

Workshop on black carbon

# **Research Progress of Black Carbon Geochemistry – Soot and char in the environment**

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# What's black carbon?

“Combustion derived black particulate carbon having a graphitic microstructure” by atmospheric scientist of Novakov (1982);  
“Charcoals from biomass burning and soot from fossil fuel and wood combustion” by Goldberg (1985).

Thereafter, the soil and sediment sciences focus mainly on the refractiveness of BC. They followed the Goldberg's definition and clarified that there are two formation pathways for BC (Kulbusch et al., 1997; Hedges, 2000; Masiello, 2004, Hammes et al., 2007): the combustion residues by pyrolysis and the combustion condensates in flames via gas-to-particle conversion.

In atmospheric science, people cared more about the light-absorbing property of BC and assertively defined it as soot carbon.

# Classifying carbon in atmospheric science

Terms describing carbonaceous aerosol including BC are defined according to the methods they measured. No any considerations are given to how they are formed and what they are.

*Thermochemical  
classification*

*Molecular structure*

*Optical  
classification*

<b>Elemental carbon (EC)</b>	<b>Graphene layers</b>	<b>Black carbon (BC)</b>
<b>Refractory organics</b>	<b>Polycyclic aromatics, Humic-like substances, biopolymers</b>	<b>Colored organics</b>
<b>Non-refractory organics (OC)</b>	<b>Low-MW hydrocarbons</b>	<b>Colorless organics (OC)</b>

Light Absorbing Carbon

# Recent definition in atmospheric science

## 2.1. What Is Black Carbon?

[52] Black carbon is a distinct type of carbonaceous material, formed only in flames during combustion of carbon-based fuels. It is distinguishable from other forms of carbon and carbon compounds contained in atmospheric aerosol because it has a unique combination of the following physical properties:

[53] 1. It *strongly absorbs visible light* with a mass absorption cross section of at least  $5 \text{ m}^2\text{g}^{-1}$  at a wavelength of 550 nm.

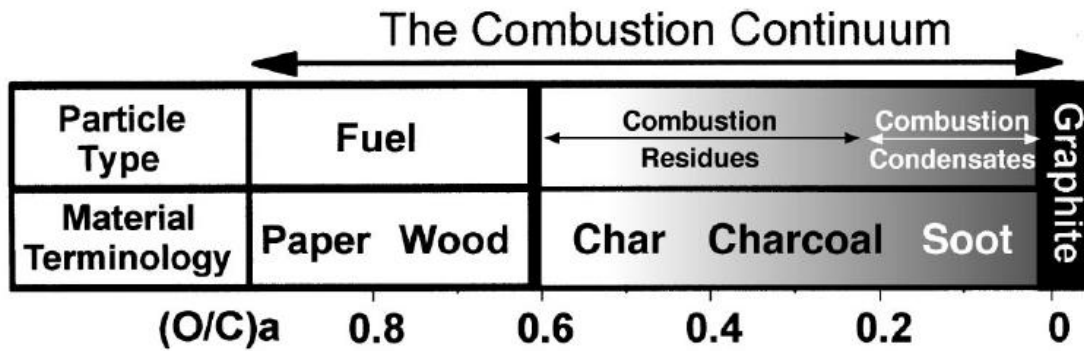
[54] 2. It is *refractory*; that is, it retains its basic form at very high temperatures, with a vaporization temperature near 4000K.

[55] 3. It is *insoluble* in water, in organic solvents including methanol and acetone, and in other components of atmospheric aerosol.

[56] 4. It exists as an *aggregate* of small carbon spherules.

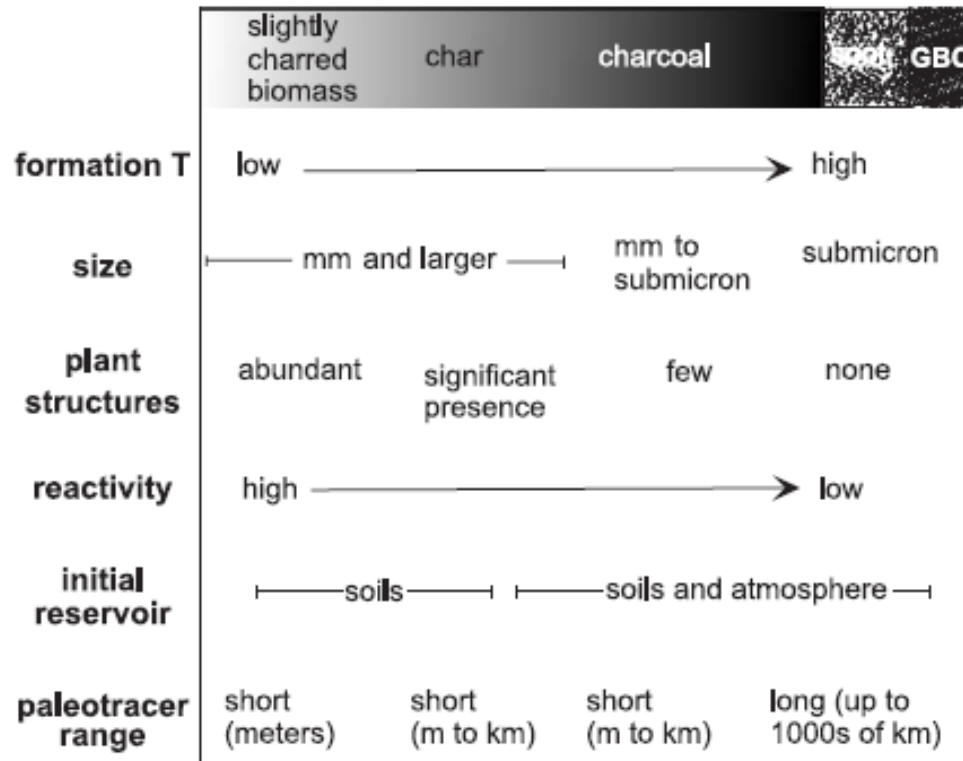
[57] The strong absorption of visible light at all visible wavelengths by black carbon is the distinguishing characteristic that has raised interest in studies of atmospheric radiative transfer. No other substance with such strong light absorption per unit mass is present in the atmosphere in significant quantities. BC has very low chemical reactivity in the atmosphere; its primary removal process is wet or dry deposition to the surface. BC is generally found in atmospheric aerosol particles containing a number of other materials, many of which are co-emitted with BC from a variety of sources.

The definition is much clearer, However, is it practical?  
**Doubtful**



Hedges, 2000

Fig. 3. The combustion continuum of black carbon (from Jones and Chaloner, 1991; Goldberg, 1985). Increased heating and chemical reformation yields a spectrum of progressively carbon-rich and refractory organic materials. (O/C)<sub>a</sub> indicates typical atomic ratios of oxygen to carbon in the various black carbon types.



**In soil and sediment studies, BC was considered as the refractory part of the combustion continuum, and it separates BC into two subtypes, the combustion residues and the combustion condensates, based on their formation pathways. However, there was still no method to differentiate between them.**

Fig. 1. The black carbon combustion continuum.

Masiello, 2004

# We follow the definition from soil and sediment science that two subtypes, char and soot, exist with different formation pathways

**Soot** are submicron particles ( $< 1 \mu\text{m}$ ) formed from the condensation of hydrocarbon radicals at high temperature ( $>600^\circ\text{C}$ ) **via gas-to-particle conversion**.

