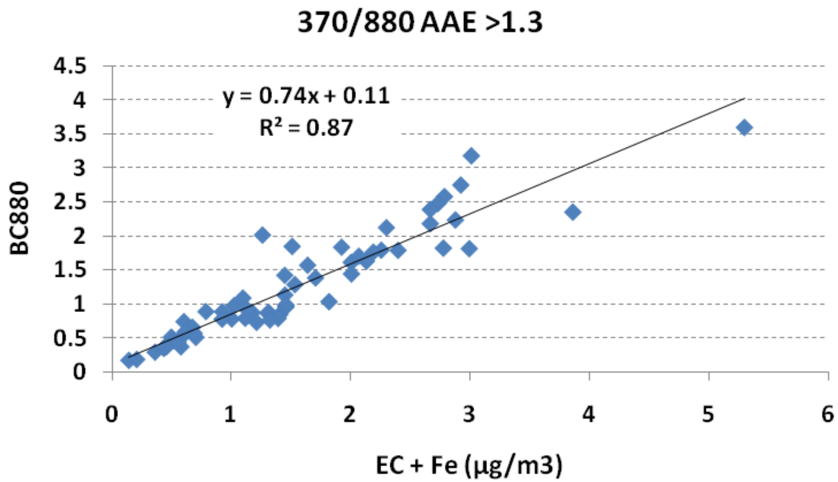




Again, iron oxides have a minor effect, but improve correlations







Relationships among TOT EC, HIPS b_{abs}, Fe, and Aethalometer BC (interpolated to 633 nm).

				HIPS σ(633 nm)				Aeth σ(633 nm)
AAE range	**N**	**Avg b_{abs} (Mm^{-1})**	**Avg TOT EC (μg/m^3)**	**Avg b_{abs}/ TOT EC (m^2/g)**	**R^2**	**Avg b_{abs}/ (Ec+Fe)**	**R^2**	**Avg b_{abs}/BC (m^2/g)**
<1.1	72	9.61	0.60	16.13	0.373	12.50	0.497	9.04
1.1-1.3	64	9.99	0.69	14.54	0.738	11.78	0.807	7.96
>1.3	63	10.68	0.80	13.37	0.713	12.03	0.746	8.00

AAE Range	**N**	**EC1**	**EC2**	**EC3**	**OC1**	**OC2**	**OC3**	**OC4**	**OP**	**EC**	**OC**
<1.1	72	0.357	0.023	0.001	**0.054**	0.197	0.228	0.149	**0.139**	0.242	0.758
1.1<AAE<1.3	64	0.362	0.018	0.001	**0.080**	0.170	0.230	0.139	**0.116**	0.264	0.736
AAE>1.3	63	0.336	0.012	0.000	**0.120**	0.172	0.231	0.128	**0.088**	0.261	0.739

OC1 is higher and OP is lower when AAE>1.3

Comparison of IMPROVE sampler TOR and TOT abundances for OP and EC, by AAE range.

AAE Range	N	TOR OP	TOT OP	TOR EC	TOT EC
<1.1	72	0.139	0.221	0.242	0.160
1.1<AAE<1.3	64	0.116	0.215	0.264	0.166
AAE>1.3	63	0.088	0.204	0.261	0.145

TOT OP > TOR OP, potentially due to increased charring of organic vapors or liquid particles within the filter as opposed to deposited on the surface

IMPROVE network analysis

- No multi-wavelength b_{abs} available at IMPROVE sites
- At Fresno, high AAE was associated with high abundance of OC1 (average 0.054 for AAE<1.1, 0.08 for AAE=1.1-1.3, 0.12 for AAE>1.3)
- Set criteria for suspected high AAE for IMPROVE network as OC1 abundance>0.08, total carbon >4 $\mu g/m^3$
- Criteria met for 1396/54131 samples (2.6%)
- 10% of samples had OC1/TC>0.08; 4% of samples had TC >4 $\mu g/m^3$
- 67% of samples with TC > 4$\mu g/m^3$ had OC1/TC > 0.08, so about 2/3 of high TC samples, but only 2.6% of all samples met criteria for suspected high AAE
- Look at HIPS b_{abs} to EC ratios for high suspected AAE and other cases

Summary data for expected high and low AAE cases, IMPROVE network 2005-2008. N=52,575 for low expected AAE, 1,396 for high expected AAE.

