Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance

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[1]   Sequestration in sediments of black carbon (BC) from vegetation fires and fuel combustion may constitute a significant sink of otherwise rapidly cycling carbon from the atmosphere-biosphere cycle. It also has the potential to provide a historical record of atmospheric BC loadings. Previous treatments of BC as one homogeneous entity are being replaced with the growing awareness of a BC combustion continuum, a range spanning from slightly charred biomass to soot and graphite. Here the relative recalcitrance of different BC forms is evaluated, and implications for both BC quantification and environmental stability are considered. The stabilities of four BC reference materials against thermal oxidation in air were quite distinct with $T_{50\%BC}$ values (i.e., the temperature where 50% BC remained in the residue) of 444°C (diesel soot–BC), 388°C (n-hexane soot–BC), 338°C (wood char–BC), and 266°C (grass char–BC). The implications for BC quantification have been illustrated for a thermal oxidation (the CTO-375) method commonly applied to study BC in sediments. This technique measured BC:TOC ratios of 78.3 ± 1.3% for the diesel soot–BC and 45.3 ± 6.1% for n-hexane soot–BC, whereas no CTO375-BC was detected for the two analyzed char-BC materials. The greater lability of char-BC compared to soot-BC likely reflects higher accessibility to internal microporosity in char-BC, facilitating internal O_2 transfer. Decreasing the temperature cutoff below 375°C to also include char-BC is not possible as thermograms of nonpyrogenic reference materials indicated that such material would then be artifactually quantified as BC. The presence of mineral oxides in the sediment matrix may lead to a catalytically mediated lowering of the activation energy for soot-BC oxidation but not for char-BC or nonpyrogenic organic material. Several recent studies combine to challenge the proposition of complete recalcitrance of BC. Particularly, the thermal lability of char-BC from grassland fires deserves further attention in order to improve the understanding of BC in the global carbon cycle.

1.   Introduction

[2]   Black carbon (BC) is formed from incomplete combustion of fossil and biomass fuels as well as from vegetation fires and these particles are involved in many important processes throughout the biogeosphere. In the atmosphere, the BC particles affect Earth's radiative heat balance [*Crutzen and Andreae*, 1990] and may be the second most important greenhouse "substance" [*Jacobson*, 2001]. BC

sequestered in sediments and soils has been suggested to represent a sink for carbon from the fast bio-atmospheric cycle and a source for the long-term geological carbon cycle [*Kuhlbusch and Crutzen*, 1995; *Gustafsson and Gschwend*, 1998; *Masiello and Druffel*, 1998]. However, recent studies suggest that at least some portion of the BC may be subject to degradation [*Middelburg et al.*, 1999; *Baldock and Smernik*, 2002; *Hamer et al.*, 2004; *Masiello*, 2004]. In aquatic sediment systems, many hydrophobic organic contaminants sorb 10–1000 times stronger to BC than to non-BC organic matter, affecting the solid water partitioning of contaminants and thereby reducing their bioavailability [*Bucheli and Gustafsson*, 2000; *Accardi-Dey and Gschwend*, 2002; *Cornelissen et al.*, 2005].

[3]   BC is not one chemical compound or a group with well-defined characteristics, but can best be understood

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Figure 1. BC combustion continuum model where T is temperature, P is pressure, and O/C is the atomic oxygen to carbon ratio (modified after *Hedges et al.* [2000] and *Masiello* [2004]. Reprinted with permission from Elsevier).

through the "combustion continuum model" (Figure 1). Combustion products range from slightly charred biodegradable material to highly condensed refractory soot-BC and therefore they possess different physical and chemical properties. Nevertheless, all BC matter shares a common origin as combustion-derived products, which separates them from other types of carbon-rich material.

[4] BC particles can be broadly separated into two groups; soot and char. Soot-BC is formed at high temperatures from the condensation of hydrocarbons in the vapor phase. It consists of a more randomly ordered inner core and a more crystallized outer shell [*Ishiguro et al.*, 1997; *Schmidt and Noack*, 2000; *Gustafsson et al.*, 2001; *Stanmore et al.*, 2001]. The primary soot-BC particles are tens of nanometers in size and cluster together into loose agglomerates of 0.1 to 1 μm size. Char-BC are larger particles (diameter range generally from 1 to 100 μm) and are the solid residue of combustion [*Griffin and Goldberg*, 1975; *Fernandes et al.*, 2003; *Nguyen et al.*, 2004]. They are formed at lower temperatures and therefore the fuel material is not fully altered and some morphological features of the source material may be retained. As a result of their different formation mechanisms, these two BC classes differ also in other physicochemical properties. For instance, the lower formation temperatures for char-BC generally result in higher O/C ratios (presence of heteroatoms) and greater internal microporosity, accessible for diffusion from the exterior by gases such as oxygen. Both of these factors suggest a greater reactivity of char-BC compared to the more recalcitrant soot-BC. This difference in lability of different BC forms is likely to impact both the operational returns of different BC quantification methods and the longevity of different BC forms in the environment. The main objective of this study is to evaluate the relative recalcitrance of different BC forms as this carries considerable implications for determining both what part of the BC spectrum that is actually quantified by different methods as well as for the environmental stability of BC. To this end, this study (1) tests the thermal oxidation stabilities of several soot-BC reference materials and of several char-

BC reference materials, (2) models the relative thermal stabilities of BC-containing material, and (3) further investigates the influence of matrix-assisted mineral-catalyzed BC oxidation.