**Char** is combustion residues by **pyrolysis**, retaining the morphology of their source material, and than soot.

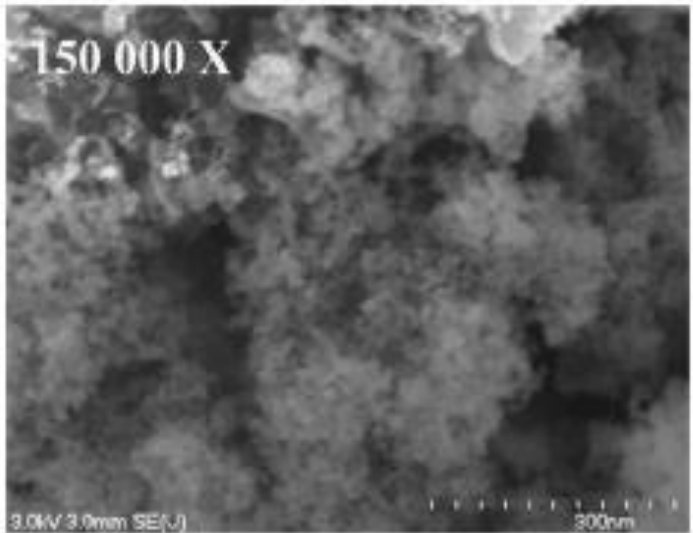
Atomic Ratio						
H/C	1.7	1.3	1.0	0.6	0.3	0.0
O/C	1.0	0.8	0.6	0.4	0.2	0.0

Sediments	(Nonrefractory) Organic carbon (OC)	(Refractory) Organic carbon (OC)	Combustion residues Char (Microscope measured Charcoal)	Combustion Condensates Soot	Graphite
	Low-Molecular-Mass Hydrocarbons and Derivatives (Colorless) Organic carbon (OC)	Polycyclic aromatics, Humic and humic-like Substances, Biopolymers, etc (Colored) Brown Carbon (BrC)	Highly Polymerized and aromatic	Graphene layers (graphitic or turbostratic)	
Molecular Structures					
Aerosol			Combustion residues Char	Combustion Condensates Soot	Graphite

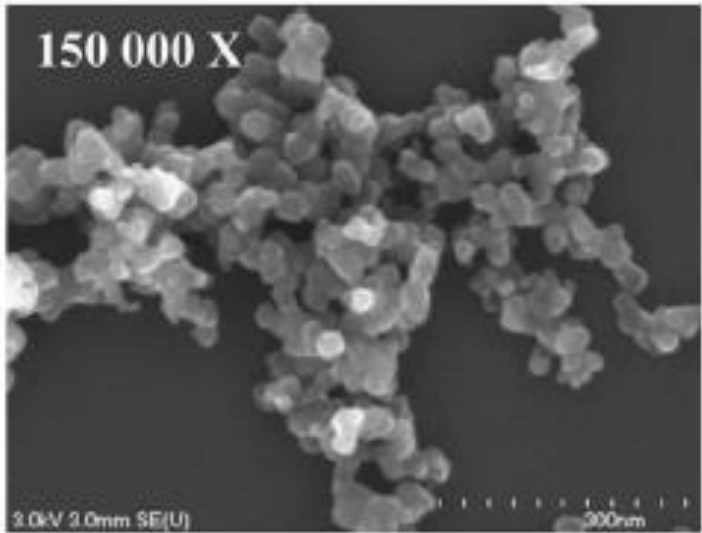
Optical Absorption Non Spectral dependence Uniform

Han et al., 2007a, Chemosphere; Zhang, Han et al., 2014, Springer book

# Morphological characteristics for char and soot suggests that they are different materials with similar origin (combustion)

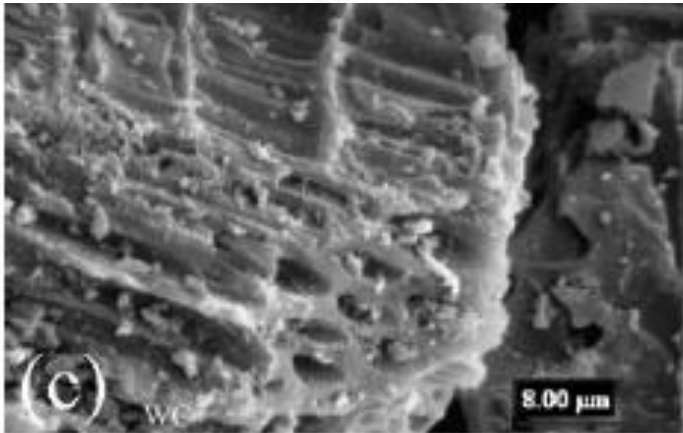


(c)

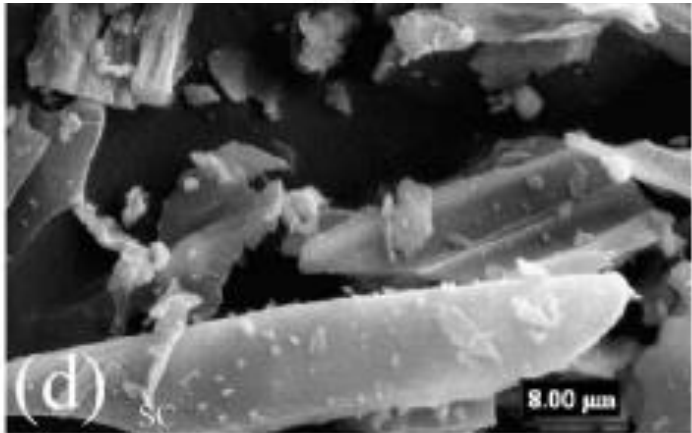


(d)

Soot



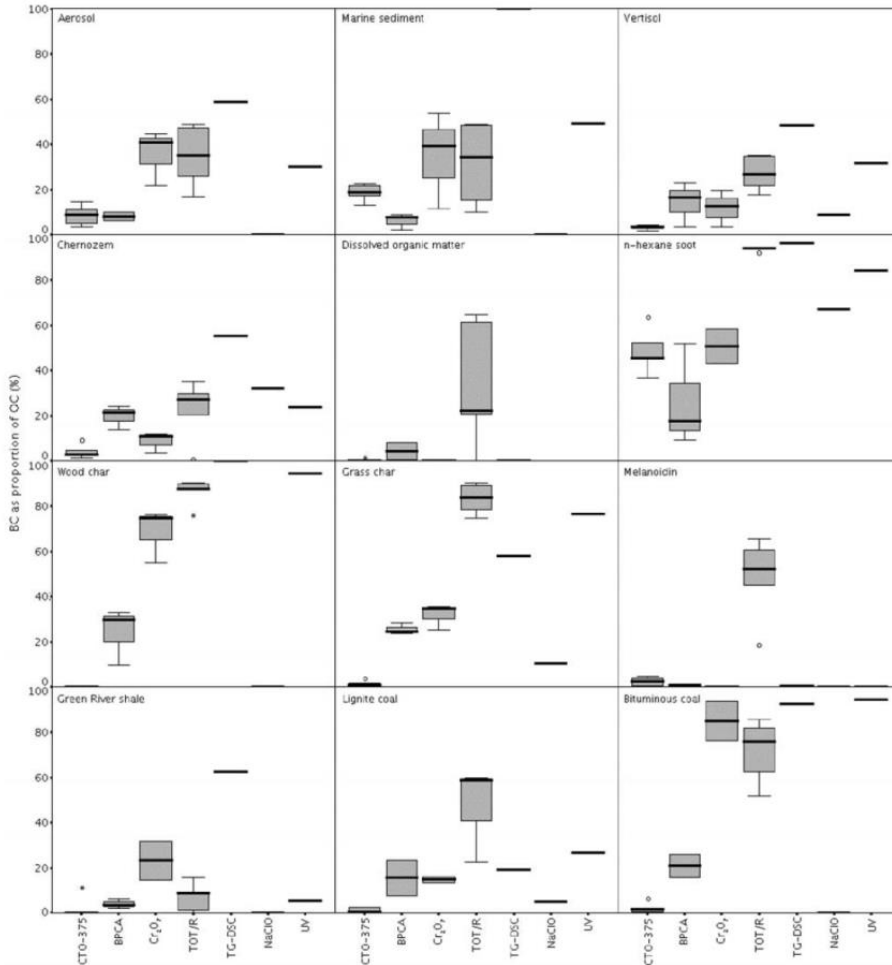
(c)



(d)

Char

# There is no universally accepted method for BC quantification. Great differences exist among the different methods (and protocols).



