

Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere

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[1] Black carbon (BC), the product of incomplete combustion of fossil fuels and biomass (called elemental carbon (EC) in atmospheric sciences), was quantified in 12 different materials by 17 laboratories from different disciplines, using seven different methods. The materials were divided into three classes: (1) potentially interfering materials, (2) laboratory-produced BC-rich materials, and (3) BC-containing environmental matrices (from soil, water, sediment, and atmosphere). This is the first comprehensive intercomparison of this type (multimethod, multilab, and multisample), focusing mainly on methods used for soil and sediment BC studies. Results for the potentially interfering materials (which by definition contained no fire-derived organic carbon) highlighted situations where individual methods may overestimate BC concentrations. Results for the BC-rich materials (one soot and two chars) showed that some of the methods identified

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most of the carbon in all three materials as BC, whereas other methods identified only soot carbon as BC. The different methods also gave widely different BC contents for the environmental matrices. However, these variations could be understood in the light of the findings for the other two groups of materials, i.e., that some methods incorrectly identify non-BC carbon as BC, and that the detection efficiency of each technique varies across the BC continuum. We found that atmospheric BC quantification methods are not ideal for soil and sediment studies as in their methodology these incorporate the definition of BC as light-absorbing material irrespective of its origin, leading to biases when applied to terrestrial and sedimentary materials. This study shows that any attempt to merge data generated via different methods must consider the different, operationally defined analytical windows of the BC continuum detected by each technique, as well as the limitations and potential biases of each technique. A major goal of this ring trial was to provide a basis on which to choose between the different BC quantification methods in soil and sediment studies. In this paper we summarize the advantages and disadvantages of each method. In future studies, we strongly recommend the evaluation of all methods analyzing for BC in soils and sediments against the set of BC reference materials analyzed here.

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1. Introduction

[2] The incomplete combustion of fossil fuels or biomass leads to the formation of carbon-rich (>60%), aromatic residues (char) and condensates (soot) [Novakov, 1984; Goldberg, 1985; Akhter et al., 1985]. These residues and condensates, collectively called elemental carbon (EC, used in atmospheric sciences) or black carbon (BC, used in soil and sediment sciences), seem to be ubiquitous in the atmosphere, marine sediment, soil, and water, and influence a wide range of biogeochemical processes [Schmidt and Noack, 2000; Watson et al., 2005]. In this paper we will use the term black carbon (BC) to imply both BC and EC as originally defined for soil and sediments and atmospheric studies respectively. Readers are encouraged to refer to Andreae and Gelenčsér [2006] where clear definitions of EC and BC are given. A recent escalation in interest in BC can be attributed to its potential role in global warming. In fact, BC is of interest in this field for two quite different and independent reasons. First, BC has a direct effect on Earth's radiative heat balance and visibility [Crutzen and Andreae, 1990; Watson et al., 2005]. Here it is the literally the "blackness" of BC that is important. Second, and for the purposes of this paper, BC in soils and sediments is defined as a carbonaceous substance of pyrogenic origin, which is resistant to thermal or chemical degradation under the conditions applied in the methods under discussion. According to estimates found in literature, >80% of BC produced ends up in the soil, where it can reside for hundreds to thousands of years, being relatively resistant to biological and chemical breakdown [Forbes et al., 2006; Preston and Schmidt, 2006]. Black carbon therefore represents a pool of C with a long residence time: in essence BC is a carbon sink. For soils and sediments, the light-absorbing characteristics of the substance are not part of our definition of black carbon. What is important is the chemical and thermal stability (and hence longevity) of BC either due to chemical recalcitrance that is evident from its aromatic

structure or physical protection due to its surface functionality and binding with minerals and other organic compounds [Brodowski et al., 2005a; Forbes et al., 2006]. A consequence of BC playing a different role in the atmosphere to that played in terrestrial and marine environments is that two different sets of methodologies have been developed for its quantification. In atmospheric sciences, BC is usually quantified using optical methods that rely on the light-absorbing properties of BC. In contrast, methods developed for the quantification of BC in soils and sediments rely on its resistance to degradation, and in particular, oxidation. The goal of this study is to compare how different methods, designed for soils and sediments, quantify BC in a variety of environmental materials. Therefore we are focused on the resistance of BC to degradation, rather than to its light-absorbing and scattering properties. Several different techniques have been developed for quantification of BC in soils and sediments. Even though they all rely on the same basic principle, that BC is more resistant to breakdown than other forms of organic matter, the nature of the attacking species and the conditions of reaction vary widely. More tellingly, the BC contents determined by these different techniques also vary widely. In a recent intercomparison study of BC in soils, measured concentrations varied by up to a factor of 500 [Schmidt et al., 2001]. In the field of atmospheric science, a large number of inter-comparative studies of BC quantification have been published, as detailed in the review of Watson et al. [2005]. These studies generally found smaller variations in BC contents determined by different techniques or measured in different labs. However, variation was still considerable, with differences of a factor of two common [Watson et al., 2005].

[3] A major problem in quantifying BC is that it is not a single entity, but rather exists as a chemical continuum (Figure 1, top), ranging from large pieces of slightly charred biomass (1–100 μm), to submicron soot particles (30–40 nm) [Goldberg, 1985; Hedges et al., 2000; Masiello,

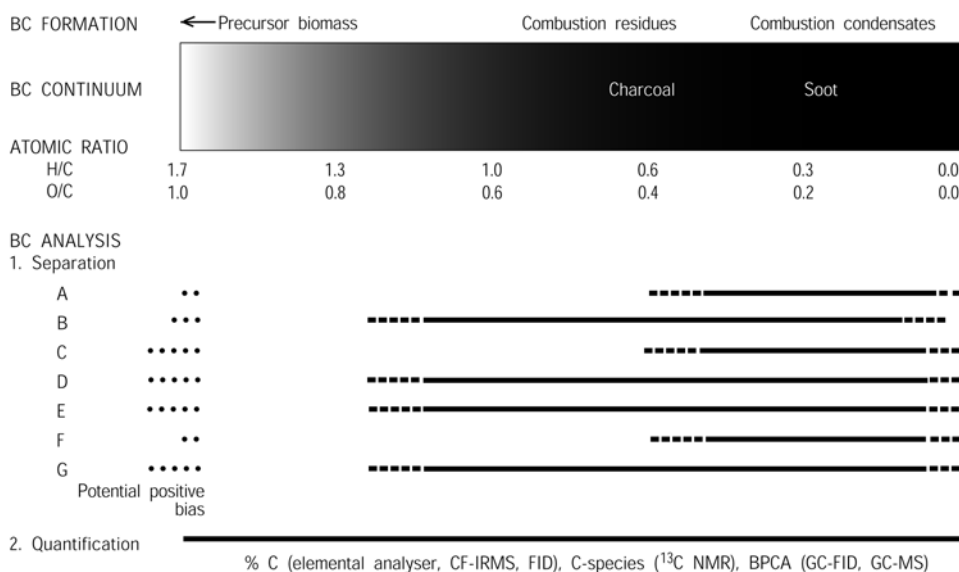


Figure 1. Conceptual summary of the comparative analyses of the seven methods to quantify black carbon (BC). The BC continuum ranges from biomass (not affected by fire) on the left-hand side to pyrogenic, highly condensed aromatic structures on the right-hand side, and is plotted along a scale of atomic H/C and O/C ratios, also used in van Krevelen plots. Note that the H/C scale is nonlinear. BC analysis has two steps: (1) Separation of BC was performed by seven methods: CTO-375, BPCA, Cr₂O₇, TOT/R, TG-DSC, NaClO, and UV. The analytical ranges of separation are conceptual only, visualized by the use of solid and dotted lines. The dashed lines at each end of the solid lines indicate the uncertainty in the range of the BC continuum that each method measures, for example, how much soot or partially charred biomass a certain method measures. The dots on the left of the figure indicate the potential for positive bias from the potential interfering materials for each method. (2) Quantification of BC in the operationally defined separates includes elemental analysis (to quantify carbon left after separation), ¹³C NMR spectroscopy (to identify condensed aromatic C), or the use of gas chromatography with different detectors (GC/FID, GC/MS) to quantify the molecular markers of black carbon (BPCA). The figure was inspired by *Hedges et al.* [2000] and *Masiello* [2004].