AAE Range	EC1	EC2	EC3	OC1	OC2	OC3	OC4	OP	EC	OC	b_{abs}	Fe
Conc low µg/m³	0.60	0.08	0.00	0.05	0.30	0.31	0.23	0.37	0.30	1.26	3.96	0.05
Conc high µg/m³	2.70	0.14	0.01	0.98	1.60	1.43	0.79	1.34	1.50	6.14	11.89	0.13
Abund low	0.381	**0.050**	0.001	0.031	0.191	0.199	**0.147**	**0.239**	0.193	0.807		
Abund high	0.353	**0.018**	0.001	0.129	0.209	0.188	**0.103**	**0.175**	0.197	0.803		

Low OP, EC2, OC4 abundances for high expected AAE cases, similar to Fresno analysis

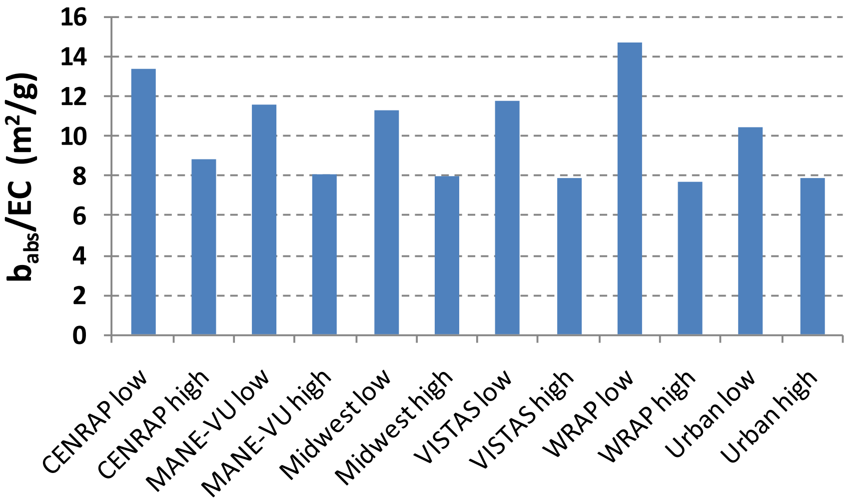
Seasonal average ratios of light absorption to EC and EC+Fe for high and low expected AAE ranges over all IMPROVE sites, 2005-2008

	All	Winter	Spring	Summer	Autumn
Percent high AAE	2.58	3.06	1.23	3.33	2.57
b_{abs}/EC high	7.91	7.68	7.88	8.09	7.99
b_{abs}/EC low	13.11	11.76	13.56	13.89	13.04
b_{abs}/(EC+Fe) high	7.29	7.08	7.20	7.50	7.32
b_{abs}/(EC+Fe) low	11.16	10.77	11.05	11.33	11.38
b_{abs}/EC low/ b_{abs}/EC high	1.66	1.53	1.72	1.72	1.63
b_{abs}/(EC+Fe) low/b_{abs}/(EC+Fe) high	1.53	1.52	1.53	1.51	1.55

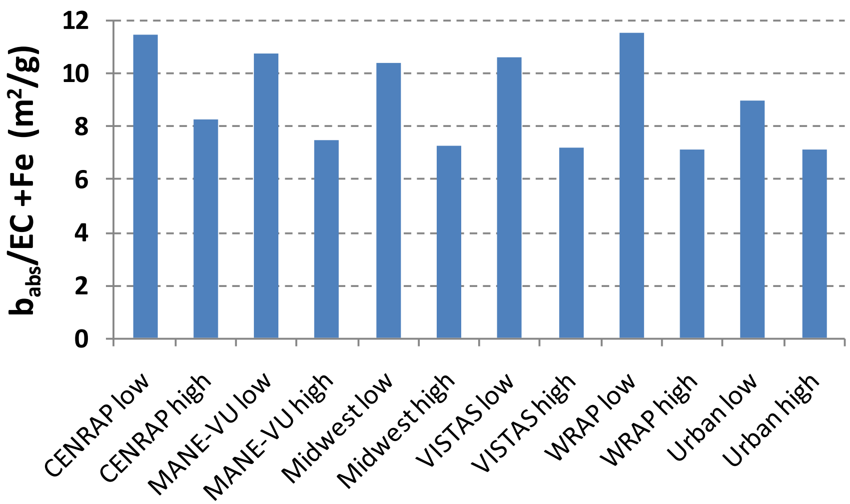
At high suspected AAE, HIPS σ(633 nm)=b_{abs}/EC and b_{abs}/(EC+Fe) lower than for expected low AAE cases, similar to Fresno results. Winter has least affect of including Fe, spring and summer the most effect. Ratio of absorption efficiency for low and high AAE cases shows almost no seasonal variation when including Fe.