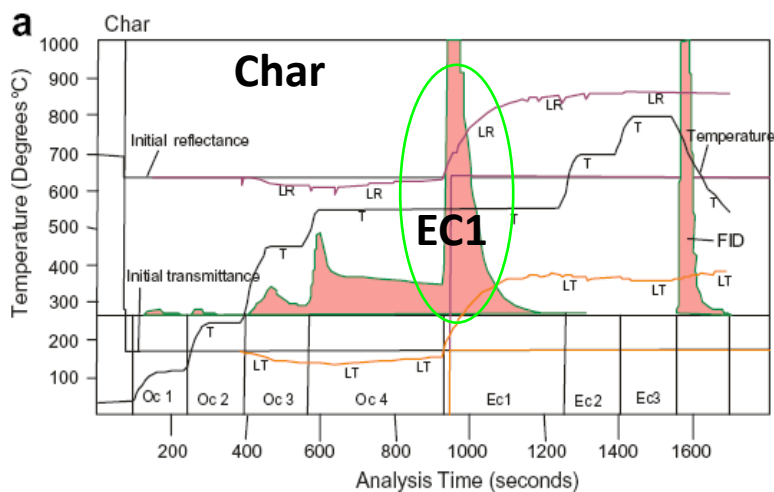
It is suggested that the different methods may measure different fractions of BC. However they are all called BC.

Thus, the careless use of the term BC and no differentiation between and soot often lead to confusion and sometimes infer wrong properties. It is, I think, very important for discrimination between char and soot in the environment.

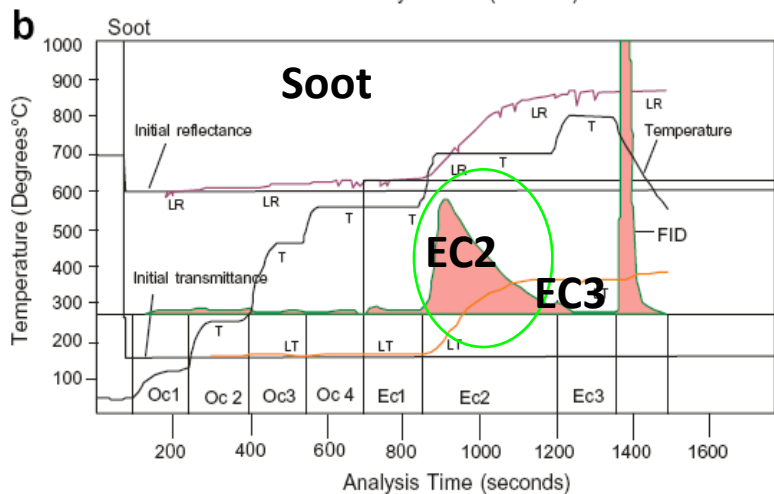
Differences among the different methods (Hammes, 2007)



# We tried to find an existing method that can be extended to discriminate between char and soot



Char and soot reference materials evolve in different elemental carbon fractions in the IMPROVE protocols because of their different refractiveness



Example thermograms for char and soot using the IMPROVE TOR method

- A) Char evolves at the EC1 oxidation step ;
- B) Soot with the single peak at EC2;
- C) Carbon black, with the peaks mainly from EC2 and EC3 with negligible EC1.

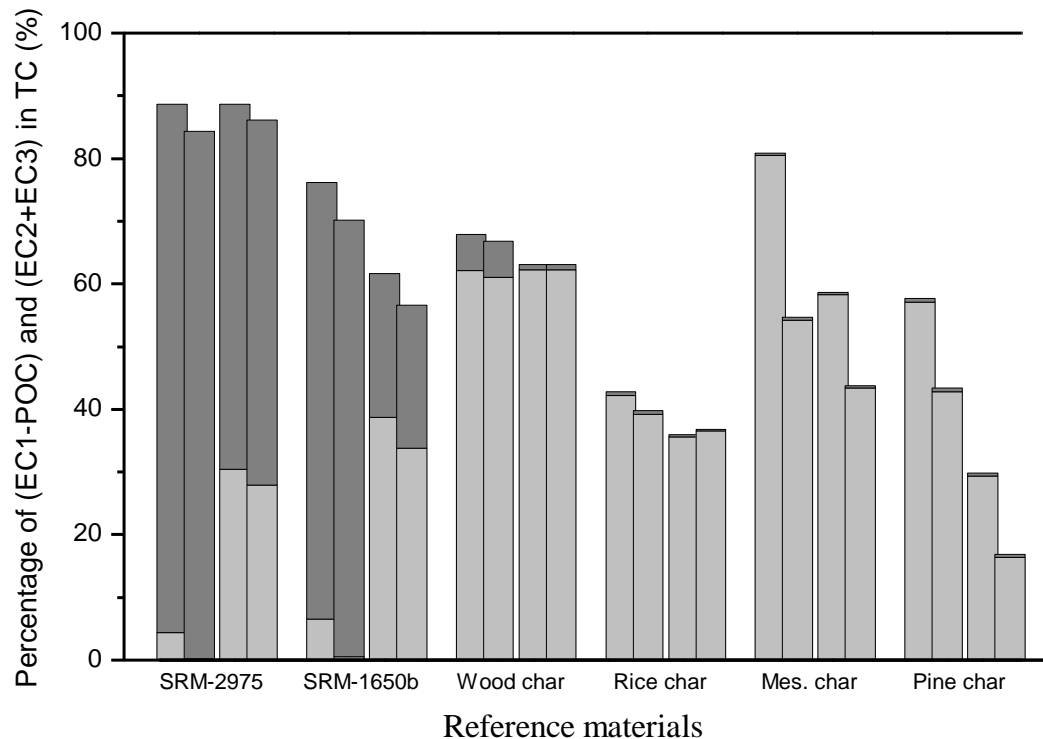
Thermograms for the char and soot reference materials

# Test of the evolution of char and soot reference materials under the different peak-inert temperatures using the IMPROVE protocol

Sample ID	ECT <sup>2</sup>					EC1-POC (T) <sup>2</sup>					EC2+EC3				
	480 <sup>1</sup>	520 <sup>1</sup>	550 <sup>1</sup>	580 <sup>1</sup>	610 <sup>1</sup>	480	520	550	580	610	480	520	550	580	610
SRM-2975	70.0±5	84.7±6	84.4±4.9	86.2±3	74.4±3	-19.6±5	-4.4±3	0.2±4	28.0±20	60.8±4	89.5±1	89.1±4	84.2±1	58.2±18	13.6±2
SRM-1650b	40.2±11	58.0±2	69.2±0.7	56.7±6	63.0±6	-33.7±12	-13.9±2	0.6±3	33.8±17	53.9±2	74.0±1	71.9±0	69.6±1	22.9±25	9.2±4
Wood char	70.7±3	69.7±13	66.9±6	63.1±10	61.5±8	13.7±2	42.9±10	61.1±5	62.3±9	61.5±8	57.0±4	26.7±3	5.8±1	0.8±1	0.0±0
Rice char	49.8±3	43.4±9	39.8±8.1	37.0±7	29.0±1	48.2±9	42.4±9	39.3±8	36.6±7	28.4±1	1.6±0	0.9±0	0.5±0	0.3±0	0.5±0
Mes. char	65.7±5	60.2±3	54.7±1.2	43.7±6	35.1±9	60.2±4	59.4±3	54.3±1	43.4±6	34.7±9	5.5±2	0.8±0	0.4±0	0.4±0	0.4±0
Pine char	53.7±3	47.2±7	41.5±5.6	16.9±4	17.3±4	53.1±3	46.9±7	42.8±5	16.4±4	16.7±4	0.6±0	0.3±0	0.6±0	0.5±0	0.6±0
Sample ID	ECR <sup>2</sup>					EC1-POC (R) <sup>2</sup>					EC2+EC3				
	480	520	550	580	610	480	520	550	580	610	480	520	550	580	610
SRM-2975	90.6±5	93.8±8	88.7±4	88.7±1	79.1±7	1.2±4	4.7±3	4.5±3	30.5±18	65.6±8	89.5±1	89.1±4	84.2±1	58.2±18	13.6±2
SRM-1650b	49.5±9	71.3±4	76.2±0	61.6±6	69.0±6	-24.4±21	0.6±4	6.6±2	38.8±20	59.8±5	74.0±1	71.9±0	69.6±1	22.9±25	9.2±4
Wood char	78.9±8	72.5±20	68.1±15	63.1±18	66.8±17	21.8±5	45.8±17	62.2±8	62.3±18	66.8±17	57.0±4	26.7±3	5.8±1	0.8±1	0.0±0
Rice char	57.3±7	49.2±12	42.8±8	36.1±6	27.9±6	55.7±7	48.2±12	42.3±8	35.7±6	27.3±6	1.6±0	0.9±0	0.5±0	0.3±0	0.5±0
Mes. Char	80.2±6	77.9±5	80.9±3	58.6±2	37.2±21	74.7±5	77.2±5	80.5±2	58.3±2	36.8±21	5.5±2	0.8±0	0.4±0	0.4±0	0.4±0
Pine char	79.0±4	67.2±7	57.6±2	29.9±8	23.7±8	78.3±4	66.9±7	57.1±1	29.4±8	23.1±8	0.6±0	0.3±0	0.6±0	0.5±0	0.6±0