2004]. The chemistry of these materials varies with the degree of fire exposure and the production mechanism [Kuhlbusch *et al.*, 1996; Baldock and Smernik, 2002; Czimczik *et al.*, 2002; Nguyen *et al.*, 2004a]. While char retains some plant chemistry and morphology [Sharma *et al.*, 2004], soot is produced from the condensation of gas phase intermediates, and its geochemistry reflects combustion conditions and not plant or fuel precursors. During combustion, both residues (char material) and condensates (soot) can form simultaneously, and may coexist in environmental samples [Poirier *et al.*, 2000, 2002; Schmidt *et al.*, 2002; Jonker and Koelmans, 2002; Fernandes *et al.*, 2003; Brodowski *et al.*, 2005a]. Depending on the formation conditions (e.g., temperature), chars and soot can have overlapping properties, such as specific surface area and oxidative kinetics, confounding the detection of these different forms of BC. Chemical variations of BC within this combustion continuum cause methodological problems, because each BC method may be intentionally or inadvertently optimized to detect a particular form of BC. Regional or even global black carbon budgets based on measurements of different components of the black carbon continuum (remaining charred biomass, released soot) in different matrices (soil, atmosphere, water, sediments) obtained with different methods will likely underestimate the true loading

of BC. Conversely, the biases associated with each method (charring, false positive for refractory kerogens) will lead to an overestimate of the true loading of BC.

[4] The need for a wide-ranging comparative study of methods used for quantification of BC in soils and sediments is clear. There has only been one other comparative study for soils (Schmidt *et al.*, 2001). The current study is the first wide-ranging study (multimaterial, multimethod, multilab) comparing quantification methods for soils and sediments. This study should serve as a basis for further systematic studies on these methods, to answer the myriad of questions that will surely arise from this study. A set of reference materials was selected for this intercomparison, covering a broad spectrum of environmental conditions [Schmidt *et al.*, 2003]. These reference materials included (1) five BC-containing environmental matrices for which BC quantification is often sought, (2) three laboratory-produced BC-rich materials, and (3) four potentially interfering materials containing little or fire-derived carbon. Seventeen laboratories, using seven different analytical approaches (with variations), analyzed these samples for black carbon.

[5] This intermethod comparison is a step in the direction of refining BC quantification methods used in soil and sediment studies in order to better compare data from

different methods. Within the scope of BC quantification in soils and sediments, we address the following questions in this paper: (1) how is BC defined for each method? (2) how BC values from different methods and laboratories compare? (3) what are potential biases for each method? and (4) what are the strengths and weaknesses of each method?

2. Experimental Section

2.1. Reference Materials

[6] Twelve reference materials in three categories were used: (1) potential interfering materials (melanoidin, shale, lignite coal and bituminous coal), (2) laboratory-produced BC-rich materials (n-hexane soot, wood char and grass char), and (3) examples of environmental matrices that commonly contain BC (aerosol from an urban area, harbor marine sediment, a sand-rich soil (Chernozem), a clay-rich soil (Vertisol), and dissolved organic matter (DOM) from a river). Details on these materials can be found in Table 1.

2.2. Black Carbon Quantification Methods

[7] Seventeen laboratories used seven different quantification methods. The laboratories are identified in auxiliary material Text S1¹. The method details, including references to more specific parameters, are presented in Table 2.

2.3. Statistics

[8] We did not use a hidden code on the samples and, therefore, trust that each laboratory was honestly reporting its analytical precision. Basic statistics were applied to the results at intralaboratory level: standard deviation (s) and coefficient of variation (CV). Beyond that, at interlaboratory level, we used chemographical statistical tools to explore the data further, i.e., a Youden plot [Youden, 1959] and data filtering (with relative standard uncertainty, u_r).

3. Results and Discussion

3.1. Comparative Study Set-Up

[9] Black carbon concentrations in the twelve reference materials were determined by 17 laboratories using seven distinct methods described earlier (Table 2). Three to five laboratories used methods CTO-375, BPCA, Cr₂O₇, TOT/R, whereas single laboratories used methods TG-DSC, NaClO and UV. The results of these analyses are summarized in Figure 2 (expressed as BC as proportion of OC as determined by each laboratory individually (%)) and presented in auxiliary material Text S2 (expressed as g BC kg⁻¹ material), and are discussed below by first considering the results for each reference material in turn. A discussion of intra- and interlaboratory reproducibility follows. Finally, we discuss the advantages and disadvantages of each method, and some considerations for future BC studies in soils and sediments.

3.2. Potentially Interfering Materials

3.2.1. Melanoidin

[10] The melanoidin was included in the study to act as a negative control, i.e., as a sample that contains no material

produced by combustion. Melanoidins have been suggested to have similar chemistry to that of natural organic matter [Benzing-Purdie and Ripmeester, 1983]. It should be noted that melanoidin is not the perfect negative control sample. Any environmental matrix (e.g., soil or sediment) will contain, along with any BC, non-BC organic matter in a myriad of forms, some of which may have a similar chemistry to melanoidin, but most of which probably will not. However, there are clear practical constraints on the number of samples that can be included in an exercise such as this, and in this comparative study melanoidin was chosen to serve as a single negative control.

[11] On average, the highest BC/OC% values were reported by laboratories using method TOT/R (44.8–65.5% BC/OC; one outlier: 18.1%). This method relies on the transmittance and reflectance of a material after oxidation, and the dark color of this material probably aided premature oxidation in the melanoidin [Currie et al., 2002]. This raises some concern as to how this method discriminates between organic carbon and black carbon, since the method was developed specifically for the analysis of small quantities of aerosols collected on filters in situ, to study radiation effects in the atmosphere [Schauer et al., 2003; Chow et al., 2004]. It would appear that this method, as it was used in the study, is not suitable for the analysis of bulk solid residues as is done in soil and sediment studies. However, resuspension of solids should be possible under certain circumstances. Other methods (CTO-375, BPCA and TG-DSC) measured about 10 times less BC/OC in the melanoidin, while methods Cr₂O₇, NaClO and UV reported BC/OC of zero percent. For method BPCA this confirms that the condensed aromatic structures forming the markers detected by this method can be present in low concentrations in nonpyrogenic material, such as melanoidin [Brodowski et al., 2005b]. However, it should be noted that these markers were found at 30–50 times higher concentrations in the char and soot samples (Figure 2 and auxiliary material Text S2). For method CTO-375, charring of the melanoidin during heating would seem the most likely cause of nonzero BC values determined by this method [Gustafsson et al., 2001].

3.2.2. Shale

[12] The shale was included in the study because it contains chemically resistant OC that has low aromaticity [Trewthella et al., 1986]. The OC (kerogen) in this shale is derived mainly from the alkyl biopolymers that constitute the cell walls of certain species of algae. The kerogen has undergone little thermal change and so retains its aliphatic character. Nonetheless, it does contain some aromatic C, at least some of which is in fused aromatic structures [Trewthella et al., 1986].

[13] The highest BC concentration for the shale was reported by method TG-DSC (62.6%), and the second highest by method Cr₂O₇ (average BC/OC 23.3%). These methods potentially overestimate BC, since they quantify chemically recalcitrant carbon, irrespective of the nature of the carbon, and TG-DSC also reports weight losses from dehydration of clay minerals in samples of this type. Most other laboratories reported BC/OC <10% (apart from one extreme value for one laboratory from method CTO-375

¹Auxiliary materials are available in the HTML. doi:10.1029/2006GB002914.

Table 1. Black Carbon Reference Materials Used in Ring Trial With Selected Characteristics