2. Methods

2.1. Chemothermal Oxidation Method

[5] Chemothermal oxidation at 375°C in air (CTO-375 method) has been broadly used for the quantification of BC,
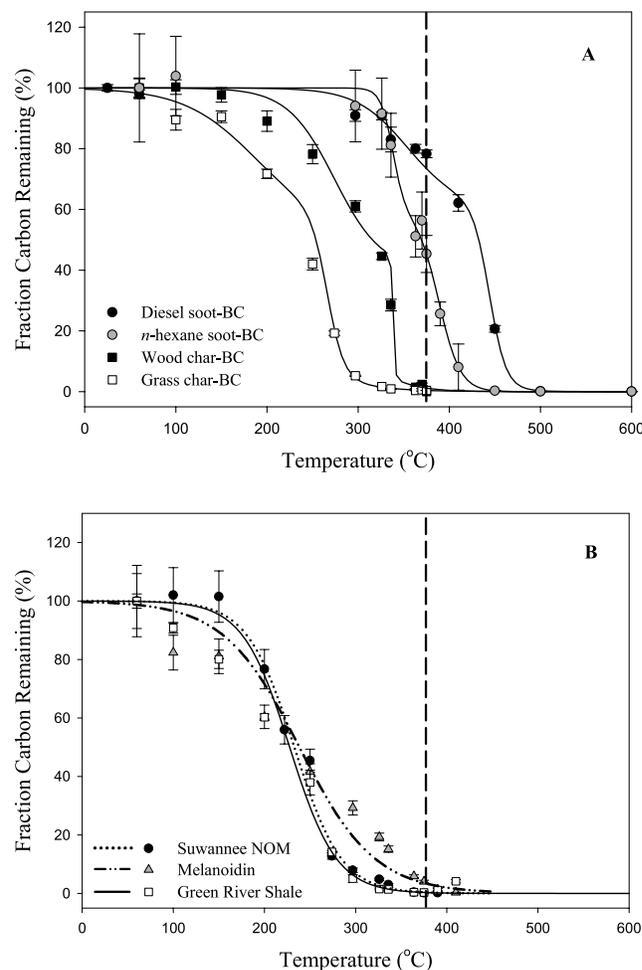
Figure 2. CTO method thermograms for (a) positive BC material and (b) negative BC material, showing the mass percentage carbon remaining after chemothermal oxidation at various temperatures. Positive reference materials displayed are diesel soot-BC SRM-2975 (solid circles), *n*-hexane soot−BC (gray circles), wood char−BC (solid squares), and grass char−BC (open squares). The negative standard materials are represented by Suwannee natural organic matter (solid circles), synthetical melanoidin (gray triangles), and Green River shale (open squares). For comparison of the various materials with each other, a Boltzmann sigmoidal function was fitted to the data (equation (1)). Error bars represent one standard deviation of triplicate measurements, and the dashed vertical line indicates a combustion temperature of 375°C.
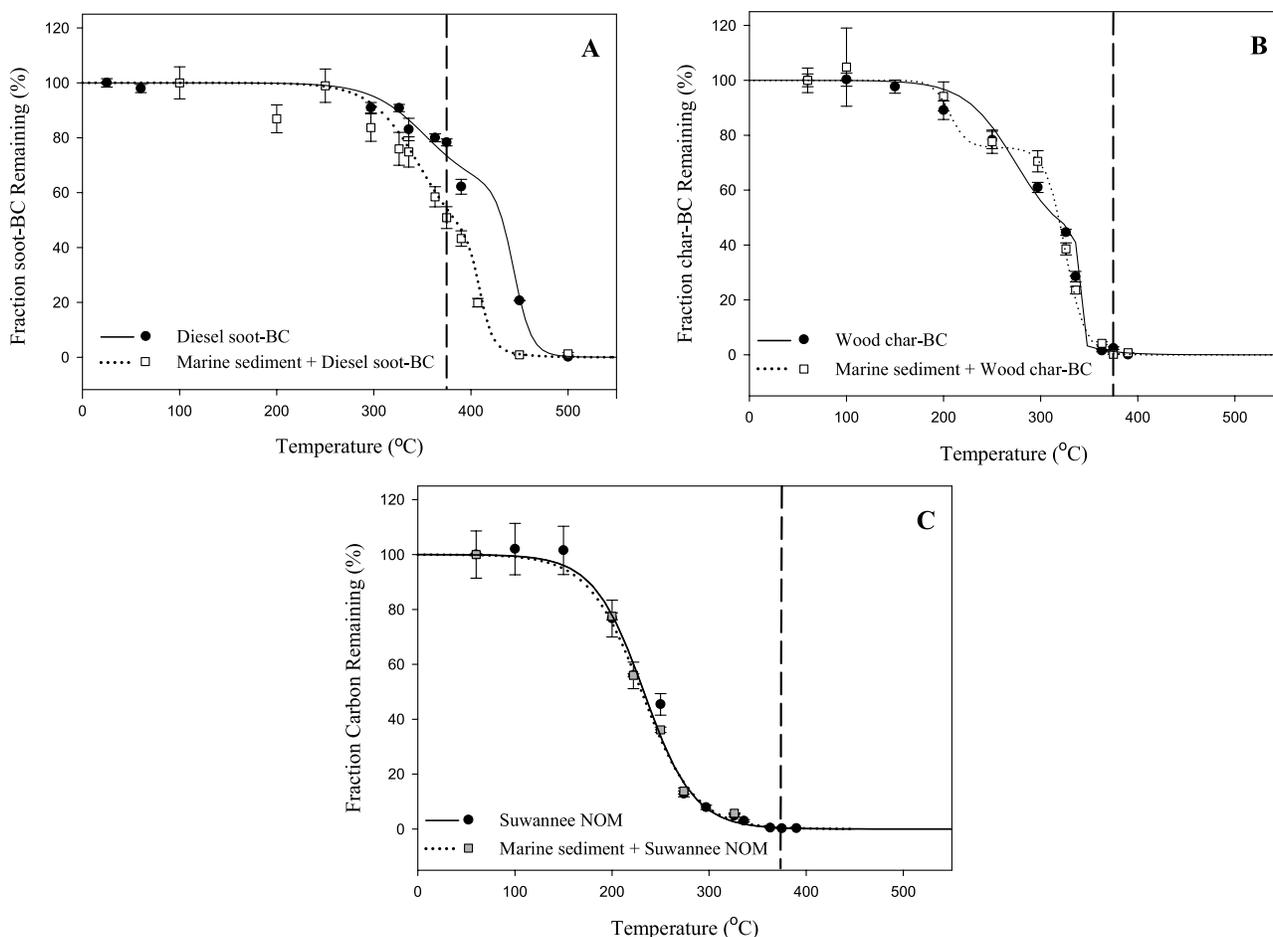
Figure 3. Evaluation of matrix-assisted oxidation. (a) Thermograms for the reference diesel soot-BC SRM-2975 in pure form (solid circles) and mixed with precombusted marine sediment SRM-1944 (open squares). (b) Thermogram for the reference wood char–BC in pure state (solid circles) and mixed with precombusted marine sediment SRM-1944 (open squares). (c) Thermogram for the negative non-BC reference material Suwannee natural organic matter in pure state (solid circles) and mixed with precombusted marine sediment SRM-1944 (open squares). Error bars represent one standard deviation of triplicate measurements. For comparison of the various materials with each other, a Boltzmann sigmoidal function was fitted to the data (equation (1)). The dashed vertical line shows a combustion temperature of 375°C.

mainly in marine sediments; and the methodology has been described in detail elsewhere [*Gustafsson et al.*, 1997, 2001; *Elmquist et al.*, 2004]. Briefly, about 10 mg of sediment (dried and ground for 20 min in automatic ball grinder to ≤100 μm) is weighed into silver capsules (5 × 9 mm, Säntis Analytical, Uppsala, Sweden) and combusted in a tube furnace (375°C, 18 h) under an active airflow of 200 mL min^{-1} to oxidize organic matter. Thereafter, the samples are wetted with 25 μL distilled water and small portions (3 × 25 μL) of 1M hydrochloric acid (HCl) are added to remove carbonates. The remaining carbon after the treatments is quantified as BC with combustion isotope ratio mass spectrometry (Europa Hydra 20/20). For the thermogram study, every parameter was kept constant as in ordinary CTO-375 except the combustion temperature that was varied over the studied temperature interval.