Percentages of the EC carbon fractions in total carbon (TC) in the different standard reference material (SRM) samples used in this study

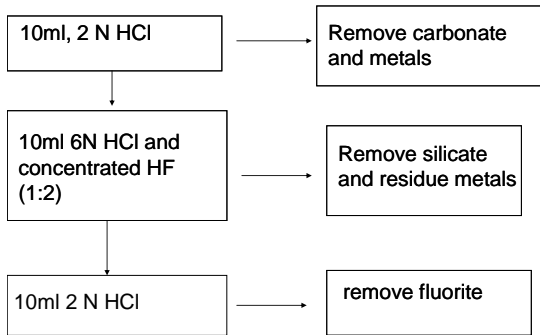
# We proposed the IMPROVE protocol for differentiating between char and soot at the peak-inert temperature of 550 °C using the transmittance correction



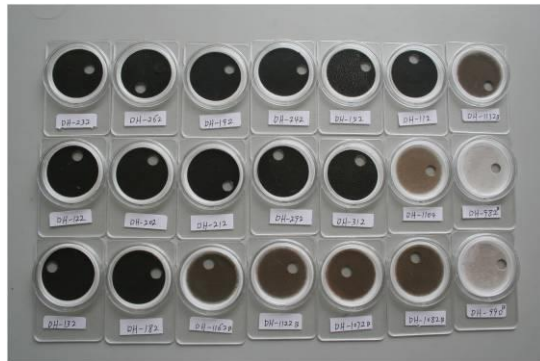
Char and soot are also operationally defined:  
Char = EC1 – POC  
soot = EC2+EC3

Comparison of the percentage of char (EC1-POC, in grey) and soot (EC2+EC3, in dark) and EC (the sum of char and soot) in standard reference materials (SRMs) measured with the IMPROVE TOR and TOT methods at 550°C and 580°C, respectively. From left to right, the four corresponding protocols used for each SRM were TOR at 550°C, TOT at 550°C, TOR at 580°C, and TOT at 580°C.

# Extension of the IMPROVE protocol for the measurement of BC in soils and sediments after chemical pretreatment



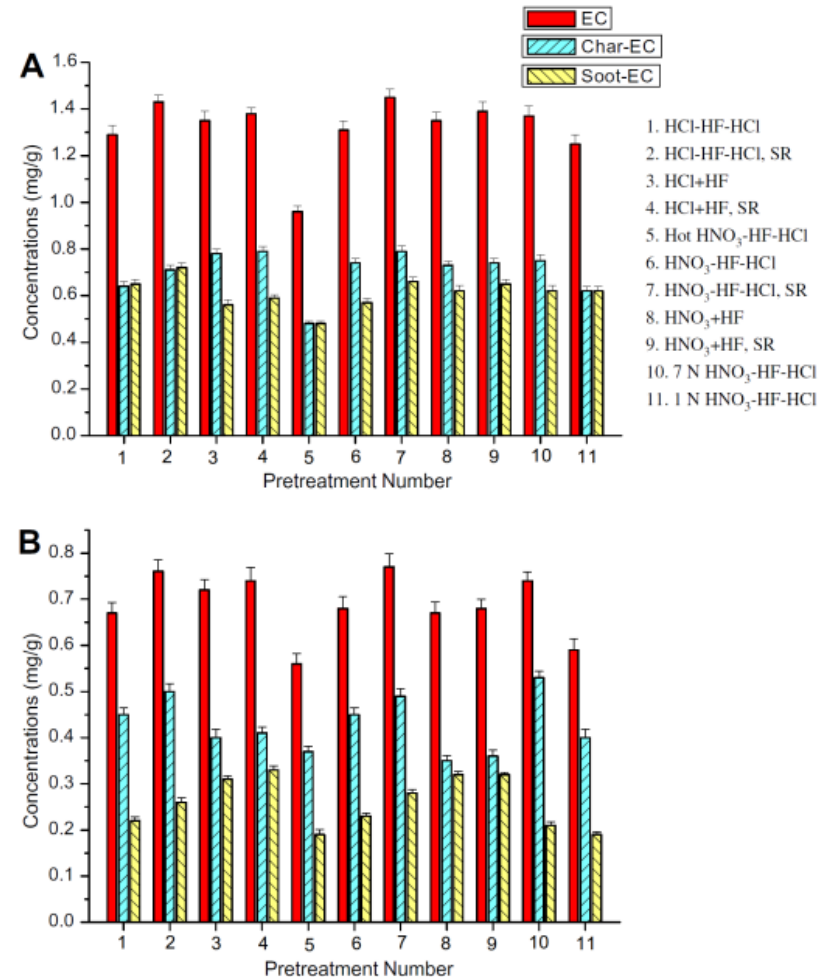
Pretreatment



Filtered samples



Quantification



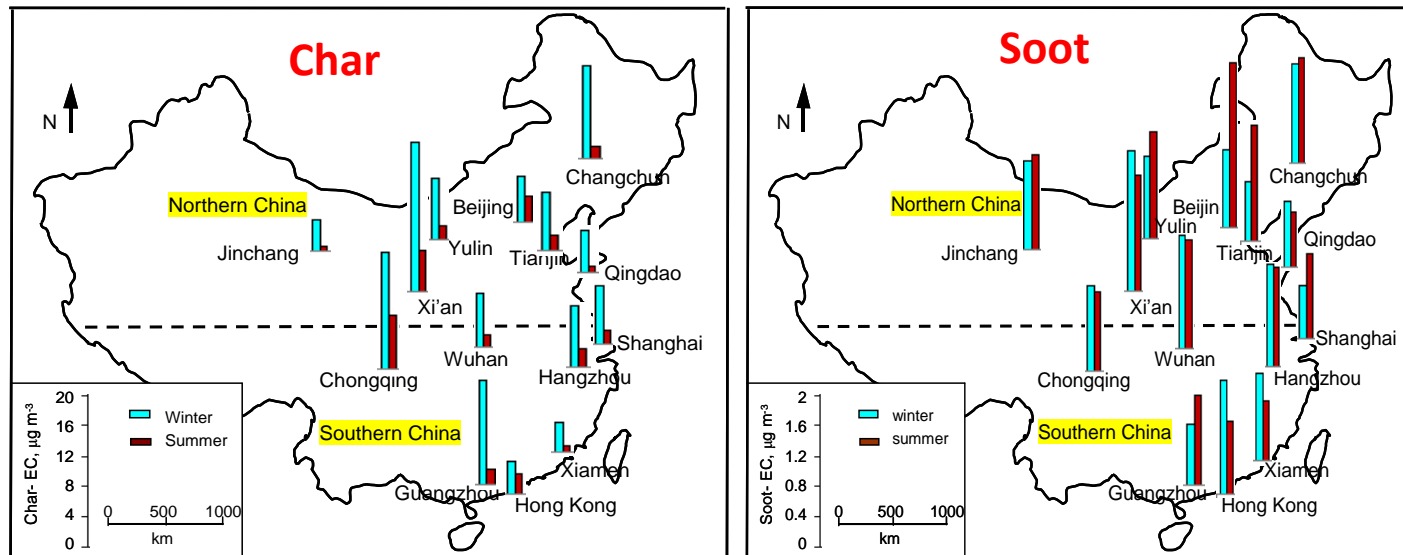
Comparison of BC, char, and soot concentrations with different acids pretreatment