Material	Selected References	Production/ Collection Method	Organic Carbon, ^a g kg ⁻¹ mass	Surface Area, m ² g ⁻¹	Lightness, L	Rationale
Melanoidin	<i>Elmqvist et al.</i> [2006]	<i>Group 1: Potential Interfering Materials</i> residue formed on reaction of urea with glucose at 90°C for 30 days sampled from the Mahogany zone of the Green River formation (Utah, USA) sampled in Mercer County (North Dakota, USA) sampled in Buchanan County (Virginia, USA)	541.3 (30.1)	2.9	8.1	negative control: contains no pyrogenic BC contains chemically resistant carbon but has no pyrogenic origin
Green River shale	<i>Petsch et al.</i> [2001], <i>Elmqvist et al.</i> [2006]		272.5 (12.9)	0.8	44.4	an immature coal to differentiate coal from pyrogenic BC
Beulah-Zap lignite coal	<i>Vorres</i> [1990]		589.6 (101.3)	1.6	0.4	a mature coal to differentiate coal from pyrogenic BC; can contain up to 10% inertinite in some cases
Pocahontas bituminous coal	<i>Vorres</i> [1990]		846.1 (62.6)	1.9	9.2	
n-hexane Soot	<i>Akhter et al.</i> [1985], <i>Smith and Chughtai</i> [1995]	<i>Group 2: Laboratory-Produced BC-Rich Materials</i> produced by open n-hexane flame and collected from the top of the flame on an inverted funnel surface	921.3 (32.9)	73.9	0.1	represents BC produced in the gas phase (condensate) from a fossil fuel
Wood char	<i>Elmqvist et al.</i> [2006], <i>Hammes et al.</i> [2006]	chestnut hardwood (<i>Castanea sativa</i>) char was produced at 450°C for 5 hours (holding time) in inert N atmosphere (Fessin, Switzerland)	744.4 (45.6)	2.0	6.0	represents BC produced in the solid phase (residue) from wood material (biomass)
Grass char	<i>Elmqvist et al.</i> [2006], <i>Hammes et al.</i> [2006]	grass char (<i>Oryza sativa</i>) was produced at 450°C for 5 hours (holding time) in inert N atmosphere (Fessin, Switzerland)	591.4 (32.0)	5.9	5.7	represents BC produced in the solid phase (residue) from grass material (biomass)
Urban dust (SRM 1649a)	<i>Currie et al.</i> [2002], <i>Masiello et al.</i> [2002], <i>National Institute of Standards and Technology</i> [2001]	<i>Group 3: Environmental Matrices</i> sampled in 1976–1977 as atmospheric particulate matter from the Washington DC area (USA)	178.4 (6.3) ^b	3.7	15.4	represents BC soot in a aerosol matrix ^c
Marine sediment (SRM 1941b)	<i>Elmqvist et al.</i> [2006], <i>National Institute of Standards and Technology</i> [2004]	sampled from the Baltimore Harbor in the Chesapeake Bay area (USA)	30.7 (4.0) ^b	28.6	53.5	Represents BC soot in a sediment matrix
Vertisol	<i>Schmidt et al.</i> [2001]	sandy clay soil sampled at a 0–10 cm depth at Urbræe (South Australia), 37% clay	31.3 (2.3)	57.3	30.7	represents BC char in a soil matrix with a high clay content
Chernozem	<i>Schmidt et al.</i> [2001]	light sandy clay soil sampled at a 20–60 cm depth in the Hildesheim-Braunschweig region (Harsum, Germany), 19% clay collected from the Suwannee River using reverse osmosis (Georgia, USA)	19.3 (0.9)	9.0	32.0	represents BC char in a soil matrix with a low clay content
Dissolved organic matter (DOM)	<i>Serkiz and Perdue</i> [1990], <i>Elmqvist et al.</i> [2006]		459.4 (37.6)	-	25.9	could contain soluble condensed aromatic structures

^aOrganic carbon content for each material averaged over all the laboratories (standard deviation in brackets).^bOrganic carbon for TOT/R methods is total carbon minus black carbon.^cCalled EC in atmospheric sciences [see *Currie et al.*, 2002].

Table 2. Methods Employed in Ring Trial and Individual Modifications

Lab	Selected References	Pretreatment				Oxidation				Detection
		Acid	Mode ^b	Time	Initial Oven Temperature	Temperature Ramp	Atmosphere	Temperature	Instrument	
Chemo-Thermal Oxidation at 375°C (CTO-375) ^a										
1	<i>Gustafsson et al.</i> [1997], <i>Nguyen et al.</i> [2004a]	1 HCl	crucible (except soot and chars)	24 hours	360°C	2.5°C min ⁻¹ to 375°C	air	24 hours	360°C	elemental analysis on residue between before oxidation and after
5	<i>Gustafsson et al.</i> [1997]	0.7 M H ₂ SO ₃	Ag capsule	24 hours	23°C ^c	60°C min ⁻¹ to 360°C 30°C min ⁻¹ to 370°C 3°C min ⁻¹ to 375°C	air	24 hours	23°C ^c	Mass difference before oxidation and after
7a	<i>Gustafsson et al.</i> [1997, 2001]	1 M HCl	Ag capsule with automatic ball grinder	18 hours	23°C ^c	10°C min ⁻¹ to 350°C 0.5°C min ⁻¹ to 375°C	air	18 hours	23°C ^c	CF-IRMS, followed by coulometric quantification of CO ₂ ^d
7b ^c	<i>Gustafsson et al.</i> [1997], <i>Gustafsson et al.</i> [2001], <i>Elmqvist et al.</i> [2004]	32% HCl	crucible - vapor	18 hours	23°C ^c	11°C min ⁻¹ to 375°C	air	18 hours	23°C ^c	CF-IRMS, followed by coulometric quantification of CO ₂
12a	<i>Gustafsson et al.</i> [1997, 2001], <i>Gélinas et al.</i> [2001]	10% HF/1 M HCl wash	crucible - vapor	18 hours	23°C ^c	11°C min ⁻¹ to 375°C	air	18 hours	23°C ^c	CF-IRMS, followed by coulometric quantification of CO ₂
12b	<i>Gustafsson et al.</i> [1997, 2001]	32% HCl	crucible - vapor	18 hours	23°C ^c	11°C min ⁻¹ to 375°C	air	18 hours	23°C ^c	CF-IRMS, followed by coulometric quantification of CO ₂
Method B: Benzene Polycarboxylic Acids (BPCA) ^f										
Lab	Selected References	Pretreatment			Oxidation			Detection		
		Time	Temperature	Acid	Time	Temperature	Acid	Instrument	Temperature Program	
2	<i>Glaser et al.</i> [1998], <i>Brodowski et al.</i> [2005b]	4 hours	105°C	4 M TFA	8 hours	170°C	65% HNO ₃	GC-FID 30 m × 0.32 mm i.d., 0.25 μm film	100°C held for 2 min 20°C min ⁻¹ to 240°C held for 7 min 30°C min ⁻¹ to 300°C held for 10 min	
6	<i>Glaser et al.</i> [1998], <i>Brodowski et al.</i> [2005b]	4 hours	105°C	4 M TFA	8 hours	170°C	65% HNO ₃	GC-FID 30 m × 0.25 mm i.d., 0.25 μm film	100°C held for 2 min 20°C min ⁻¹ to 240°C held for 7 min 30°C min ⁻¹ to 300°C held for 10 min	
14	<i>Glaser et al.</i> [1998], <i>Brodowski et al.</i> [2005b]	4 hours	105°C	4 M TFA	8 hours	170°C	65% HNO ₃	GC-MS 50 m × 0.2 mm i.d., 0.33 μm film	70°C held for 2 min 15°C min ⁻¹ to 200°C held for 5 min 5°C min ⁻¹ to 300°C held for 15 min	

Table 2. (continued)

Lab	Selected References	Method C: Acid Dichromate Oxidation (Cr ₂ O ₇) ^g										
		Pretreatment			Oxidation							
		Time	Temperature	Acid	Time	Temperature	Acid					
11	<i>Bird and Gröcke</i> [1997], <i>Rumpel et al.</i> [2006]	24 hours	22.5 ± 2°C	10 % HF	24 hours	80°C	0.1 M K ₂ Cr ₂ O ₇ / 2 M H ₂ SO ₄	elemental analysis; mass difference between before and after oxidation				
13	<i>Wolbach and Anders</i> [1989]	20 hours	60°C	6 M HCl/53% HF	400 hours	22.5 ± 2°C	0.25 M K ₂ Cr ₂ O ₇ / 2 M H ₂ SO ₄	elemental analysis; mass difference between before and after oxidation				
16b	<i>Lim and Cachier</i> [1996], <i>Song et al.</i> [2002]	20 hours	60°C	6 M HCl	10 min	23°C in ultrasonic bath ^f	0.1 M K ₂ Cr ₂ O ₇ / 2 M H ₂ SO ₄					
		20 hours	60°C	6 M HCl/22 M HF	60 hours	55°C in water bath						
		10 hours	60°C	6 M HCl								
17	<i>Lim and Cachier</i> [1996]	15 min	23°C in ultrasonic bath ^f	3 M HCl	15 min	23°C in ultrasonic bath ^f	0.5 M K ₂ Cr ₂ O ₇ / 2 M H ₂ SO ₄	elemental analysis; mass difference between before and after oxidation				
		24 hours	23°C ^e		48 hours	55°C						
		15 min	23°C in ultrasonic bath ^e	10 M HF/1 M HCl								
		24 hours	23°C ^e									
Method D: Thermal/Optical Transmittance and Reflectance (TOT/R) ^h												
Lab	Selected References	Oxidation										
		Pretreatment	First Heating Step			Second Heating Step			Third Heating Step			Detection
			Temperature	Atmosphere	Temperature	Atmosphere	Temperature	Atmosphere	Temperature	Atmosphere		
3	<i>Chow et al.</i> [1993]	no	23°C to 550°C ^c	He	up to 800°C under	2% O ₂ /He					He-Ne laser reflectance (632 nm) plus FID	
9a	<i>Huang et al.</i> [2006]	no	23°C to 550°C ^c	He	up to 870°C	He	up to 900°C	10% O ₂ / 90% He			integrated fraction of plateau at 900°C plus FID	
9b	<i>Chow et al.</i> [1993], <i>Huang et al.</i> [2006]	no	23°C to 550°C ^c	He	up to 870°C	He	up to 900°C	10% O ₂ / 90% He			He-Ne laser transmittance (632 nm) plus FID	
10	<i>Chow et al.</i> [1993], <i>Schauer et al.</i> [2003], <i>Huebert et al.</i> [2004]	no	from 250°C to 870°C	He	cooling to 550°C	He	up to 900°C	10% O ₂ / 90% He			He-Ne laser transmittance (632 nm) plus FID	
16a	<i>Chow et al.</i> [1993], <i>Chen et al.</i> [2005]	HCl vapor	from 310°C to 840°C	He	cooling and then heat to 550°C	He	up to 860°C	10% O ₂ / 90% He			He-Ne laser transmittance (632 nm)	