2.2. Thermograms and Black Carbon Stability

[6] Thermograms show the stability of different carbon phases during combustion and are used to find the cutoff temperature between nonpyrogenic organic carbon (OC) and black carbon (BC) material [*Kuhlbusch*, 1995; *Gustafsson et al.*, 1997, 2001; *Nguyen et al.*, 2004]. They are constructed by plotting the mass percent carbon remaining in the residue after combustion over a broad temperature interval (Figures 2 and 3). The materials were divided into positive BC materials (containing both OC and BC material) and negative BC materials (containing OC but are practically void of BC matter). To facilitate comparison of the various materials, a Boltzmann sigmoidal function is fitted to the data (equation (1), modified after *Accardi-Dey* [2003]). Since the positive BC reference materials comprise both OC and BC fractions, an extra term describing BC

Table 1. Characteristics of Studied Materials[a]

Material	TOC, mg gdw^{-1}	BC, mg gdw^{-1}	$T_{50\%OC}$,[b] °C	$T_{50\%BC}$,[b] °C
Positive BC Reference Materials				
Diesel soot SRM-2975	844 ± 9	661 ± 8[e]	354	444
Diesel soot SRM-1650	714 ± 6	457 ± 26	300[d]	427[d]
n-hexane soot	943 ± 120[e]	428 ± 19[f]	338	388
Wood char	760 ± 18	ND	274	338
Grass char	639 ± 14	ND	188	266
Negative BC Reference Materials[g]				
Suwannee River natural organic matter	415 ± 36	0.79 ± 0.052	233	
Green River shale	276 ± 4.7	0.87 ± 0.036	228	
Urea-glucose melanoidin	619 ± 41	25 ± 2.2	238	
Pocahontas bituminous coal	665 ± 86	39 ± 8.5[e]	270	
Beulah-Zap lignite coal	557 ± 14	14 ± 0.35	NA	

[a]Errors represent one standard deviation of triplicate measurements. ND, nondetected; NA, not analyzed.
[b]The $T_{50\%}$ parameter is the temperature when 50% of respective carbon phase (i.e., OC or BC) remains in the residue.
[c]*Gustafsson et al.* [2001] reported a BC concentration of 682 ± 9 mg BC gdw^{-1}, and *Nguyen et al.* [2004] reported a value of 630 ± 41 mg BC gdw^{-1} for the same material.
[d]Data from *Gustafsson et al.* [2001] were used for the calculation of $T_{50\%}$.
[e]Error represents one standard deviation of nine replicates.
[f]*Nguyen et al.* [2004] reported a BC concentration of 440 ± 53 mg BC gdw^{-1}.
[g]Related as negative BC standards, but several of these may contain a minimal amount of geological BC such as pyrofusinite [*Scott*, 2002].

oxidation (whole right-hand term of equation (1), below) is here included in the model. Only the OC term is used for the negative BC materials.

$$FCR = Bottom + \left[\frac{Top_{OC} - Bottom_{OC}}{1 + \exp\left(\frac{T - T_{50\%OC}}{Spread_{OC}}\right)} \right] + \left[\frac{Top_{BC} - Bottom_{BC}}{1 + \exp\left(\frac{T - T_{50\%BC}}{Spread_{BC}}\right)} \right],$$

(1)

where

FCR the fraction carbon remaining in the residue;
Bottom bottom boundary of the thermogram, usually equal to 0%;
Top_{OC} top boundary of the thermogram, equal to 100%;
Top_{BC} (=$Bottom_{OC}$) variable boundary between OC phase and BC phase;
$Bottom_{BC}$ bottom boundary of the thermogram, equal to 0%;
$T_{50\%OC}$ the midtemperature (in °C units) between the top and bottom boundaries of the organic carbon phase;
$T_{50\%BC}$ the midtemperature (in °C units) between the top and bottom boundaries of the black carbon phase;
$Spread_{OC}$ the temperature range for the OC part of the thermogram;
$Spread_{BC}$ the temperature range for the BC part of the thermogram;
T the combustion temperatures of the thermogram study.

When the BC term is included, the "$Bottom_{BC}$" is set to 0% and "$Bottom_{OC}$" equals "Top_{BC}". For the analyzed positive BC samples in pure state (Figure 2 and Table 1), the "Top_{BC}"(= "$Bottom_{OC}$") value was typically in the range

of 40–61%. The Top (100%) and Bottom (0%) boundaries were set to fixed values whereas the $T_{50\%}$ and the spread were used as variables. The curve fitting was performed by minimizing the sum of the squared residuals between measured and fitted values of FCR.

2.3. Positive BC Materials

[7] The positive BC materials tested are of both soot-BC and char-BC types (Figure 2a and Table 1). The U.S. National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) provides standard reference material (SRM) of diesel particulate matter from the exhausts of an industrial forklift truck (SRM-2975) and diesel particulate matter from a truck (SRM-1650). The properties of these SRMs are extensively described in each material certificate [*National Institute of Standards and Technology (NIST)*, 1991, 2000] and elsewhere [e.g., *Gustafsson et al.*, 2001]. Another soot-BC reference material was prepared under laboratory conditions from combustion of *n*-hexane (distributed by D. Smith, Denver, USA, as part of a BC intercomparison study, www.geo.unizh.ch/phys/bc/index.html).

[8] A different group of positive BC materials are the chars. This group has not previously been extensively tested with the CTO method mainly due to lack of representative reference materials [*Jonker and Koelmans*, 2002; *Fernandes et al.*, 2003; *Nguyen et al.*, 2004]. Two char-BC materials, which were distributed for the BC intercomparison study in 2004, are investigated here. Lignocellulosic char-BC was prepared by combustion at 450°C (held for 5 hours) of wood from Chestnut trees (wood char–BC) in nitrogen atmosphere (500 mL h^{-1}). A second type of char-BC was made from combustion of rice straw (grass char–BC) under identical conditions as described above (both chars were provided by M.W.I. Schmidt and K. Hammes, Zürich, Switzerland, www.geo.unizh.ch/phys/bc/

Table 2. Characteristics of Environmental Matrix Samples

Environmental Matrix	Reference ID	TOC, mg gdw^{-1}	BC, mg gdw^{-1}	
			Direct CTO-375	Standard Additions CTO-375
Marine sediment from Baltimore Harbor	SRM-1941b	29.7 ± 0.32	5.7 ± 0.28[a]	3.8 ± 1.5[b]
Sediment from New Jersey/New York waterways	SRM-1944	42.0 ± 1.5	8.6 ± 1.2[c]	7.2 ± 0.60[b]
Urban dust from Washington, D. C.	SRM-1649a	168 ± 3.2	18.3 ± 0.27[d]	15.8 ± 1.6[b]

[a]Previously published values have been measured with the CTO-375 method to 5.8 ± 0.5 [*Gustafsson et al.*, 2001].