*Han et al., 2007b, Chemosphere; 2011, ES&T*

# Char and soot in PM<sub>2.5</sub> have different distribution characteristics

Char concentrations are different in different cities;

Soot concentrations are almost similar in different cities



Char and soot in 14 Chinese cities during the winter and summer seasons

**Implications: char and soot have different transport pathways. Char is of local sources, while soot is of regional transport. The local pollution control may be useful for char materials, while soot reduction needs a regional activities from different regions**

# A paired observational study from the urban, sub-urban and rural sites in North America confirms that soot is of regional transport and char is more local

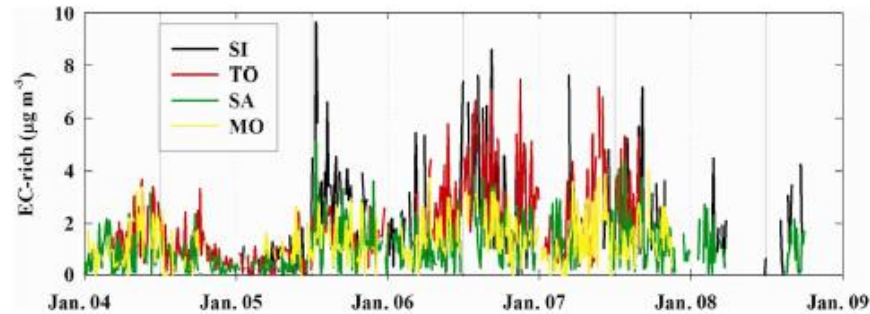
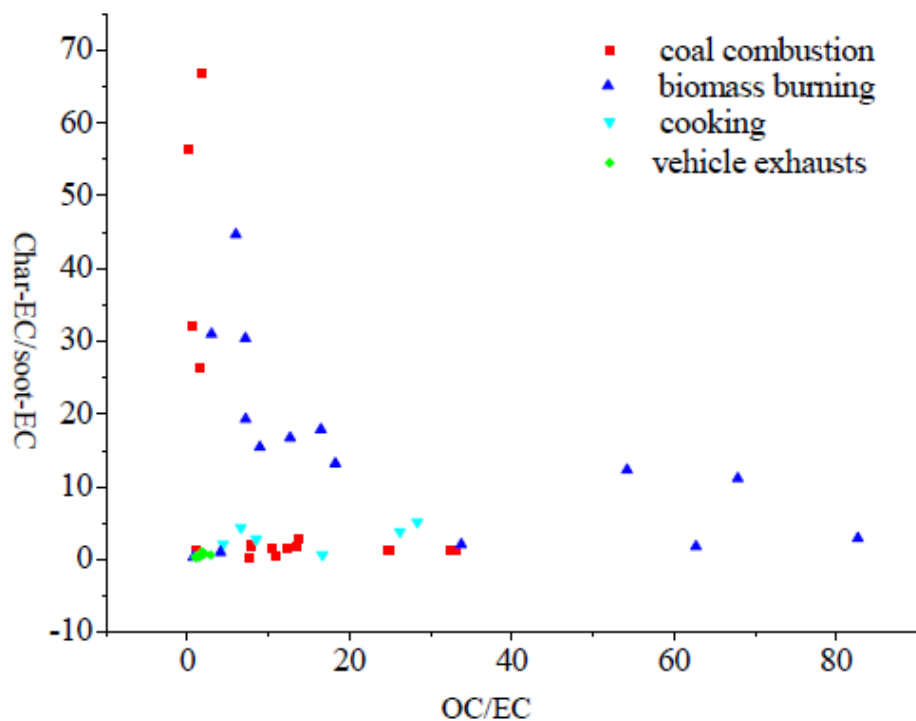


Figure 3. Temporal variations of the EC-rich factor at the Simcoe (SI), Toronto (TO), St. A (SA), and Montreal (MO) sites.

statistically significant difference according to a paired  $t$  test ( $p < 0.05$ ). The EC1 fraction (or char-EC) was considerably higher at the urban areas, reflecting the influence of local combustion emissions on the increase of char-EC at the urban sites.<sup>15</sup> However, the EC2 and EC3 fractions (or soot-EC) accounted for ~89% in Simcoe, ~85% in St. Anicet, ~70% in Toronto, ~60% in Montreal of the total EC mass concentration. Interestingly, the average concentrations of EC2 were similar at all the sites and there was no statistical difference between the two furthest sites, rural Simcoe and urban Montreal. The strong temporal correlation of EC2 concentrations among the four sites suggests that a similar regional source was impacting everywhere (SI Figure S4). The concentrations of EC2 showed a similar temporal pattern for all sites, with high concentrations in summer (June–September) and low concentrations in winter (December–March) (SI Figure S5). In contrast, the lowest concentrations of char-EC were in summer with higher concentrations in the urban as compared to rural areas. The increased soot-EC in summer is

**We also found that char and soot have different dominant sources. For example, biomass burning emits more char, while vehicle exhausts give more soot. Char/soot ratios were suggested to be an indicator for source identification in aerosol studies**



Char/soot ratios from different sources in the literature

*Han et al., 2010, Atmos. Chem. Phys.*

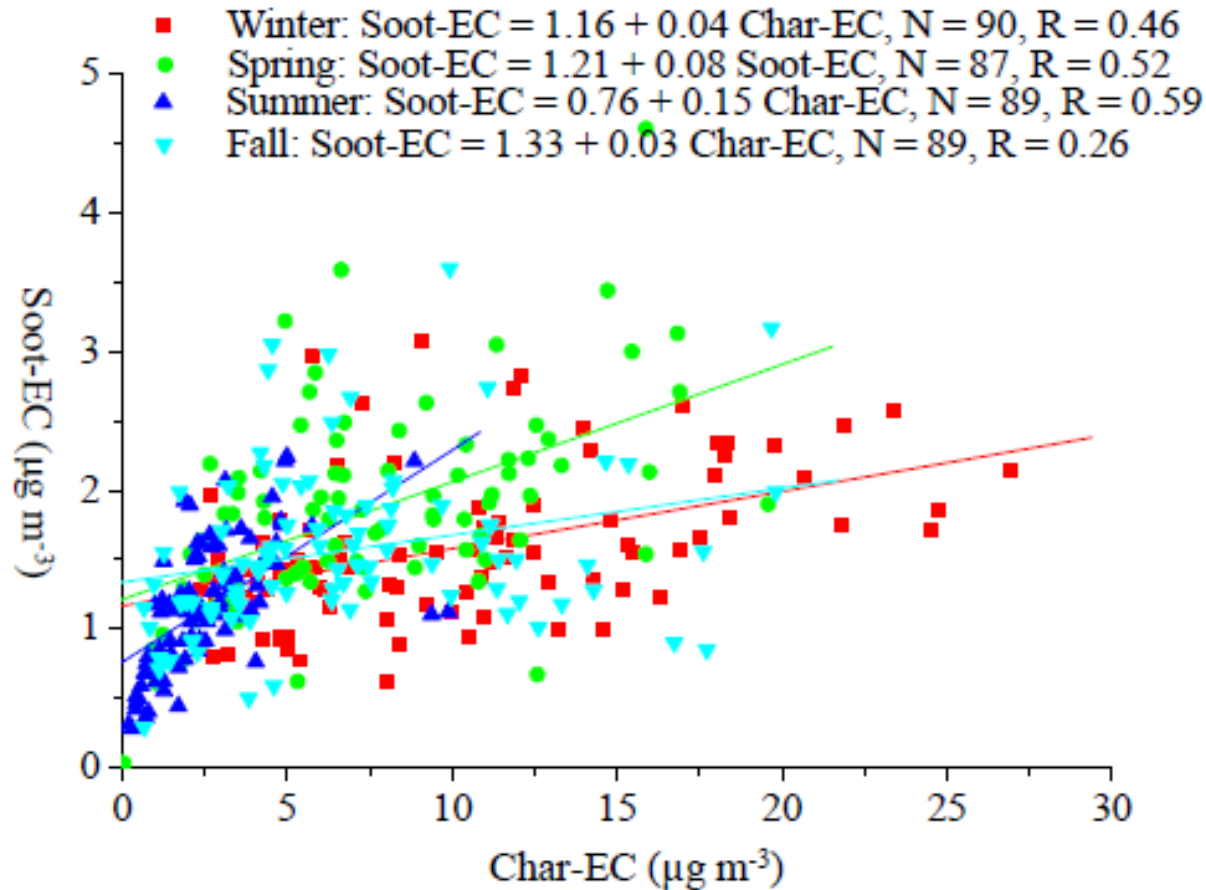
Contents lists available at SciVerse ScienceDirect  
 Atmospheric Environment  
 ELSEVIER  
**Chuang et al., AE, 2012**  
 ATMOSPHERIC ENVIRONMENT