Table 2. (continued)

Lab	Selected References	Method E: Thermogravimetry and Differential Scanning Calorimetry Analysis (TG-DSC) ⁱ					
		Pretreatment	Temperature	Atmosphere	Detection		
4	<i>Dell'Abate et al.</i> [2000, 2003], <i>Plante et al.</i> [2005], <i>Lopez-Capel et al.</i> [2005]	no	20°C to 990°C (20°C min ⁻¹)	20% O ₂ /80% He	mass difference during heating, over specific intervals that correspond to decomposition of individual components of the sample		
Method F: Sodium Hypochlorite Oxidation (NaClO) ^j							
Lab	Selected References	Pretreatment		Oxidation (Repeat 3 Times)			
		Time	Acid	Time	Temperature	Detection	
8	<i>Simpson and Hatcher</i> [2004a, 2004b]	12 hours	6 M HCl	4 hours	23°C	¹³ C NMR; Elemental analysis; mass difference between before and after oxidation	
Method G: UV Photooxidation (UV) ^k							
Lab	Selected References	Pretreatment		Oxidation			
		Time	Acid	Time	Temperature	Wash	Detection
15	<i>Skjennstad et al.</i> [1996, 1999]	wet sieved < 53 μm	< 53 μm 2 % HF	2 hours	23°C	UV photooxidation at 2.5 kW in oxygen-saturated water	¹³ C NMR; elemental analysis; mass difference between before and after oxidation

^aIn this method, samples are pretreated with acid to remove carbonates and then thermally oxidized to eliminate labile carbon and leave a resistant residue for quantification as BC.

^bCrucible acidification is made ex situ, Ag capsule acidification made in situ.

^cHere 23° is assumed room temperature.

^dCF-IRMS denotes Continuous Flow Isotope Ratio Mass Spectrometer.

^eStandard addition of incremental amounts of standard reference material SRM 2975 to marine sediment and urban dust. Rest of procedure as for 7a.

^fIn this method samples are pretreated to remove metals and carbonates. The samples are then oxidized to isolate aromatic structures that are converted into benzene polycarboxylic acids. Black carbon is quantified as the sum of the threefold to sixfold carboxylated benzoic acids that are measured using gas chromatography and flame ionization detection (GC/FID). Black carbon yields were multiplied by a conversion factor of 2.27 to estimate BC quantities.

^gSamples are pretreated to remove carbonates. Black carbon is defined as the organic carbon that survives oxidation with dichromate. Oxidation of carbon in the residue is modeled as first-order exponential loss process, with a "fast" component (~6 hours) corresponding to labile, non-BC oxidation, an intermediate component corresponding to kerogen, and a "slow" component (100–1000 hours) corresponding to BC.

^hBC is defined as the integrated part after the split point where the laser transmittance or reflectance equals the initial laser value.

ⁱThis method measured carbonaceous species being thermally oxidized while recording mass loss. Initial weight loss is due to exothermic decomposition of labile aliphatic and carboxylic groups (~300°C), while exothermic loss of more refractory aromatic carbon occurs at higher temperatures (~450°C). The positions of the DSC peaks reflect the structure and chemical composition of the material.

^jSamples are oxidized in NaClO to remove components that overlap with the signal of BC, such as lignin and other non-BC aromatic compounds. This is followed by organic carbon and ¹³C nuclear magnetic resonance (NMR) analyses of the residue to determine BC from the relative amount of aromatic carbon (110–140 ppm in solid-state ¹³C NMR).

^kThis method relies on the relative stability of char to high-energy UV oxidation compared to other soil organic carbon fractions.

and one high value for one laboratory from method TOT/R) (Figure 2).

3.2.3. Coal

[14] The coals were included in the study to determine whether the BC quantification techniques would identify coal as BC. Coal is naturally present in a minority of soils and sediments, but is an abundant contaminant in many industrialized environments. In such environments it may be important to be able to differentiate coal from pyrogenic BC. Since coal chemistry varies greatly, two coals were chosen at either end of the maturity scale, a lignite coal (immature) and a bituminous coal (mature). The bituminous coal may contain about 10% inertinite from ancient fire occurrences [Vorres, 1990].

[15] The bituminous coal was found to have a higher BC content than the lignite coal for every technique. The highest BC/OC% for lignite coal was reported by method TOT/R (50.2%), followed by method UV (26.9%) and one laboratory of the BPCA method (23.4%). Most other methods reported values <20%, while methods CTO-375 and NaClO reported $\leq 5\%$. For the bituminous coal, laboratories using methods TOT/R, TG-DSC, Cr₂O₇ and UV all reported BC/OC of >70% (Figure 2); that is, most of carbon in this sample was found to be BC using these methods. The bituminous coal was not analyzed using method NaClO. Method BPCA reported 15.8–25.9% BC/OC for the bituminous coal, indicating that it only partly consists of highly condensed material. Laboratories using method CTO-375 reported the lowest BC concentrations in both coals. In fact, the BC concentrations determined using method CTO-375 were generally at least an order of magnitude lower than those measured by other techniques.

[16] In summary, all methods except CTO-375 and NaClO measured more than 10% BC/OC for one or more of the potential interfering materials. These materials have properties shared by BC-rich materials, like high C content or dark color, but do not have pyrogenic origins. These potential biases should be kept in mind when analyzing environmental matrices like soils and sediments where such contaminants could be present, since it could lead to an overestimation of the BC content of the material [Chow *et al.*, 2004].

3.3. Laboratory-Produced BC-Rich Materials

[17] Three materials were produced as BC-rich standards for this comparative study. These were designed to cover a range of the BC continuum, and included soot (produced in the gas phase from an inefficiently combusting hexane flame) and two chars (solid residues of combustion of solid materials under oxygen-free conditions). The two chars were produced from wood and grass residues to test whether chars produced from different starting materials are detected differently by the various BC quantification methods.

[18] Method CTO-375 clearly differentiated between the soot and the chars: Laboratories using this method reported zero BC/OC in the wood char, no more than 1.5% BC/OC in the grass char and around 48.5% BC/OC in the soot (one outlier in method CTO-375: 36.6%; Figure 2). Similar results were reported for method NaClO: A value of zero was found for the wood char, 10.4% for the grass char, and

67.0% for the soot (Figure 2). In both methods where zero values were found, there was no residue left to measure. The CTO-375 and NaClO methods both quantified more BC in the grass char than the wood char, which is the opposite of the other five methods. There could be specific structural properties of the grass char that resulted in it partially surviving the oxidation at 375°C and NaClO oxidation. For example, grasses typically contain organic carbon trapped within silica phytoliths and this carbon is protected from oxidation under these conditions. Of the other methods, laboratories using method BPCA reported the lowest BC concentrations for the soot and chars (around 26%), although these varied quite widely (by up to a factor of three) between the different laboratories that used this method (Figure 2). The other methods (Cr₂O₇, TOT/R, TG-DSC and UV) reported large concentrations of BC in all three of these materials, although the values varied by up to a factor of two (auxiliary material Text S2).

[19] In summary, methods CTO-375 and NaClO were able to differentiate between the soot (which gave high BC values) and the chars (which gave zero and low BC values). Method BPCA gave intermediate values for BC content, whereas methods Cr₂O₇, TG-DSC and UV gave high values for BC content for all of these materials, based on the high thermal and chemical resistance of these materials [Lim and Cachier, 1996; Skjemstad *et al.*, 1999, Lopez-Capel *et al.*, 2005]. It is possible that the dark color of these materials created problems for the TOT/R method in that the split between OC and BC became hard to discern [Chow *et al.*, 2004].

3.4. Environmental Matrices

[20] As has been found previously [Schmidt *et al.*, 2001], the BC contents reported by each of the laboratories in this study for the five environmental samples varied widely. However, by knowing how the different methods detected BC in the potentially interfering and BC-rich materials discussed above, we can draw some conclusions from these variations.

3.4.1. Aerosol

[21] The highest BC/OC% was reported for method TG-DSC (58.9%). Method TG-DSC can overestimate BC concentrations in samples that contain clays or carbonates, which lose water or CO₂ during heating [Lopez-Capel *et al.*, 2005]. Methods Cr₂O₇ and TOT/R reported BC/OC ranging from about 16–50%. Laboratories using methods CTO-375 and BPCA reported similar BC/OC% (3.7–14.3%) in a lower range than the other methods, although a wider range of values was reported using method CTO-375 than method BPCA (Figure 2). The aerosol was not analyzed using method NaClO. This aerosol was first studied in detail by Currie *et al.* [2002], where 19 different chemical and thermal methods, including CTO-375, TOT/R, reported 6.9–52.0% EC/TC (BC/OC). This gave the first evidence that comparative results are likely to be method and matrix-dependent [Currie *et al.*, 2002].