[b]Standard deviations were calculated from the uncertainty of the *y* intercept as extrapolated from the linear regression achieved from triplicate measurements at each concentration level.

[c]Previously published values have been measured with the CTO-375 method to 6.6 ± 1.6 [*Gustafsson et al.*, 2001], 8.0 ± 0.2 [*Reddy et al.*, 2002], and 4.4 ± 0.6 [*Nguyen et al.*, 2004].

[d]Previously published values have been measured with the CTO-375 method to 13.6 ± 0.7 [*Gustafsson et al.*, 2001] and 14.0 ± 0.1 [*Reddy et al.*, 2002].

index.html). These two synthetic chars were produced at relatively low combustion temperature [e.g., *Nguyen et al.*, 2004].

2.4. Negative BC Materials

[9] The negative BC materials are nonpyrogenic carbon-rich matter that is void, or practically void, of any BC. In this study, the following negative materials were tested: urea-glucose melanoidin (prepared by K. Hammes, Zürich, Switzerland), Suwannee River natural organic matter (Suwannee NOM; International Humic Substances Society, St. Paul, MN, USA), Green River shale SGR-1 (U.S. Geological Survey, Denver, CO, USA) (Figure 2b). Two coals of different maturity, Pocahontas bituminous coal and Beulah-Zap lignite (Argonne National Laboratory, Argonne, IL, USA), were also included. Properties of these coals are extensively described in each certificate and elsewhere [*Vorres*, 1990]. For instance, the O/C (oxygen to carbon ratio) varies between the two coals with 0.02 for Pocahontas bituminous coal and 0.21 for Beulah-Zap lignite.

2.5. Environmental Matrices

[10] Environmental materials contain BC and are here represented by urban dust from Washington D.C. (SRM-1649a), marine sediment from Baltimore Harbor (SRM-1941b) and sediment from New Jersey/New York waterways (SRM-1944) (Table 2). SRM-1649a has a total organic carbon (TOC) reference value of 176.8 ± 1.9 mg gdw^{-1} whereas the TOC values for the two sediments are 29.9 ± 2.4 mg gdw^{-1} (SRM-1941b) and 44 ± 0.3 mg gdw^{-1} (SRM-1944) [*NIST*, 1999, 2001, 2004a]. While their BC contents have been reported (Table 2), none of them have NIST-certified BC concentrations. An NIST certified value is a value for which NIST has the highest confidence in its accuracy where all known or suspected sources of bias have been investigated or accounted for by the NIST.

## 2.6. Synthetically Mixed Matrices to Test Smearing Effects and Catalyzed Oxidation

[11] Earlier studies have shown an enhanced BC oxidation when positive BC material is mixed with sediment [*Accardi-Dey*, 2003; *Elmquist et al.*, 2004; *Nguyen et al.*, 2004]. This enhanced oxidation has been proposed to be the result of increased oxygen accessibility when BC aggregates are broken up and smeared out onto mineral grains. Another possibility is that when certain mineral oxides

within the sedimentary matrix come in close contact with BC particles, they may act as catalysts making the oxidation process more effective by lowering the activation energy [*Elmquist et al.*, 2004].

[12] Several mixtures were prepared to test the importance of smearing and mineral-catalytic effects using the CTO-375 method (Figure 3). The first types of mixed matrices were made by adding about 3% of diesel soot–BC (SRM-2975) or wood char–BC into two portions of silica (silica gel 6, Merck). The mixtures were first mixed with a spatula and then ground together in an agate mortar with pestle. The second mixed material sample was made with reference sediment SRM-1944 and the following materials were mixed with this sediment: diesel soot–BC (SRM-2975, SRM-1650), wood char–BC, grass char–BC, melanoidin and Suwannee NOM. The silica-amended materials were used to test the smearing effect, while the sediment mixtures were used to test the combined smearing and mineral-catalytic effect. Both the sediment and the silica were precombusted (600°C, 18 h) to remove all natural organic matter and native BC before the mixtures were prepared. The mass percent of added material for all BC and non-BC mixtures was kept at concentrations of 2–5%. Triplicate subsamples were taken from samples standing in room temperature at 25°C or heated at various temperatures between 60°C and 600°C for 18 h (Figure 3).