Characterization of aerosol chemical properties from near-source biomass burning in the northern Indochina during 7-SEAS/Dongsha experiment  
 Ming-Tung Chuang<sup>a</sup>, Charles C.-K. Chou<sup>b</sup>, Khajornsak Sopajareepom<sup>c</sup>, Neng-Huei Lin<sup>d</sup>, Jia-Lin Wang<sup>e</sup>, Guey-Rong Sheu<sup>c</sup>, You-Jia Chang<sup>a</sup>, Chung-Te Lee<sup>a,\*</sup>

Several studies have pointed out that the ratio of char-EC (EC1-OP) to soot-EC (the sum of EC2 and EC3, EC2 + EC3) in PM<sub>2.5</sub> is useful in identifying the sources of carbonaceous aerosols (Han et al., 2007, 2009). The reason is that char-EC is formed under lower combustion temperatures such as BB activities, whereas soot-EC is formed under higher combustion temperatures, such as coal combustion and internal engine combustion (Zhu et al., 2010). Chow et al. (2004) and Chen et al. (2007) reported that the char-EC to soot-EC ratio could reach as high as 20 for BB and less than 2.0 for coal combustion and vehicle exhaust. In the present study, the char-EC to soot-EC ratio is  $9.4 \pm 3.8$  for PM<sub>2.5</sub> (Fig. 6), similar to the value of 11.6 from BB sources (Cao et al., 2005). For PM<sub>10-2.5</sub>, the char-EC to soot-EC values vary greatly from 0.7 to 13.7 because the amounts of char-EC and soot-EC in PM<sub>10-2.5</sub> are very low and variable (char-EC:  $0.07 \pm 0.05 \mu\text{g m}^{-3}$ ; soot-EC: 0.02–0.15  $\mu\text{g m}^{-3}$ ).



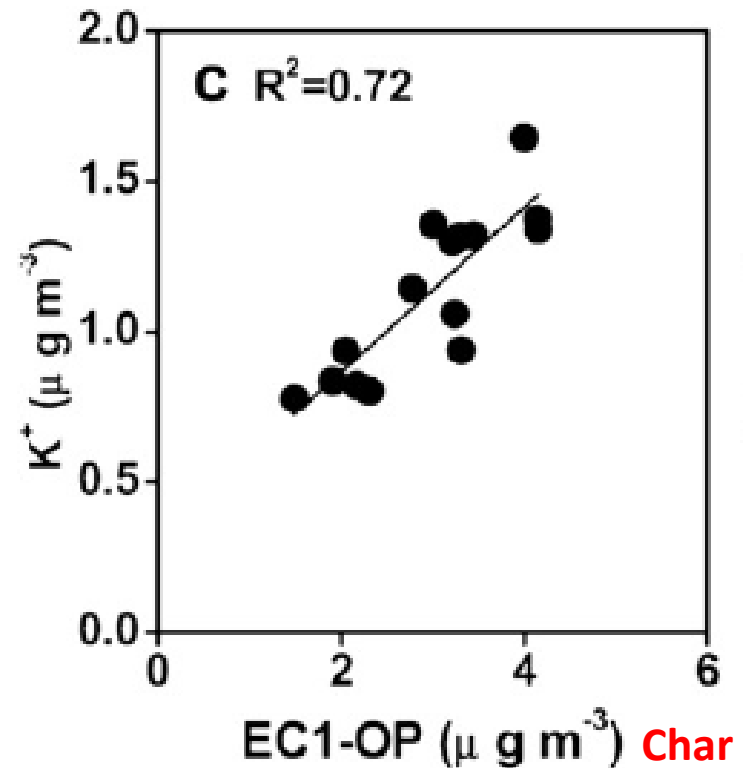
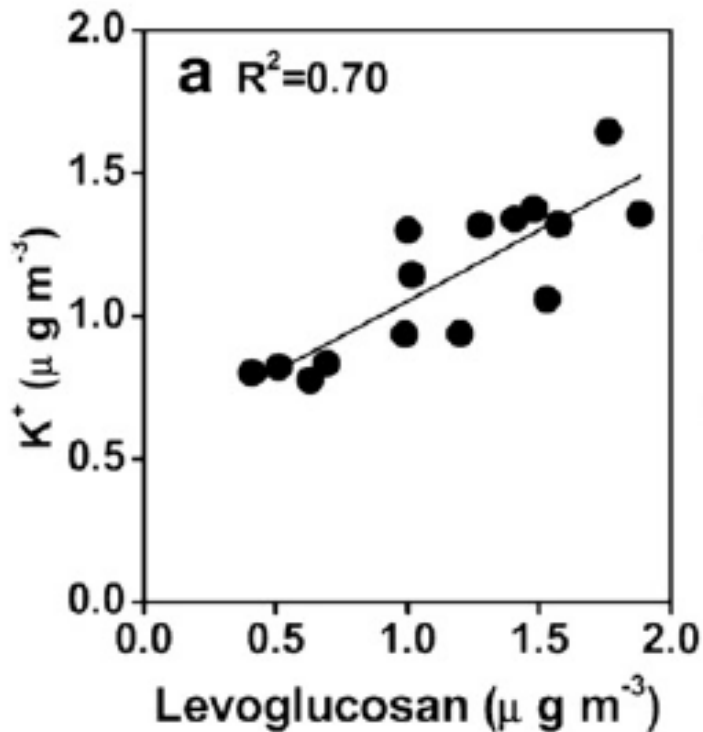
# The lower slopes of PM<sub>2.5</sub> soot to char correlations in winter and fall seasons are in good agreement with the increase in biomass burning and coal combustion contributions



Char and soot correlations in different seasons in Daihai, a rural region



**Good correlation between char and potassium ion, an indicator of biomass burning, further confirms the main source of char from biomass burning in rural areas**



# The long-term trend of PM<sub>2.5</sub> char and soot aerosol variations: the decrease in BC and char concentrations and the increase in soot concentrations

From 2004 to 2013:

BC decreased from 8.3 to 5.6  $\mu\text{g m}^{-3}$

Char decreased from 6.8 to 3.8  $\mu\text{g m}^{-3}$

While soot increased from 1.5 to 1.8  $\mu\text{g m}^{-3}$

This trend is related to the decrease in the emissions of biomass burning and coal combustion, while the vehicle emissions increased.

	IMPROVE				
	Min.	Max.	Average	SD	CV
TC $\mu\text{g m}^{-3}$	10.04	84.20	26.79	14.60	0.54
TOR OC $\mu\text{g m}^{-3}$	7.11	51.99	17.52	9.08	0.52
TOR POC $\mu\text{g}/\text{m}^3$	1.13	19.28	4.85	3.80	0.78
TOR EC $\mu\text{g m}^{-3}$	2.93	32.21	9.27	5.72	0.62
TOR OC/EC	1.36	3.66	2.04	0.48	0.24
TOT POC $\mu\text{g}/\text{m}^3$	2.36	34.21	8.49	6.15	0.72
TOT OC $\mu\text{g m}^{-3}$	8.58	66.92	21.16	11.47	0.54
TOT EC $\mu\text{g m}^{-3}$	1.45	17.28	5.62	3.32	0.59
TOT OC/EC	2.28	6.74	4.06	0.97	0.24
TOR Char $\mu\text{g m}^{-3}$	1.41	30.22	7.45	5.68	0.76
TOT Char $\mu\text{g m}^{-3}$	-0.07	15.29	3.81	3.25	0.853
Soot $\mu\text{g m}^{-3}$	0.62	3.50	1.82	0.60	0.33
TOR Char/soot	0.92	15.23	4.55	3.67	0.81
TOT Char/soot	-0.05	7.84	2.31	2.04	0.88

Table 1. Seasonal variations of mass, total carbon (TC), organic carbon (OC), elemental carbon (EC), OC/EC, char-EC, soot-EC, and char-EC/soot-EC.