[22] The relatively high BC concentration detected using method CTO-375 (8.6%) indicates a high soot content for this sample (Currie *et al.*, 2002). This soot may have been underdetected using method BPCA, as this method recorded

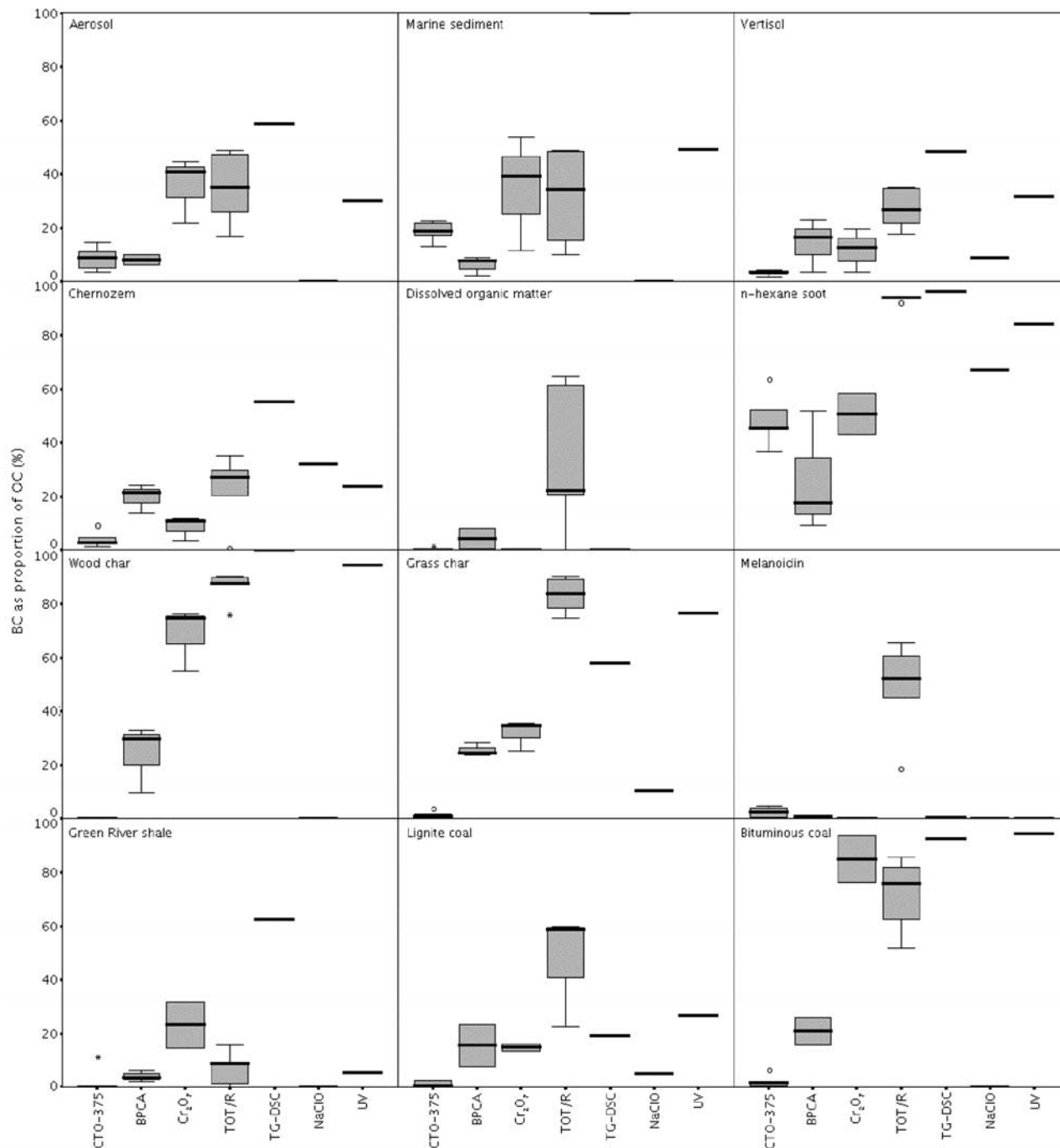


Figure 2. Black carbon concentrations for each BC reference material quantified by seven different methods. The top line of each grey bar is the highest value measured, the bottom line is the lowest value measured, and the black line inside each bar is the average BC concentration for each method. For method CTO-375, $N = 6$; for BPCA, $N = 3$; for Cr_2O_7 , $N = 4$; for TOT/R, $N = 5$; for TG-DSC, $N = 1$; for NaClO, $N = 1$; and for UV, $N = 1$.

relatively low BC concentrations for the most condensed aromatic structures (soot, char and bituminous coal). On the other hand, method BPCA also detects small units of condensed aromatic systems. Therefore a likely explanation for the similar BC contents reported using methods CTO-375 and BPCA would be that the aerosol contains a mixture

of large and small units of condensed aromatic structures, the former of which is detected more efficiently by method CTO-375, the latter by method BPCA. Such an explanation also would be consistent with the higher BC contents recorded using methods Cr_2O_7 and UV, since these two

methods detected a wide range of aromatic structures as BC in the BC-rich materials (both soot and char BC).

3.4.2. Marine Sediment

[23] The highest BC/OC% for the marine sediment was reported by method TG-DSC (100%), an unlikely value attributed to the interference of mineral impurities in the sediment [Manning *et al.*, 2005]. The lowest BC/OC% for the marine sediment were reported by laboratories using method BPCA (2.0–8.6%). Laboratories using method CTO-375 reported BC/OC in the range 12.8–22.6%. Method TOT/R showed large variation in the results (9.9–48.7%). Three of the four laboratories using method Cr₂O₇ reported BC/OC in the range 11.3–39%, and 49.4% for the UV method.

[24] That BC concentrations were higher for method CTO-375 than method BPCA may indicate that BC in this sample is predominantly highly condensed (soot-like). However, the higher BC concentrations reported using methods Cr₂O₇, TG-DSC and UV indicate the presence of additional BC with less condensed structures. These methods also measured high values for the shale and coals, thus also suggesting that methods Cr₂O₇, TG-DSC and UV overestimated the BC in the marine sediment.

3.4.3. Soils

[25] The lowest BC/OC for the two soils were reported by the laboratories using method CTO-375, ranging between 1.2 and 8.7% (Figure 2). Higher BC/OC in the range 3.5–35.5% were generally reported for laboratories using methods BPCA, Cr₂O₇, TOT/R and NaClO, although there were some lower values reported using method Cr₂O₇ (Figure 2). Method Cr₂O₇ produced a wide range of values, especially for the Vertisol (3.5–19.4%) but also for the Chernozem (3.8–11.7%). The highest BC concentrations in the soils were reported by methods TOT/R, TG-DSC and UV (Figure 2). Owing to the inefficient removal of interfering matrices (clays, carbonates, paramagnetics), it could be that these methods may have overestimated the BC in the soils [Currie *et al.*, 2002; Plante *et al.*, 2005]. The random and systematic differences between the methods for these soils are further discussed in section 3.7.

[26] The lower BC concentrations reported using method CTO-375 for the soils as compared to the aerosol and marine sediment are consistent with differences in the source of the BC in these materials. Both the aerosol and the marine sediment were collected in highly industrialized environments in which fossil fuel burning is a major source of BC. On the other hand, the soils were collected from agricultural sites where vegetation burning is the major BC source. As discussed above, method CTO-375 specifically detects the most condensed BC and this is more prevalent in BC produced by fossil fuel burning than vegetation burning.

3.4.4. Dissolved Organic Matter

[27] BC-derived material has been identified as part of the dissolved organic matter fraction in river water [e.g., Hockaday *et al.*, 2006]. Methods Cr₂O₇ and UV were bound to find zero BC contents for DOM as each of these techniques identifies BC as an insoluble, solid residue. Laboratories using method CTO-375 also generally reported zero or near-zero BC contents for the DOM (Figure 2). This seems plausible, as this technique only identifies the most

highly condensed aromatic structures (e.g., soot) as BC, and such structures are unlikely to be water-soluble. Methods TG-DSC and NaClO did not analyze the DOM. Method TOT/R reported the highest content for this material (average 33.9%) but with large variation (0–62%). Method BPCA gave two extreme values for the DOM (0.6% and 8.3%, Figure 2). It is certainly conceivable that the DOM does contain condensed aromatic structures, and that these are pyrogenically formed. Such soluble condensed aromatic structures would owe their water solubility to the presence of polar substitutions (e.g., carboxyl groups) and small molecular size [Hockaday *et al.*, 2006].