2.7. Standard Additions Approach

[13] The standard additions method is a more elaborate version of the CTO technique to quantify BC in sediments and it has also been used to look at the efficiency of the standard CTO-375 method [*Elmquist et al.*, 2004]. Briefly, a positive standard reference material, here represented by diesel soot–BC (SRM-2975), was added in incremental amounts to sediments (SRM-1941b and SRM-1944) and to urban dust (SRM-1649a). The mixtures were first mixed with a spatula and then ground together with an agate mortar and pestle until no lumps or aggregates were visible. Thereafter, subsamples were taken for quantification by CTO with combustion temperatures of 375°C and in one case 360°C. The SRM-2975 was added to reference sediment SRM-1941b with the following starting concentrations: 4.9, 14.0, 21.2, 27.4 and 34.6 mg BC gdw^{-1} and for the other reference sediment, SRM-1944, the starting concentrations were: 2.9, 5.8, 10.0, 20.9 and 31.1 mg BC gdw^{-1}. The standard soot-BC concentrations resulting after addi-
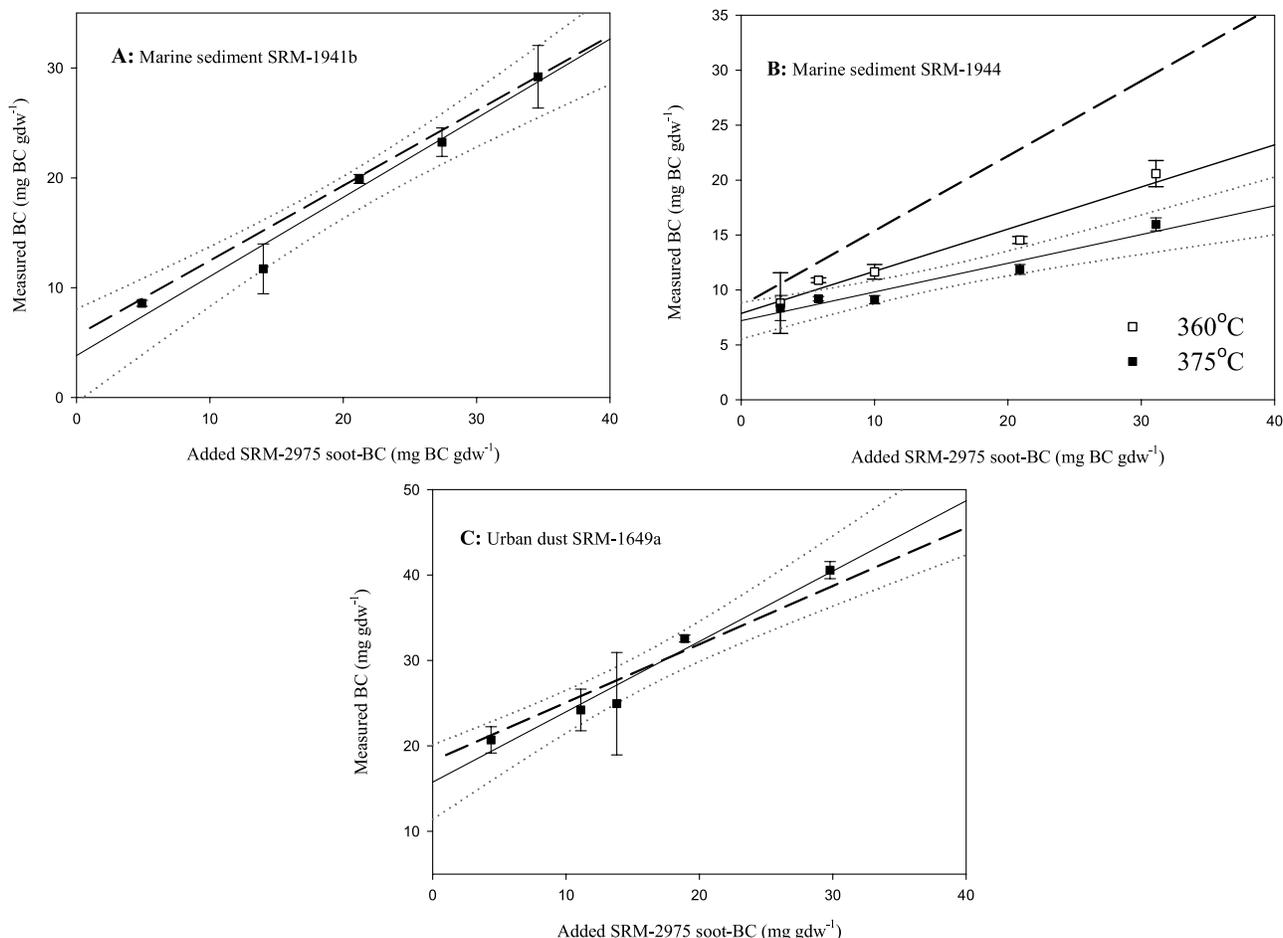
Figure 4. Standard addition curves for incremental amounts of SRM-2975 diesel soot−BC added to three separate reference materials of ambient geomatrices: (a) marine sediment SRM-1941b, (b) marine sediment SRM-1944, and (c) urban dust SRM-1649a. Solid lines represent linear regression for the CTO-360 and CTO-375 experiments. Dashed lines represent predicted BC from additions of SRM-2975, based on a BC concentration of the pure SRM-2975 standard of 68.2 ± 0.9% [*Gustafsson et al.*, 2001]. Error bars show one standard deviation of triplicate measurements. The regression line for the CTO-375 method (solid black line) is shown with its 95% confidence interval (dark gray dotted line).

tions of SRM-2975 to urban dust SRM-1649a were: 4.4, 11.1, 13.8, 18.9 and 29.8 mg BC gdw^{-1}. The original native BC content of each environmental matrix is then given by the y intercept in a plot of measured total BC concentration after chemothermal oxidation (y axis) and added soot-BC concentration from SRM-2975 (x axis) (Figure 4). All soot additions were recalculated to their respective BC concentration, from the SRM-2975 additions, and the BC concentration applied for SRM-2975 was 68.2% ± 0.9% [*Gustafsson et al.*, 2001]. The dashed line in Figure 4 represents the predicted total concentration of BC, coming from both the added soot-BC from SRM-2975 and the natural concentration in sediment or urban dust. The starting values for the different materials were measured with ordinary CTO-375 method to be 5.7 ± 0.28 mg BC gdw^{-1} (SRM-1941b), 8.6 ± 1.2 mg BC gdw^{-1} (SRM-1944) and 18.3 ± 0.27 mg BC gdw^{-1} (SRM-1649a) (Table 2). The recovery of SRM-2975 soot-BC is determined from com-

paring the regression slopes of the dashed line with the linear return from the standard additions approach (Figure 4).

3. Results and Discussion

3.1. Thermograms: Varying Stability of Different BC Forms and Resulting Cutoff Between Positive and Negative BC Materials

[14] A thermogram shows the fraction carbon remaining (FCR) in the residue of a sample subjected to increasing combustion temperatures. With the operational cutoff temperature of 375°C, the SRM-2975 diesel soot−BC FCR is 78.3 ± 1.3% (Figure 2 and Table 1). Other studies have measured similar FCRs of 78.2 ± 1.1% [*Gustafsson et al.*, 2001] and 78.3% [*Nguyen et al.*, 2004] for this same sample. The thermally resistant phase is the soot-BC whereas the oxidized organic carbon probably comes from an organic coating that condenses on the particle as the

temperature decreases further away from the combustion flame [*Hamins*, 1993; *Gustafsson et al.*, 2001]. The FCR after combustion at 375°C is lower for *n*-hexane soot-BC of 45.3 ± 6.1%. Neither of the two char-BCs contained any carbon that was thermally resistant at 375°C, even though the wood char shows a higher thermal stability than grass char by the appearance of their thermograms (Figure 2a). Solid state ^{13}C nuclear magnetic resonance cross-polarization analysis (^{13}C NMR CP) did not reveal any major difference in aromatic intensity between the two chars [*Hammes et al.*, 2005]. The two materials also had similar H/C and O/C atomic ratios. For the wood char, a temperature of 350°C would be necessary to detect any carbon remaining in the residue and the temperature would have to be even lower for the grass char (Figure 2a). Lowering the cutoff temperature of the CTO method to such values would cause unwarranted inclusion of NOM into the quantified BC fraction (Figure 2b), and is thus not possible. The $T_{50\%BC}$ values were modeled for the positive BC materials with equation (1) and ranged from 444°C to 266°C in the order diesel soot–BC > *n*-hexane soot-BC > wood char–BC > grass char–BC (Table 1).