Analysis by Regional Planning Organization

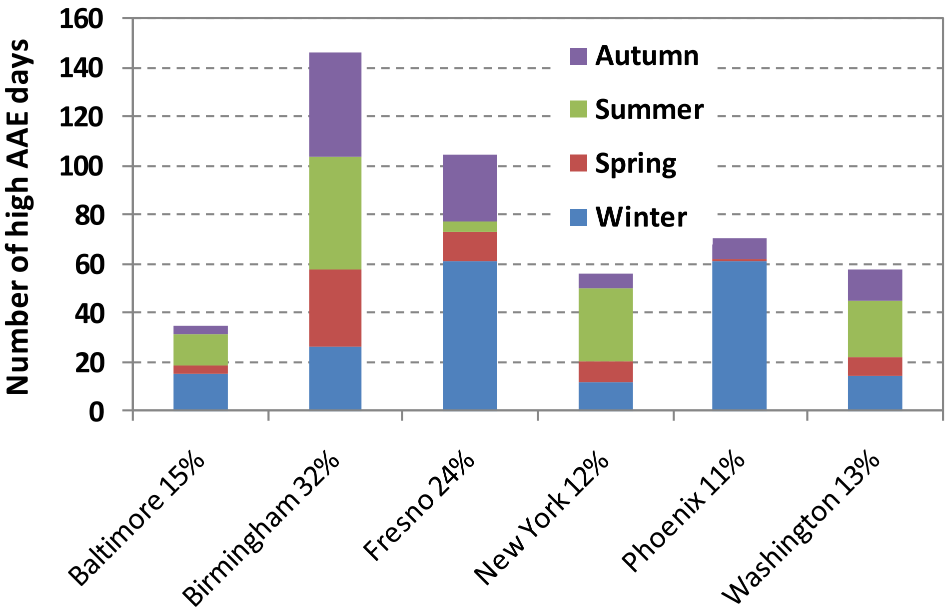
All RPO's experience lower HIPS σ(633 nm) at high suspected AAE, greatest effect for WRAP, least for urban sites (suspect criteria may not work well for urban sites)



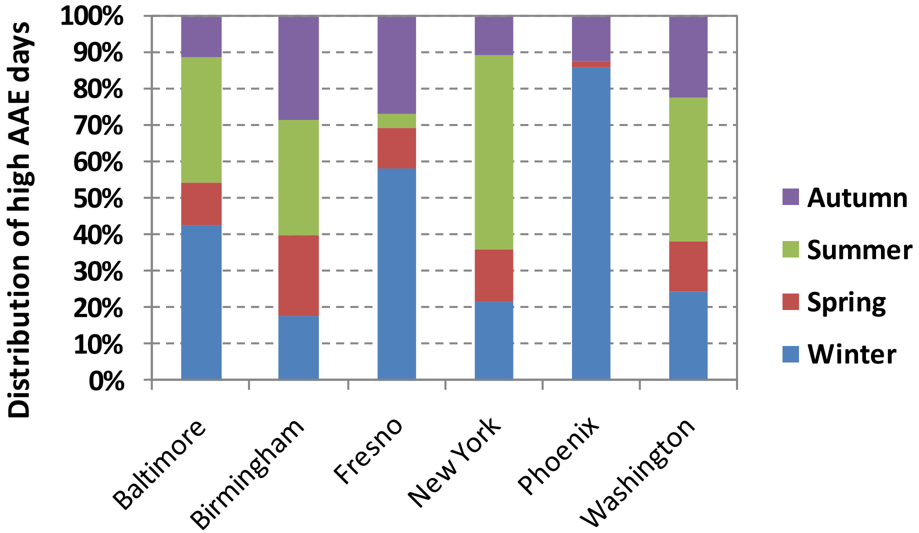
Accounting for Fe partially offsets decreased mass absorption efficiency