[28] In summary, for the environmental materials, methods TOT/R and TG-DSC are influenced by interfering matrices like carbonates and clays, in the former case because the method has been developed for samples with little or no inorganic matrix, and in the latter because clay minerals potentially decompose at similar temperatures to BC, thus giving interfering weight losses that cannot be discriminated [Manning *et al.*, 2005].

3.5. Intralaboratory Reproducibility

[29] Most laboratories made replicate BC measurements for each of the reference materials, which enable intralaboratory reproducibility to be gauged. The results of these replicate measurements are shown in auxiliary material Text S2 in terms of coefficients of variance (CV) in the replicate measurements, expressed as a proportion (%) of the mean BC concentration reported by that laboratory. The mean CV increased in the order: Method TOT/R (5.1%) < CTO-375 (11.9%) < Cr₂O₇ (14.9%) < BPCA (17.0%) < NaClO (19.4%). For the latter (method NaClO) only data for seven of the twelve reference materials were reported. The order was different when considering the range of CV, which increased in the following order: method TOT/R (0–20.3%) < NaClO (2.5–30.6%) < BPCA (0–42.9%) < CTO-375 (0–57.1%) < Cr₂O₇ (0–91.1%). The largest CV value (91.1%) originated from duplicate analysis of the marine sediment with low absolute BC concentrations (3.7 g BC kg⁻¹ dry matter) and large standard deviation (±3.4 g BC kg⁻¹). Methods TG-DSC and UV were not replicated, and thus we could not assess reproducibility. However, for method TG-DSC, three to five replicates typically yield CV of less than 10%, and for method UV, laboratory 15 pooled four sub samples per reference material for the final quantification step on one sample using NMR.

3.6. Interlaboratory Reproducibility (Within Methods CTO-375, BPCA, Cr₂O₇, and TOT/R)

[30] Variations in BC contents reported by laboratories using the same method (for methods CTO-375, BPCA, Cr₂O₇, TOT/R) were generally greater than the intralaboratory variation discussed above. The most likely reason for this is that there were some variations in the exact methodology used (Table 2).

3.6.1. Method CTO-375

[31] Six data sets were generated by four laboratories, which used different pretreatment and oxidation conditions. The pretreatment removes organic matter, carbonates and

silicate minerals before thermal combustion takes place, that can otherwise be charred and lead to BC overestimation. The original method uses a 24-hour oxidation time, but it has been shown for some low-condensed chars the char carbon is fully removed after 18 hours [Nguyen *et al.*, 2004a]. The systematic differences found between the laboratories are further discussed in section 3.7.

3.6.2. Method BPCA

[32] The three laboratories performing this method used essentially the same pretreatment and oxidation conditions. Actions that could influence results include the following. (1) Material could be lost from the filter papers after the pretreatment wash (worse for fine BC-rich materials than environmental matrices). (2) Care has to be taken not to exceed an aliquot volume of 2 mL (sample in HNO₃), to avoid the deterioration of the citric acid internal standard [Brodowski *et al.*, 2005b]. Nevertheless, an incomplete recovery of the internal standard at least offers a method-inherent control of accuracy. Results could be affected by (3) slightly differing derivatization conditions (duration, temperature, standing time after derivatization), (4) column specifications and temperature program of the gas chromatograph, and (5) the type of calibration curve set up (one-point calibration versus calibration curve).

3.6.3. Method Cr₂O₇

[33] Four laboratories used this method, with pretreatment and oxidation conditions varying widely. Since this method quantifies the resistant carbon residue after a specific time of Cr₂O₇ oxidation, the different oxidation conditions led to substantial differences in results among laboratories.

3.6.4. Method TOT/R

[34] Four laboratories generated five data sets using this method. Differences in sample weight as well as pretreatment and heating conditions led to substantially different results among laboratories. Laboratories using this method had difficulty spreading the material homogeneously on the filter paper, leading to uneven oxidation sites and sometimes an unreliable split between OC and BC.

3.7. Statistical Evaluation of Variability

[35] We used two chemographical tools to identify patterns across laboratories and classes of methods. This approach could serve as a first step to aid in the process of asking qualitative and quantitative questions about underlying (artifactual, scientific) causes of the patterns.

[36] First, we tried to reveal outliers as well as random and systematic differences within and between laboratories by using a correlation (Youden) plot (Figure 3). This graphical data analysis technique visualizes variability within a laboratory as well as variability between laboratories. Basically, crossplotting data from sample 1 (*x* axis) and sample 2 (*y* axis) helps to reveal if all laboratories behave the same. Plotting the data for the two soils (Vertisol, Chernozem, Figure 3) for all the methods, systematic differences are seen between laboratories, spanning about 2 orders of magnitude along the diagonal line (log scale on both axes). Outliers are indicated by deviations from the pattern or the diagonal, respectively. Several key observations became clear: (1) All method CTO-375 results fall substantially below those of the other methods, (2) The

systematic errors occur between and within methods, suggesting that subtle intramethod details may be responsible for significant differences, and (3) outlying results of laboratory 17 (method Cr₂O₇) and laboratory 9b (method TOT/R) could not be explained at first sight. Possible reasons for the observed differences between laboratories using nominally the same method are the modification in oxidation time (method CTO-375 and Cr₂O₇), and the use of an internal standard (method BPCA), which is very sensitive to chemical degradation.

[37] Second, to reveal systematic differences within one method we selected the results from method CTO-375 as example, since it had the most data points to use (Figure 4). The data were filtered to exclude results where less than three laboratories reported data, and relative standard uncertainty (*u_r*) was larger than 10. The filtering elucidated ordered, and even semiquantitative patterns (systematic differences) among all BC reference materials, except the soot and wood char, where the results were indistinguishable. For all the environmental samples, laboratory 5 always exceeded laboratory 7a (except for DOM), while the potential interfering materials showed exactly the opposite trend (except for shale). Compatible data (overlapping numbers) were obtained for marine sediment, soot, and wood char, but not for the other materials. This method was developed for measuring soot in marine sediments. The differing results for the reference materials are probably due to differences in acid pretreatment procedures and thermal oxidation time as explained above. The other methods did not reveal such systematic differences, owing to either random differences or lack of data points after data filtering.

3.8. Choosing Between Methods

[38] The seven BC quantification methods described here are very different: they rely on a range of different properties (color, thermal and chemical stability) to differentiate BC from coexisting non-BC components and were originally developed for specific types of sample (e.g., soil, sediment, aerosol) or to quantify a specific type or range of BC (e.g., soot or char or both). The methods are also at different stages of method development: Some have been used widely (though usually only for a limited range of sample types), whereas others are more recent and have only been used by a few laboratories, or perhaps only by the person/laboratory that developed them. The methods also vary in their ease of use and cost. All of these factors will come into play when choosing a BC quantification technique for a given application. A major goal of this exercise was to provide assistance in making this choice for BC quantification in soil and sediment studies. Below we summarize what we see as the advantages and disadvantages of each method, based mainly on the results of the comparative study.

3.8.1. Method CTO-375

3.8.1.1. Advantages

[39] This method provided excellent differentiation between the soot and chars analyzed in this study and so is best suited for quantifying the most condensed forms of BC, irrespective of its source. It also did not identify coal as BC. It should be noted that while the BC concentrations deter-

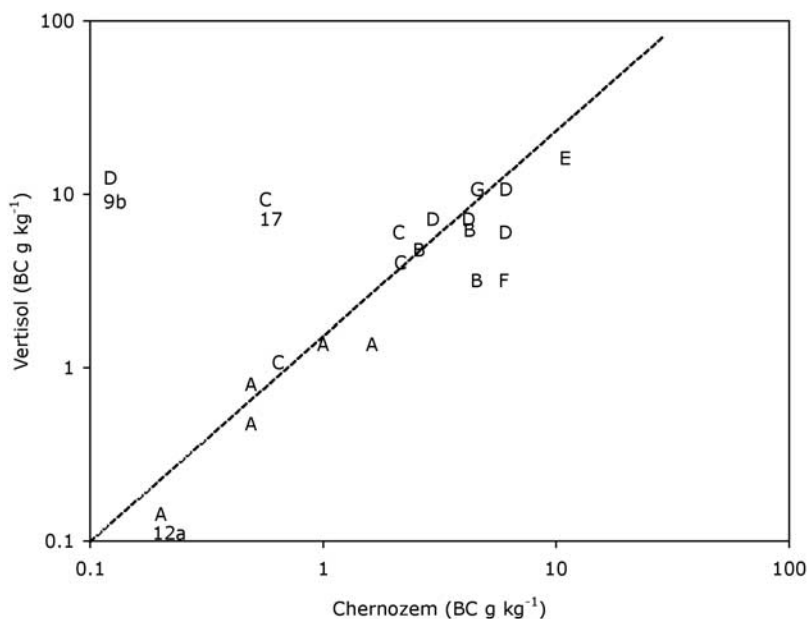


Figure 3. Correlation (Youden) plot of Vertisol (y axis) versus Chernozem (x axis), showing broad systematic differences, and major discrepancies (Laboratories 9b and 17). The letters A to G correspond to the seven classes of methods and the numbers identify laboratories. The best fit line is seen as a diagonal trend line along which most of the data lie.