[15] The slope of the thermogram holds information on the homogeneity of the sample. Here, the *n*-hexane soot-BC has steeper slope than the diesel soot–BC (SRM-2975) (Figure 2a). Also, the two chars show oxidation over a large temperature interval (Figure 2a). A homogenous material oxidizes more uniformly at a similar starting temperature while heterogeneous materials oxidize at a range of temperatures most likely because they contain carbon phases spanning a greater range in bond strengths. Structural differences between BC types may be explained by differences in source material, combustion temperature, durations and atmosphere, all affecting the carbonization degree [*Czimczik et al.*, 2002; *Baldock and Smernik*, 2002]. Also, the reactivity of different carbon phases during combustion reflects the density of free-edged carbon sites and the presence of heteroatoms, with higher occurrence of either leading to increased reactivity [*Rodriquez-Reinoso et al.*, 1974; *Radovic et al.*, 1983]. The lower the concentration is of such carbon sites, the more energy is needed to break the strong internal carbon-carbon π bonds in order to oxidize the material. The steeper slope seen in the thermogram for the *n*-hexane may thus reflect the formation conditions with a single source material and controlled flame combustion. The structurally more heterogeneous starting materials of diesel, wood and grass lead to BC material with various functional sites, which require different activation energies to oxidize. Hence the thermograms of the diesel soot–BC and the two tested char-BCs show oxidation over a larger temperature range.

[16] Another important factor that controls the oxidation rate is the tertiary structure of BC. Soot-BC particles are primarily made up by two different nanostructures with an outer shell and an inner core [*Ishiguro et al.*, 1997; *Gustafsson et al.*, 2001]. The inner core is randomly ordered due to a rapid decrease in formation temperature while the outer shell contains graphene sheets that are oriented parallel to the external surface. This shell structure limits the oxygen transfer to the inner oxidation sites of the particle. The char-BC on the other hand, lacks this shell structure, which may explain part of its lower resistance toward higher combustion temperatures (Figure 2 and *Nguyen et al.* [2004]). When the fuel material that is combusted is of solid state (e.g., wood, grass, leaves), the resulting BC phase has increased microporosity, leading to higher oxygen accessibility as compared with BC phases stemming from combustion of liquid fuels (e.g., oil and natural gas). Plant-derived chars have been shown to have lower aromatic content and lower volatility compared with fossil fuel derived soots [*Fernandes et al.*, 2003]. This will have an effect on the structural organization of the aromatic sheets leading to a less ordered matrix that can be more easily broken down by thermal treatment.

[17] The BC formation temperature also plays an important role in determining its survival potential during the CTO thermal treatment. For instance, *Nguyen et al.* [2004] found that chars produced at higher temperatures (e.g., 900°C or 1000°C) survived the CTO method to a higher degree than chars formed at moderate temperatures (e.g., <750°C). For comparison, the two char-BC materials, prepared for the BC intercomparison study and used here, were produced at significantly lower temperatures (450°C). For the high-temperature chars, 44% carbon was detected as BC with the CTO-375 method compared with 0% for low-temperature chars [*Nguyen et al.*, 2004]. Also, the low-temperature chars had a higher O/C ratio compared with high-temperature chars, 0.16 and 0.02 respectively, and higher percentage of hydrogen within the structure [*Nguyen et al.*, 2004]. This latter observation is consistent with heteroatoms affecting BC reactivity [*Rodriquez-Reinoso et al.*, 1974; *Radovic et al.*, 1983]. This information is of particularly high relevance for the environmental cycling/recalcitrance of BC since natural wildfires produce BC material at various formation temperatures with a range from smoldering grassland fires (50°C to 80°C) to hot scrubland fires (700°C to 1000°C) [*Schmidt and Noack*, 2000]. Hence it may be anticipated that thermal oxidation-based "soot-BC" methods would detect less of the BC produced from grassland fires, and that grassland-produced BC would have a lower recalcitrance than BC from scrubland and forest fires.

[18] Suwannee NOM, synthetic melanoidin, Green River shale (GRS) and two coals of different maturity (Pocahontas bituminous coal and Beulah-Zap lignite) represented the negative BC materials. Negative BC materials interfere with BC quantification if they are not completely removed during combustion. The GRS and the Suwannee NOM were completely removed at 375°C with FCR of 0.2 ± 0.02% and 0.3 ± 0.01%, respectively (Figure 2b). Therefore they clearly do not interfere with the CTO-375 method. Melanoidin measured a FCR of 4.1 ± 0.5% after combustion at 375°C. Also, the Pocahontas and the Beulah-Zap coals had FCRs of 5.9 ± 1.5% and 3.4 ± 0.1%, respectively. Given that soot-BC has a FCR on the order of 60% (as for SRM-2975 and *n*-hexane), such carbon forms would only interfere with soot-BC quantification if they were 10 times more abundant than soot-BC in a sediment sample. The relatively high coal FCR could either reflect coal carbon matter that is not completely removed during the thermal

treatment or remnants of ancient BC incorporated during coal formation [*Dickens et al.*, 2004]. It should further be noted that a previous study reported lower FCRs for two very similar materials with values of only 0.45% (Pocahontas bituminous coal) and 0.031% (Beulah-Zap lignite) [*Gustafsson et al.*, 1997]. For this study, new ampoules from the Argonne National Laboratory were broken and analyzed within a few months time whereas the two coals used in the *Gustafsson et al.* [1997] study had been stored for a longer time period. So, this discrepancy could be an effect of differences in storage of the coal materials.

[19] Three environmental matrices of unknown ambient BC concentrations were also analyzed with the CTO-375 method (Table 2). The sediment SRM-1941b contained 5.7 ± 0.28 mg BC gdw^{-1} and the sediment SRM-1944 revealed a slightly higher BC concentration of 8.6 ± 1.2 mg gdw^{-1} (Table 2). The BC concentration of the urban dust SRM-1649a was measured to be 18.3 ± 0.27 mg gdw^{-1}. These environmental matrices all showed BC concentrations that were consistent with values reported in earlier studies [*Gustafsson et al.*, 2001; *Currie et al.*, 2002; *Reddy et al.*, 2002; *Nguyen et al.*, 2004].