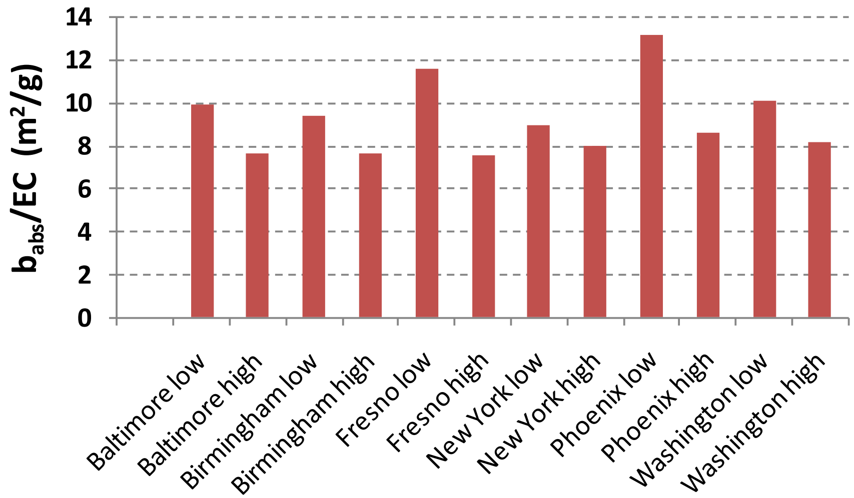
14% of days at urban sites met high AAE criteria, compared to 2.6% at all sites

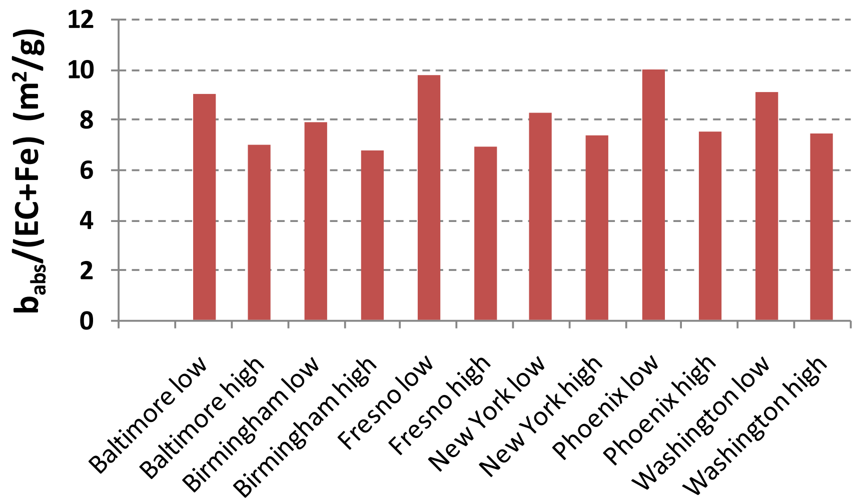


Phoenix and Fresno most high AAE sites in winter; New York, Birmingham, Washington most in summer



Fresno and Phoenix greatest differences in HIPS σ(633 nm) between low and high AAE cases





Observations

- Seven λ aethalometer provides an estimate of deviations from the λ^{-1} assumption.
- AEEs>1.3 are found more frequently in winter at Fresno, consistent with known contributions from residential wood combustion
- σ(633 nm) and σ(880 nm) lower for AAE>1.3 than for AAE <1.3 for IMPROVE_A TOR EC
- IMPROVE_A TOT EC does not show a decrease in σ(633 nm) or σ(880 nm) at AAE>1.3, possibly due to dominance of the pyrolysis correction by graphitic carbon formation within the filter rather than the surface deposit
- OC1 is higher for AAE>1.3 in the IMPROVE data base. OC1 may be a good indicator of higher AAE and associated sources (e.g. biomass burning)

Recommendations

- Obtain multi-wavelength transmittance and reflectance measurements on IMPROVE filters with high and low OC1 to evaluate relationship
- Create a multi-wavelength capability in the carbon analyzer and examine the extent to which $\sigma(\lambda)$ changes during analysis
- Determine the extent to which the OC/EC split might be related to the λ used to determine the split for samples from biomass smoldering, biomass flaming, and other sources