mined using method CTO-375 were very low for the chars analyzed in this study (which were produced at 450°C), *Nguyen et al.* [2004a] found that chars produced at higher temperatures (e.g., 1000°C) partially survived the CTO-375 method. The lower formation temperature of the chars in this study allowed for more cellulose and lignin to be preserved in the material, inducing a premature oxidation of BC. The same phenomenon was found when forklift diesel soot was combined with apple leaves to make a hybrid RM. The presence of the biopolymer component led to a premature oxidation of a major part of the soot [*Currie and Kessler, 2005*]. Most soot survives primarily because of the combination of largely graphitic outer surfaces, natural aggregation into larger particles, and perhaps a relative lack of oxygen access to internal locations, compared to chars, which are organized in smaller, less condensed units. Lowering the oxidation temperature would include recalcitrant nonpyrogenic OM as artifact, leading to an overestimation of BC.

[40] A higher BC content has been reported for diesel soot using this method [*Gustafsson et al., 1997, 2001; Elmquist et al., 2004, 2006*]. The relative degree of thermal oxidative stability was explicitly and quantitatively demonstrated by *Elmquist et al.* [2006] to be wood char < grass char < hexane soot < diesel soot.

3.8.1.2. Disadvantages

[41] Since this method only quantifies highly condensed BC, it cannot give a representative view of the whole BC continuum like some gentler oxidation methods can; that is, if low-condensed char BC is present, it will not be detected. Also, gentler oxidation methods reported higher soot BC concentrations than the CTO-375 method, which is related to the relative degree of thermal oxidative stability as

discussed above. As for all BC methods tested, a central challenge also for method CTO-375 is to avoid significant positive biases (e.g., charring). While this method returned the lowest interference potential for 3 out of the 4 potentially interfering materials, results for melanoidin (average 2.4% BC/OC) indicate the risk for positive bias. Such interference potential should be compared with the fraction of carbon remaining for BC material (e.g., 700 g kg^{-1} TOC for diesel soot-BC [*Elmquist et al., 2006*]) and the expected relative abundances of the interfering and target substances in the studied environmental matrix. Laboratory 12a used a washing step to remove labile organic matter, which consistently gave lower results (auxiliary material Text S2). However, it has been shown that the majority of hydrophobic soot-BC may be lost during this ex situ washing [*Elmquist et al., 2004*].

3.8.2. Method BPCA

3.8.2.1. Advantages

[42] Method BPCA is the method best suited for identifying BC components in solution. This molecular marker method also provides information on the nature of BC beyond just an estimation of the amount, as it identifies and quantifies a number of BC markers that can be related to source and formation conditions of the BC.

3.8.2.2. Disadvantages

[43] This method is also prone to positive biases from non-BC materials, notably from the shale (average 4.1% BC/OC) and coals (15.6–20.9% BC/OC). Interlaboratory reproducibility should be improved by further standardization, as BC concentrations reported by the three different laboratories that used this technique varied by a factor of at least two for six of the twelve samples analyzed, and these variations were inconsistent (different laboratories reported the highest

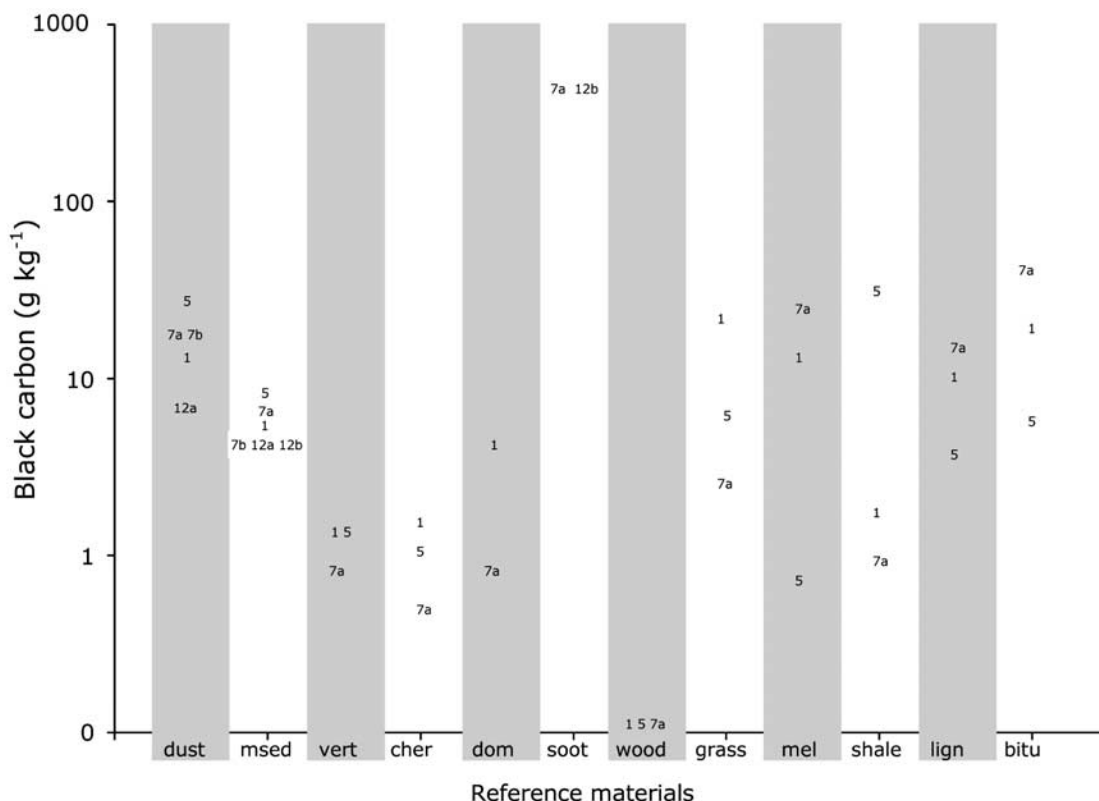


Figure 4. Log plot of CTO-375 data (y axis) versus reference materials (x axis) using selected data ($n > 2$, $u_r < 10\%$). Notation: dust, aerosol; msed, marine sediment; vert, vertisol; cher, Chernozem; dom, dissolved organic matter; soot, n-hexane soot; wood, wood char; grass, Grass char; mel, Melanoidin; shale, Green river shale; lign, Lignite coal; bitu, bituminous coal. A zero code (0.11 g kg^{-1}) was used for zero values on the log plot.

values for different samples). The BC values for the soot and chars were quite low, suggesting that the technique does not quantitatively recover the largest and most condensed BC components as BPCAs. To account for the incomplete conversion of BC to BPCAs, results were corrected with a factor, empirically determined by referencing to commercial charcoal (2.27) [Glaser *et al.*, 1998]. However, results from the measurement of other types of BC char materials suggested that using this factor only gives a conservative, minimum estimate of BC found, and is currently disputed [Brodowski *et al.*, 2005b].

3.8.3. Method Cr_2O_7

3.8.3.1. Advantages

[44] This method probably requires the least expensive or specialized equipment and so can be carried out in most laboratories. Reproducibility was reasonably good for the soot, char and bituminous coal samples, with all reported BC values within a factor of two.

3.8.3.2. Disadvantages

[45] This method assumes that all of the carbon that survives the oxidation treatment is BC, but recorded 9.6% BC/OC for the shale and 14.7–85.0% BC/OC for the coals. This assumption has also elsewhere been shown to be invalid in at least some cases where kerogen has been isolated along with black carbon [Song *et al.*, 2002; Masiello, 2004]. This problem could be overcome characterizing the residue by

solid-state NMR spectroscopy, as is done for the related chemical oxidation methods NaClO and UV. However, this would increase the complexity and cost of the technique, as enough material would need to be isolated for NMR analysis. The residue would need to be pretreated for NMR analysis (e.g., with HF), NMR itself is expensive, and the paramagnetic Cr may also interfere with the NMR analysis. Reproducibility was not so good for the sediment and soil samples, with BC concentrations reported by the four different laboratories that used this technique varying by a factor of at least three for these samples.

3.8.4. Method TOT/R

3.8.4.1. Advantages

[46] Both intra- and inter-laboratory variability was lower than for the other methods for most samples. The method thermally discerns between organic carbon and black (elemental) carbon, although it was not equally successful for all materials tested here. Only further testing can determine if this method could be used in soil and sediment studies.