3.2. Matrix-Assisted Oxidation

[20] The sediment matrix may facilitate the oxidation of BC particles during combustion due to increased oxygen accessibility when the BC aggregates are smeared out onto sediment grains. Also, metal oxides and possibly the composite of metal oxides and chloride may increase soot-BC oxidation [*Elmquist et al.*, 2004]. In fact, these processes are used exactly for this purpose in the regenerative filters of exhausts systems [*Ahlström and Odenbrand*, 1990; *Ciambelli et al.*, 1990; *Mul et al.*, 1995; *Neeft et al.*, 1996b; *Neri et al.*, 1997]. A similar soot-BC oxidation enhancement may be occurring between certain mineral oxides (e.g., V_2O_5, CuO, K_2O, Fe_2O_3 [*Ahlström and Odenbrand*, 1990; *Neri et al.*, 1997]) and BC particles during the CTO-375 method (CuO [*Elmquist et al.*, 2004]). These two effects (smearing and catalytic oxidation) may cause some underestimation of the BC concentration in a sediment sample [*Accardi-Dey*, 2003; *Elmquist et al.*, 2004; *Nguyen et al.*, 2004]. The thermograms used in this study for testing such matrix-assisted oxidation are shown in Figure 3.

[21] The FCR obtained for sediment-amended soot-BC (SRM-2975) was significantly lower than the FCR of the pure-state soot-BC (paired *t* test, $\alpha = 0.05$, n = 9). The model-derived $T_{50\%BC}$ values for these measured data were 444°C for pure-state soot-BC and 409°C for soot-BC mixed with precombusted marine sediment (SRM-1944) (Figure 3a). Similar results were obtained for another diesel soot–BC (SRM-1650) where the modeled $T_{50\%BC}$ decreased from 427°C for the pure-state material to 411°C when amended with sediment (data not shown in Figure 3), these latter values being statistically lower (paired *t* test, $\alpha = 0.05$, n = 9). In contrast, the FCR of pure-state char-BC for the wood char–BC mixtures was not significantly different from the FCR of sediment-amended char-BC (paired *t* test, $\alpha = 0.05$, n = 9). Thus no "matrix-assisted oxidation" could be established for char-BC (Figure 3b). Similarly, there was no matrix-assisted oxidation observable when testing the Suwannee NOM in pure and in sediment-amended form (paired *t* test, $\alpha = 0.05$, n = 6; Figure 3c). The grass char–BC and melanoidin mixtures led to inconclusive results as they revealed higher $T_{50\%}$ values when sediment was amended than when measured in the pure state. Conclusively, only the two diesel soot-BC materials were affected by matrix-assisted oxidation whereas the other tested materials were unaffected. On the basis of the mechanisms elaborated below, we hypothesize that this difference in matrix-assisted oxidation of soot versus char-BC stems from char-BC having already been oxidized at lower temperatures and thus been removed before the temperature interval is reached where mineral catalysis becomes significant. Catalytic soot-BC oxidation has been reported to start at temperatures of 350°C to 500°C depending on which catalyst system that is studied [*Ahlström and Odenbrand*, 1990; *Mul et al.*, 1995; *Neeft et al.*, 1996b].

[22] Mixtures were also made of SRM-2975 diesel soot–BC with silica and wood char–BC with silica in order to investigate if there is any smearing effect when the BC aggregate is distributed over a larger surface. The FCR of the silica-amended soot-BC (data not shown in Figure 3) was statistically lower from the FCR of the pure-state soot-BC, but not from the FCR of the sediment-amended material (paired *t* test, $\alpha = 0.05$, n = 9). So, mixing soot-BC with either silica or sediment lowers its oxidation temperature. For char-BC, no effect of mixing with silica (data not shown in Figure 3) or sediment could be statistically identified (paired *t* test, $\alpha = 0.05$, n = 9). This study of matrix-oxidation suggests that either there is only a smearing effect for the tested soot-BC mixtures when amended with another matrix or, alternatively, SiO_2 also acts to catalyze soot-BC oxidation. In fact, *Wang and Haynes* [2003] found a soot oxidative effect of SiO_2 when testing different metal oxides and metal chlorides, though the effect was in the lower rank of the tested substances. If there were solely a smearing effect occurring, it would probably have been present for char-type BC as well, since both soot-BC and char-BC materials tend to coagulate into lumps in the pure state, while being broken up when mixed with silica.

[23] The catalytic effect acts through the ability of carbon to adsorb metal-bound oxygen atoms faster than molecular-bound oxygen [*Mul et al.*, 1995; *Neri et al.*, 1997; *Stanmore et al.*, 2001]. The reaction is often thought to proceed through a reduction/oxidation mechanism where (1) the metal oxide is reduced by soot and (2) this metal catalyst is reoxidized by air [*McKee*, 1970; *Ciambelli et al.*, 1994]. Important aspects for this mechanism to be effective are the physical separation distance between soot and the metal oxide and the strength of the metal-oxygen bond [*Neeft et al.*, 1996a]. Also, the so-called "wetting" process (i.e., impregnation of chloride salts on oxides) can significantly improve the catalytic activity by facilitating the interaction between metal oxide and the soot surface, resulting in participation of a larger portion of the soot surface in the oxidation process [*Wang and Haynes*, 2003]. This Cl "wetting" effect is consistent with recent results showing enhanced matrix-assisted soot-BC oxidation in marine sediment (Cl rich) as compared with lacustrine sediment [*Elmquist et al.*, 2004]. The higher catalytic activity mea-

sured between mineral and soot-BC compared with char-BC may be due to (1) differences in surface properties with soot-BC having lower concentrations of heteroatoms and less free-edged carbon atoms and (2) the catalytic effect being more effective at higher temperatures. Oxidation of soot-BC requires higher combustion temperatures [*Nguyen et al.*, 2004] and therefore this catalytic activity may be more active for soot-BC than for char-BC. Chars generally have larger specific surface area (median of 201 m^2 g^{-1}) compared with soot-BC material (median 63 m^2 g^{-1}) and may therefore be more thermally labile [*Cornelissen et al.*, 2005].

[24] The mixed matrices tested in this study were prepared under dry conditions. For the future, it would be of interest to test the effect of wet mixing the BC material with sediment instead of the presently employed dry conditions.