Seasons	Concentrations	Mass $\mu\text{g m}^{-3}$	TC $\mu\text{g m}^{-3}$	OC $\mu\text{g m}^{-3}$	EC $\mu\text{g m}^{-3}$	OC/EC	Char-EC $\mu\text{g m}^{-3}$	Soot-EC $\mu\text{g m}^{-3}$	Char-EC/soot-EC
Winter (n = 90)	Min	59.20	14.52	10.45	3.56	2.56	2.39	0.62	1.37
	Max	651.26	217.00	192.66	29.09	9.72	26.95	3.08	14.71
	Average	235.41	74.05	61.96	12.08	5.35	10.49	1.60	6.69
	SD <sup>3</sup>	125.14	40.01	34.94	6.22	1.71	5.95	0.54	3.31
Spring (n = 87)	Min	28.40	4.66	4.18	0.42	2.04	0.19	0.23	1.08
	Max	404.48	120.35	98.87	21.48	9.89	19.58	4.61	18.92
	Average	152.14	38.04	28.67	9.37	3.27	7.52	1.85	4.14
	SD	72.76	20.48	16.10	4.86	1.11	4.44	0.72	2.61
Summer (n = 89)	Min	29.23	6.26	5.67	0.51	1.92	0.20	0.28	0.63
	Max	217.30	56.68	46.20	11.07	11.67	9.88	2.24	8.82
	Average	105.49	19.58	15.86	3.72	5.13	2.57	1.15	2.17
	SD	38.34	8.41	6.71	2.13	2.31	1.82	0.47	1.30
Fall (n = 88)	Min	28.94	5.43	4.47	0.97	2.61	0.66	0.29	0.57
	Max	627.14	145.27	123.47	22.85	8.79	19.81	3.60	20.77
	Average	179.70	47.05	38.62	8.43	4.62	6.85	1.58	4.62
	SD	115.56	30.17	25.80	4.79	1.21	4.60	0.59	3.62
Whole year	Average	178.54	44.79	36.39	8.41	4.61	6.86	1.54	4.41
	SD	113.83	33.75	28.90	5.61	1.84	5.28	0.64	3.27

西安市2004年黑碳、焦炭、烟炱浓度

西安市2013年黑碳、焦炭、烟炱浓度

# We proposed that char and soot have different light-absorbing properties

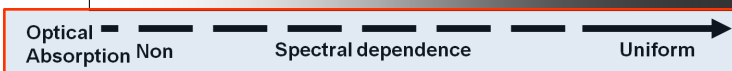
rials (Lim and Cachier, 1996). Soot has a distinctive physical morphology (Goldberg, 1985) and is composed of sub-micron particles of grape-like clusters. Although char is also light-absorbing (Bond et al., 2002; Andreae and Gelencsér, 2006), its light-absorption property is weak and has a strong spectral dependence, tending to absorb strongly in the UV spectrum (Bond, 2001; Bond et al., 2002; Kirchstetter et al., 2004, Lewis et al., 2008). Soot exhibits strong light absorption characteristics with little spectral dependence (Schnaiter et al., 2003; Kirchstetter et al., 2004). The differentiation between char and soot in the environment would help us better understand their environmental and climatic impacts.



The light-absorbing capacity of char is weak and it is of strong spectral dependence, tending to absorb strongly in the UV spectrum; while soot has strong light-absorbing characteristics with little spectral dependence.

Atomic Ratio						
H/C	1.7	1.3	1.0	0.6	0.3	0.0
O/C	1.0	0.8	0.6	0.4	0.2	0.0

	(Nonrefractory) Organic carbon (OC)	(Refractory) Organic carbon (OC)	Combustion residues Char (Microscope measured Charcoal)	Combustion Condensates Soot	Graphite
<b>Sediments</b>					
<b>Molecular Structures</b>	Low-Molecular-Mass Hydrocarbons and Derivatives (Colorless) Organic carbon (OC)	Polycyclic aromatics, Humic and humic-like Substances, Biopolymers, etc	Highly Polymerized and aromatic	Graphene layers (graphitic or turbostratic)	
<b>Aerosol</b>		(Colored) Brown Carbon (BrC)	Combustion residues Char	Combustion Condensates Soot	Graphite



**Jeong et al. (2013,ES&T) confirms that the soot-dominated aerosols have a higher positive direct radiative forcing than other aerosols**

**Table 2. Light Extinction Coefficients and Direct Radiative forcing for PMF-Resolved Sources<sup>a</sup>**

factor	$b_{\text{ext}}$ ( $\text{Mm}^{-1}$ )	$b_{\text{abs}}$ ( $\text{Mm}^{-1}$ )	$b_{\text{sca}}$ ( $\text{Mm}^{-1}$ )	direct radiative forcing ( $\text{W m}^{-2}$ )
EC-rich	9.3	3.0	6.2	0.2
secondary sulfate	19.2	0.4	12.9	-0.8
secondary nitrate	13.3	0.4	12.9	-0.5
biomass burning	0.5	0.1	0.4	0
total $\text{PM}_{2.5}$	52.1	5.4	46.7	-1.2

<sup>a</sup>In this DRF calculation, the values of the layer height and mixing factor were assumed to be 2000 m and 1.2, respectively.

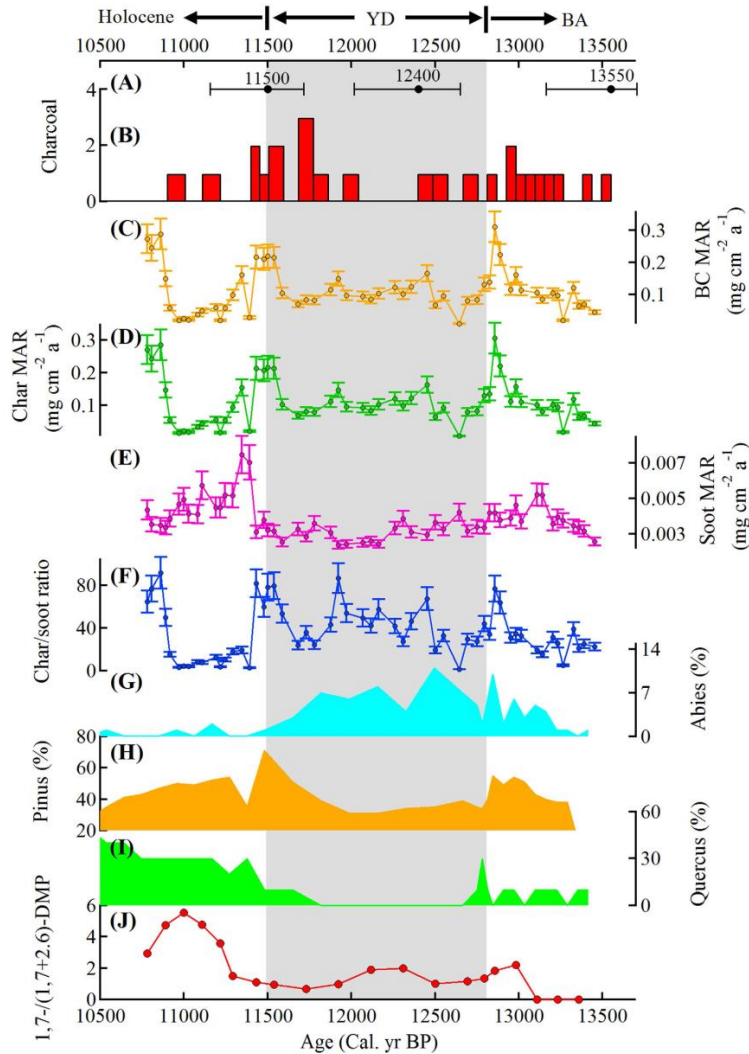
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**A recent study published in ACPD found that the EC concentrations from peat burning are far higher than their corresponding BC concentrations (measured by the optical method) and they suggests that the existing of char materials, which has a weak light-absorbing characteristics, is the reason**