3.8.4.2. Disadvantages

[47] The method did not provide adequate differentiation between BC and non-BC organic matter (as defined for soil and sediment studies), as exemplified by the very high BC values reported for DOM, melanoidin and coals (Figure 2). Care has to be taken to effectively remove the inorganic matrix of soils and sediments that can lead to interferences,

for example, premature charring. In addition, higher loaded (darker) samples probably create problems in the optical corrections procedures, when the absorption is so high that an additional blackening by charring during pyrolysis cannot be discriminated from the original absorption signal [Schmid *et al.*, 2001]. This method normally requires that the material, with little or no inorganic matrix, be collected on a filter paper in situ. Resuspension of bulk materials like soils and sediments are possible but care should be taken to spread the sample as thinly and homogeneously as possible.

3.8.5. Method TG-DSC

3.8.5.1. Advantages

[48] This method has the advantage that it is operationally very simple, and that it can detect all carbon species (including carbonates, oxalate) within a sample. In this trial, the BC values reported for the soot, chars and potentially interfering materials are in agreement with other methods for nine of the 12 samples. Disagreement arose as a consequence of mineral impurities, especially clays, in the environmental materials.

3.8.5.2. Disadvantages

[49] This method may overestimate BC in samples with low C contents (i.e., most sediments and soils) if certain impurities are present [Dell'Abate *et al.*, 2003; Lopez-Capel *et al.*, 2005], but also non-BC materials with high carbon contents like the coals (19.0–92.5% BC/OC; again, mineral contaminants may be present). Thermogravimetry measures the total weight loss during a heating profile. Therefore mineral impurities such as clays will contribute to the measured weight loss as they lose water on heating. This may be the reason why this method gave the highest BC values for the aerosol, marine sediment and soil samples (Figure 2 and auxiliary material Text S2). If calcite (CaCO_3) is present, it can be distinguished from BC as it decomposes at higher temperatures, allowing each to be quantified separately [Manning *et al.*, 2005]. Pretreatment to increase the concentration of organic matter (such as HF treatment or physical separation) may overcome the problem of impurities, and techniques such as X-ray diffraction should be used to determine independently whether or not mineral impurities are present. This technique was used by only one laboratory and no replicate measurements were made, for these specific samples; reproducibility is generally within 5%. This technique shows promise, but needs to be tested on a larger range of samples, and in other laboratories.

3.8.6. Method NaClO

3.8.6.1. Advantages

[50] This method and method A were the only ones that selectively detected soot.

3.8.6.2. Disadvantages

[51] This method was used by only one laboratory, and results were only provided for seven of the twelve samples. This technique shows promise, but needs to be tested on a larger range of samples, and in other laboratories. However, NMR quantification is expensive.

3.8.7. Method UV

3.8.7.1. Advantages

[52] This method detects BC across most of the BC continuum. The UV photooxidation appears to be “gentler” on BC than the alternative chemical oxidation methods

(Cr_2O_7 and NaClO), as evidenced by the higher BC values reported for the soot and chars (Figure 2). This method has been used extensively to quantify BC in soils, and the BC fraction isolated using this method has been shown to turnover slowly in soils [Skjemstad *et al.*, 2001, 2004].

3.8.7.2. Disadvantages

[53] Positive biases from the coals (26.9–94.3% BC/OC) were recorded with this method. Method UV was used by only one laboratory, and without replication, so it was not possible to gauge intra- or inter-laboratory reproducibility. It uses a specialized, home-built photooxidation apparatus, which is not easy to replicate. The method is also time-consuming and expensive.

4. BC Quantification: Where to Next?

[54] While there have been many intercomparisons of BC quantification for atmospheric samples, this is the first ever wide-ranging intercomparison of BC measurements for soils and sediments. This exercise was not limited to a single sample (as in work by Currie *et al.* [2002]), a single method or a single lab but a much larger effort on behalf of our community. This work may be a first, essential step in filling the gaps in the terrestrial compartment of the global BC budget. Although we lack enough information to interconvert measurements made in a variety of matrices (atmosphere, ocean, soils, sediments), we lay the groundwork for continued method validation, which will make possible the combination of data sets generated in different environments. At present we do not have enough analytical information to assess the quantitative importance in environmental matrices but we can point out several observations, some of which are also highlighted in the conceptual summary (Figure 1, bottom).

[55] 1. Reproducibility within laboratories was often in the typical range observed when analyzing environmental samples, for example, soil amino acids: 5% CV [Stevenson, 1996]. However, reproducibility among laboratories using nominally the same method was not satisfactory. This shows that these methods were sensitive to variations in analytical procedures. Standardization of methods (e.g., temperatures and acid strengths) will decrease variability within methods. However, before standard conditions can be agreed upon, we must determine which conditions give the “best” results. This will not be a simple decision, as there is scope for both under- and over-estimation of BC. Therefore it is not a simple case of choosing which conditions provide the highest or lowest BC values for a given sample. It may also be that different sets of conditions are appropriate for different sample types or different applications. Method refinement will be a continuing feature of BC quantification in the foreseeable future.

[56] 2. The TOT/R method is widely used for measuring atmospheric OC/EC concentrations on filter samples. It is important to note that the samples used in this intercomparison exercise were not provided in a manner (i.e., as solids on filters) similar to typical aerosol collections. Such aerosol analyses are predicated on collecting particles on a filter in situ. We found that attempts to replicate this by resuspending the samples and then filtering were not

successful. As a thermal oxidation method, it can potentially be used to quantify BC in soils and sediments, but would need to be adapted to deal with the problems of transmittance and reflectance related to dark materials, as well as inorganic matrices associated with soils and sediments. Worldwide atmospheric observation networks rely on TOT/R data to link atmospheric BC to climate change through the optical properties of the carbonaceous aerosols. Thus this method best serves the environmental community in the capacity for which it was developed.

[57] 3. The current definition of BC is imprecise. It is variously used to describe either a whole range or spectrum of materials, or only parts of it. Therefore it is not possible to identify a “correct” or “true” BC content for each of the reference materials. However, this is not to say that every method produces an equally valid value. There are two causes of the divergent values of BC content: (1) differing sensitivity to differing BC types and (2) under- and over-estimation of BC due to methodological differences or problems. All of the methods may be subject to the latter, though probably to differing extents. There is a clear need for users of each method to determine the nature, cause and magnitude of these problems.

[58] 4. A complete accounting of the global black carbon budget is compounded by the fact that results from the different methods investigated here did not have consistent values across methods, implying that there is no commonality or simple correlation factors among methods per se. This is to be expected when each BC method is selective for a different part of the BC continuum, for example, soot or highly condensed wood char or more amorphous wood char. For example, for a sample with a 2:1 mixture of char to soot, a factor of 2 difference between methods does not necessarily mean that one method detects only half of the total BC pool; it could simply indicate that one method quantitatively detected the soot third of the pool, while the other quantitatively detected the 2/3 of the pool composed of wood char.

[59] 5. The ultimate value of the various BC quantification methods is not how they compare to one another, but whether they provide useful information for the application for which they are used. BC quantification is not an end in itself, but rather a means to an end. On this criterion, each of the methods has already proven its value. For example, BC contents determined using the CTO-375 method correlated with other combustion markers like polycyclic aromatic hydrocarbons (PAHs) [Gustafsson *et al.*, 1997; Gustafsson and Gschwend, 1998; Persson *et al.*, 2002; Reddy *et al.*, 2002] and the BC fraction isolated UV-photooxidation (UV) has been shown to turnover slowly in soils [Skjemstad *et al.*, 2001, 2004].

[60] 6. To improve comparability between laboratories using the same method and between different methods, we strongly recommend that future BC studies include evaluation of all methods against the set of BC reference materials analyzed here. This recommendation also holds true for future methodological improvements, and the development of novel analytical approaches to quantify BC in environmental samples. Samples outside the set of twelve reference materials used here can also play a role in

future BC method evaluation. We recommend the use of well-characterized, environmentally relevant and readily accessible diesel soot standards from NIST (e.g., SRM 2975). The diesel soot SRM 2975 has been used in numerous studies to quantify BC and complement the laboratory-produced n-hexane soot as well as the urban dust, which contains among other things diesel soot from fossil fuel burning [Gustafsson *et al.*, 2001; Elmquist *et al.*, 2004; Nguyen *et al.*, 2004b; Currie and Kessler, 2005]. Specially prepared filter samples of atmospheric samples such as the prototype filter reference material prepared for the inter-comparison of the urban dust in a separate study [Currie *et al.*, 2002] can be useful to limit errors when using the TOT/R method. One or two other “negative controls,” apart from the melanoidin used here would be useful additions. We do however emphasize the advantages of using the twelve reference materials studied here: (1) their ready availability and (2) the existence of this extensive comparative study data set.

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