3.3. Standard Additions Approach

[25] The CTO standard additions approach has proved useful in investigating potential matrix effects in the direct CTO method [*Elmquist et al.*, 2004]. Here, this approach was applied to three common environmental matrix reference materials; two sediments (SRM-1941b and SRM-1944) and one urban dust (SRM-1949a). There were linear returns of the added soot-BC (SRM-2975) in the measured BC concentration for all three materials (Figure 4). The resulting soot-BC concentration determined in sediment SRM-1941b with this approach was 3.8 ± 1.5 mg BC gdw^{-1} (Figure 4a and Table 2) while the direct CTO-375 method gave a value of 5.7 ± 0.28 mg BC gdw^{-1}. For the other marine sediment, SRM-1944, the standard additions technique yielded a concentration of 7.2 ± 0.60 mg BC gdw^{-1}, which should be compared with the direct CTO-375 value of 8.6 ± 1.2 mg BC gdw^{-1} (Figure 4b and Table 2). The urban dust revealed a soot-BC concentration of 15.8 ± 1.6 mg BC gdw^{-1} with the standard additions approach and 18.3 ± 0.27 mg BC gdw^{-1} with the direct CTO-375 method (Figure 4c and Table 2). Taken together, the two methods yielded BC concentrations in substantial agreement, reflecting the robustness of the direct CTO-375 method.

[26] The slopes of the regression lines allow the detection of matrix-assisted oxidation occurring during the standard additions approach (Figure 4). The slope for the sample should be compared with the dashed line, which has a slope of 0.682 ± 0.009, corresponding to the concentration measured in the pure-state diesel soot-BC. The marine sediment SRM-1941b showed a slope of 0.72 ± 0.07 ($r^2 = 0.97$), corresponding to a recovery of added soot-BC of $106 \pm 10\%$. The marine sediment SRM-1944 had a slope of 0.26 ± 0.03 ($r^2 = 0.95$), reflecting a soot-BC recovery of only $38 \pm 4\%$. To investigate the possibility to increase the recovery in this sample, the combustion temperature was lowered to 360°C (Figure 4b). This lower temperature yielded a somewhat higher slope of the regression line of 0.38 ± 0.04 ($r^2 = 0.96$), corresponding to a recovery of $56 \pm 6\%$. However, as discussed above, decreasing the temperature may introduce artifacts from the incomplete removal of nonpyrogenic organic matter (Figure 2b), and is thus not recommended. The urban dust SRM-1649a amended with the same soot-BC had a slope of $0.82 \pm$ 0.09 ($r^2 = 0.97$), giving a soot-BC recovery of $121 \pm 13\%$. So, for two of the environmental matrices, sediment SRM-1941b and urban dust SRM-1649a, the soot-BC recoveries were close to 100% and thus no matrix-assisted oxidation of the soot-BC standard additions took place. The somewhat lower recovery in the marine sediment SRM-1944 likely reflects the mineral-catalyzed oxidation of soot-BC, discussed above, rather than a physical smearing effect since the latter would probably be observed also for the two other matrices. The SRM-1944 sediment has lower Al/Cl mass ratio (3.8) than average crust (623 [*Krauskopf*, 1982]), which show that the chlorine is not bound into the minerals. The inorganic constituents have not been measured for SRM-1941b but sediment collected from the same location (SRM-1941a and SRM-2702) has an Al/Cl ratio of 5.4. The SRM-1944 contains higher mass percentages of Cu and Ti whereas the sediment taken from the same location in Baltimore Harbor contains higher mass percentage of Fe [*NIST*, 1994, 2004b]. Both the higher chlorine content in SRM-1944 and the higher elemental values for some important catalysts may have facilitated the soot-BC oxidation in this sediment.

3.4. Concluding Discussion

[27] Soot-BC particles clearly exhibit greater resistance to oxidation than char-BC particles. We hypothesize that this results from variations across the spectrum/continuum of BC particles in key properties such as density of reactive sites and diffusive accessibility for oxygen to such sites within the particles. The lower stability of char-BCs likely stems from a greater density of both heteroatoms (reflected in higher O/C ratios) and fringe carbons (reflected in lower aromaticity) compared to soot-BC (Figures 1 and 2). Further, the greater internal microporosity of char-BC, resulting from the lower formation temperatures than for soot-BC, makes these sites accessible throughout the three-dimensional volume of the char-BC particle. This contrasts sharply with the graphene sheet shell structure of soot-BC for which the total three-dimensional surface area accessible to, for example, N_2 is very similar to the external two-dimensional surface area as estimated from high-resolution transmission electron microscopy [e.g., *Gustafsson et al.*, 2001].

[28] There is at present no one single method able to quantify the entire continuum of BC particles. The CTO-375 method detects carbon material of high thermal-oxidative resistance and is therefore well suited for quantification of soot-BC, and possibly also for char-BC formed during high combustion temperatures. We note that the two char-BC materials selected for the BC intercomparison study (www.geo.unizh.ch/phys/bc/index.html) and tested in this study, were formed at a temperature (450°C) that was low compared to other studies [e.g., *Nguyen et al.*, 2004]. For instance, scrubland fires are believed to reach 700°C −1000°C [e.g., *Schmidt and Noack*, 2000] and is thus likely to produce a more recalcitrant char-BC form. It has also been demonstrated that char-BC produced at higher temperatures is easily detectable with the CTO-375 method [*Nguyen et al.*, 2004]. The cutoff temperature of the CTO method (375°C) cannot be lowered to recover also a greater portion of the thermally labile char-BC as some nonpyro-

genic carbon would then also be artifactually quantified as BC. Other techniques such as microscopic counting [*Karapanagioti et al.*, 2001] and the benzene polycarboxylic acid (BPCA) method [*Brodowski et al.*, 2005] may be attempted to quantify larger char-BC particles of lower thermal-oxidative stabilities. On the other hand, those techniques may be limited in their ability to quantify fine and hydrophobic soot-BC because of size detection problems (microscopy) and losses during wet solution handling and transfer [*Gélinas et al.*, 2001; *Elmquist et al.*, 2004].

[29] The fraction carbon remaining (FCR) after the CTO-375 treatment of potentially interfering organic matter was low relative to FCR of soot-BC and their relative environmental abundances. While matrix-assisted oxidation for certain samples may bias the BC estimate somewhat toward low values, the standard additions approach demonstrated the robustness of the direct CTO-375 method for quantifying soot-BC in sediments and this may possibly be valid also for soils and aerosols.

[30] Black carbon reference materials in demand for the future include a soot-BC produced from biomass burning. Also, the char-BC spectrum has to be better represented by including naturally produced char-BC and synthetic char-BCs produced at higher temperatures.

[31] The results of the present study are in line with and build on other recent studies, which have implicated the possibility of BC degradation in soils [e.g., *Baldock and Smernik*, 2002; *Hamer et al.*, 2004; *Masiello*, 2004], by establishing that there are large variations in oxidative stabilities across the BC spectrum. This challenges the proposition that biomass-derived BC sequestered in soils and sediments, are a net sink of atmospheric CO_2 [e.g., *Kuhlbusch and Crutzen*, 1995]. To further develop an understanding of the role of BC in the global carbon cycle, this encourages further studies on the lability of BC with special emphasis on differentiating between different forms of this pyrogenic carbon.

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