**Stockwell et al., 2016, Atmos. Chem. Phys. Discuss.**

While EC and BC are considered approximately equivalent for some combustion sources (e.g. diesel fuel combustion), our EF EC for peat fires is noticeably larger than the EF BC although both EC and BC values are very small (Table 2) compared to typical values for combustion aerosol. This is the expected result in this case for several reasons. The peat smoke plumes sampled outdoors likely contain very small amounts of soot from rare instances of flaming and also a small amount of entrained small char particles produced by pyrolysis of the peat on site by the glowing combustion front (Santín et al., 2016). Both soot and char are detected to some extent as EC (Andreae and Gelencsér, 2006; Han et al., 2007; 2010; 2016) and our EC sub-fractions evolving at lower temperatures confirm some char was present (NIOSH, 1999). The char particles tend to be larger (1-100 microns, Han et al., 2010) and would be more efficiently sampled by the filters, which had a 2.5 micron cut-off as opposed to the PAX with a 1.0 micron cut-off. Char tends to absorb long wavelengths less efficiently than soot (Han et al., 2010) and the PAX would therefore be relatively insensitive to any sampled char for this reason also. The accuracy of both the PAX and the thermal optical EC detection is challenged by the low EC or BC to OC ratio (Andreae and Gelencsér, 2006). Yet, both measurements are useful and point to the same key results: that the aerosol is overwhelmingly organic and the organic fraction contributes most of the light absorption.

# If smoldering and flaming fires emit similar BC concentrations, does this mean that they have similar effects?



Flaming fires produce more soot, while smoldering fires produce more char. This is confirmed from our paleo-fire study. The different emissions are related to the local climate : dry climate corresponds to flaming fires and more soot is produced, while wet climate corresponds to smoldering fires and more char is produced. It is related to the combustion efficiency. If we don't differentiate between char and soot, this implies that there may be no any differences in BC emissions. However they have totally different environmental and climatic implications.

Correlations between smoldering and flaming fires with climate

*Han et al., Sci. Rep., 2016*



**In China char is the dominant part in BC aerosols because coal combustion and biomass burning are the main sources. This is far different from the west developed countries. In these countries vehicle emission is the main source and thus there should be more soot in BC. We suggest that the direct comparison of BC concentrations with no any differentiation between char and soot may “cover” some environmental and climatic implications of BC.**

**Table 1**  
Winter and summer char-EC and soot-EC concentrations in fourteen cities.

Locations	Seasons	Char-EC $\mu\text{g m}^{-3}$	Soot-EC $\mu\text{g m}^{-3}$	Char-EC/ soot-EC	N
Chongqing	Winter	15.46 ± 5.45	1.13 ± 0.67	13.66	15
	Summer	7.00 ± 2.69	1.04 ± 0.57	6.75	16
Guangzhou	Winter	13.09 ± 9.47	1.41 ± 0.49	9.28	14
	Summer	1.99 ± 0.56	1.19 ± 0.45	1.67	13
Hong Kong	Winter	4.28 ± 2.37	1.51 ± 0.86	2.84	16
	Summer	2.55 ± 1.02	0.98 ± 0.68	2.61	22
Hangzhou	Winter	8.01 ± 2.17	1.35 ± 0.27	5.94	14
	Summer	2.31 ± 1.24	1.31 ± 0.61	1.76	16
Shanghai	Winter	7.12 ± 4.96	1.20 ± 0.52	5.93	16
	Summer	1.81 ± 1.11	1.12 ± 0.61	1.61	14
Wuhan	Winter	7.11 ± 2.70	1.31 ± 1.00	5.41	13
	Summer	1.74 ± 0.48	1.26 ± 0.44	1.38	13
Xiamen	Winter	3.98 ± 1.34	1.01 ± 0.16	3.95	15
	Summer	0.81 ± 0.59	0.69 ± 0.76	1.17	12
Beijing	Winter	6.15 ± 3.44	0.91 ± 0.18	6.75	14
	Summer	3.42 ± 2.07	1.91 ± 1.59	1.79	14
Changchun	Winter	12.35 ± 4.20	1.15 ± 4.80	10.74	14
	Summer	1.63 ± 1.04	1.22 ± 0.44	1.34	16
Jinchang	Winter	3.97 ± 0.98	1.03 ± 0.28	3.84	15
	Summer	0.47 ± 0.57	1.11 ± 0.14	0.43	8
Qingdao	Winter	5.45 ± 2.32	0.86 ± 0.62	6.35	13
	Summer	0.67 ± 0.57	0.71 ± 0.36	0.94	9
Tianjing	Winter	7.73 ± 3.28	0.79 ± 0.57	9.74	16
	Summer	2.13 ± 0.99	1.54 ± 0.59	1.39	15
Xi'an	Winter	19.78 ± 5.22	1.84 ± 0.98	10.74	15
	Summer	5.47 ± 2.97	1.53 ± 0.25	3.58	15
Yulin	Winter	8.07 ± 3.91	1.09 ± 0.31	8.6	14
	Summer	1.86 ± 1.00	1.41 ± 0.57	1.31	12
Average	Winter	8.67 ± 6.19	1.26 ± 1.40	6.88	204
	Summer	2.41 ± 2.28	1.21 ± 0.72	1.98	195

Char and soot concentrations in PM<sub>2.5</sub> from 14 cities of China

# Protocol comparison conducted for EC/OC analysis in ambient aerosol study in Xi'an

Protocols		Orthogonal Fit		Ordinary Fit		t-test
x	y	Equation	r <sup>2</sup>	with zero intercept	r <sup>2</sup>	p <sup>a</sup>
EC						
IMPROVE TOR	IMPROVE_A TOR	y = 0.81x+0.43	0.94	y = 0.84x	0.94	0.17
IMPROVE TOR	EUSAAR_2 TOR	y = 1.09x-0.95	0.96	y = 1.01x	0.96	0.93
IMPROVE TOR	IMPROVE TOT	y = 0.57x+0.30	0.96	y = 0.60x	0.95	0.00
IMPROVE TOR	IMPROVE_A TOT	y = 0.45x+0.58	0.9	y = 0.49x	0.88	0.00
IMPROVE TOR	EUSAAR_2 TOT	y = 0.42x+0.41	0.83	y = 0.45x	0.82	0.00
IMPROVE_A TOR	EUSAAR_2 TOR	y = 1.34x-1.52	0.95	y = 1.19x	0.94	0.22
IMPROVE_A TOR	IMPROVE TOT	y = 0.70x+0.03	0.94	y = 0.70x	0.93	0.00
IMPROVE_A TOR	IMPROVE_A TOT	y = 0.56x+0.27	0.95	y = 0.58x	0.95	0.00
IMPROVE_A TOR	EUSAAR_2 TOT	y = 0.52x+0.12	0.86	y = 0.53x	0.86	0.00
EUSAAR_2 TOR	IMPROVE-TOT	y = 0.52x+0.85	0.92	y = 0.58x	0.9	0.00
EUSAAR_2 TOR	IMPROVE_A TOT	y = 0.41x+0.99	0.90	y = 0.48x	0.84	0.00
EUSAAR_2 TOR	EUSAAR_2 TOT	y = 0.39x+0.76	0.85	y = 0.44x	0.81	0.00
IMPROVE TOT	IMPROVE_A TOT	y = 0.79x+0.27	0.93	y = 0.83 x	0.92	0.10
IMPROVE TOT	EUSAAR_2 TOT	y = 0.75x+0.05	0.86	y = 0.75x	0.86	0.01



***Thanks for your attention***