

Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approaches

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Abstract

The highly condensed products and residues of incomplete combustion of biomass and fossil fuel termed black carbon (BC) partake in a multitude of important geochemical processes. However, ambiguity persists because different quantification methods give highly variable results, leaving it unclear whether this reflects method difficulties or that different methods simply mirror different parts of the BC spectrum. Introducing additional wet chemical ex situ pretreatment steps (Gélinas et al. 2001b), to a commonly applied chemothermal oxidation (CTO) method led to large handling and transfer losses of hydrophobic diesel-soot BC (NIST SRM-2975). The resulting yield of soot BC spiked to a coastal marine and a freshwater sediment was only $6 \pm 1\%$ and $70 \pm 4\%$, respectively, for the entire ex situ procedure. Instead, a standard addition approach yielded statistically significant linear returns of incremental soot BC additions. The slopes suggested that $51 \pm 6\%$ and $78 \pm 6\%$ of the added soot BC was accounted for in the marine and freshwater sediment, respectively. The lower recovery of soot BC in the marine sediment is likely caused by chloride enhancing the contact between BC surfaces and mineral oxides, catalyzing the BC oxidation. A consequential lowering of the oxidation energy from 375°C to 360°C resulted in increased soot BC yields of $75 \pm 7\%$ and $97 \pm 3\%$ in the marine and freshwater sediments, respectively. The standard addition approach suggests a native "soot BC-like" concentration of $0.48 \text{ mg BC/g dry weight}$ (soot BC/total organic carbon = 0.03) in the bioturbated marine sediment from Kosterfjord, Skagerrak and $6.2 \text{ mg BC/g dry weight}$ (soot BC/TOC = 0.10) in the heavily polluted Rhine River sediment.

The term black carbon (BC) is used to describe a relatively inert and ubiquitous form of condensed carbon produced by incomplete combustion of a variety of fossil fuel and biomass materials. These pyrogenic particles play important roles in a multitude of geochemical processes. For instance, BC may be an important component of sedimentary carbon preservation (Goldberg 1985; Gustafsson and Gschwend 1998; Masiello and Druffel 1998; Dickens et al. 2004) and thereby constitutes a valuable record of the global fire history (e.g., Bird and Cali 1998). Sorption of aromatic compounds to BC

is 10 to 1000 times stronger than to nonpyrogenic sedimentary organic matter (e.g., Bucheli and Gustafsson 2000; Accardi-Dey and Gschwend 2002; Jonker and Koelmans 2002; Cornelissen and Gustafsson 2004) and frequently governs the environmental distribution of many organic pollutants (Gustafsson et al. 1997; Gustafsson and Gschwend 1997; Dachs and Eisenreich 2000; Persson et al. 2002; Ribes et al. 2003). In the atmosphere, BC affects Earth's radiative heat balance (e.g., Jacobson 2001) and BC in urban air particles has been implicated as the culprit of epidemiological respiratory diseases and human deaths (Dockery et al. 1993; Künzli et al. 2000; Gerde et al. 2001).

Despite the many important roles played by BC, ambiguity persists as to the level of BC in complex matrices, such as aquatic sediments, as method comparison exercises have proved that different methods yield highly variable results (e.g., Middelburg et al. 1999; Schmidt et al. 2001; Currie et al. 2002). Method artifacts that obviously would return inaccurate results include organic matter charring (overestimation) and losses of hydrophobic soot BC during solution handling

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(underestimation). It is also possible that different methods simply probe different forms of BC.

BC particles exist as a continuum from partly charred plant material through char and charcoal to soot and graphitic-like particles. The BC continuum may be categorized into two classes (soot and char) based on physical and chemical properties, such as particle size, formation temperature, morphology, surface area, density, and carbon/hydrogen (C/H) molar ratio (Goldberg 1985; Kuhlbusch and Crutzen 1995; Schmidt and Noack 2000). Soot are sub-micron particles formed at high temperatures from the condensation of hydrocarbons followed by growth and stacking of aromatic layers, which conglomerate into grape-like structures with a low-crystallized inner core and a well-crystallized outer shell (Ishiguro et al. 1997; Schmidt and Noack 2000; Gustafsson et al. 2001; Stanmore et al. 2001). The spherules are joined together by shared carbon deposition to form loose aggregates of 0.1 to 1 μm size. Chars are larger particles formed at lower temperatures, which means that the source material is not fully destroyed and some morphological features of the original fuel particles can be retained (Griffin and Goldberg 1975; Fernandes et al. 2003; Nguyen et al. 2004). Chars range in diameter from 1 to 100 μm .

There is no generally accepted and universally applicable method to quantify BC in natural matrices, but there are several analytical approaches, including so-called optical, chemical, and thermal methods as well as hybrids thereof. A method striving to quantify BC in sediments has to differentiate between three different types of carbon: inorganic carbonate (IC), thermally unaltered organic carbon (OC), and black carbon (BC). Most approaches involve two steps: (1) demineralization and selective oxidation of non-BC carbon forms and (2) quantification of the residual carbon as BC using various detection methods, such as microscopic counting, titration, coulometry, ^{13}C NMR, and elemental analysis. Since putative problems are believed to be primarily associated with the various pretreatment strategies (Kuhlbusch and Crutzen 1995; Gustafsson et al. 1997, 2001; Middelburg et al. 1999; Schmidt et al. 2001; Currie et al. 2002; Nguyen et al. 2004), this evaluation will focus on wet chemical and dry thermal oxidation procedures, and all BC residue quantifications are here performed with elemental analysis.

The reactivity of carbon phases during oxidation is fundamentally controlled by the density of free-edge carbon and the structural presence of heteroatoms (Rodríguez-Reinoso et al. 1974; Radovic et al. 1983). The oxidation treatment thus attempts to find the oxidative strengths where weaker and more exposed carbon bonds in the amorphous nonpyrogenic organic matter is destabilized while retaining the more condensed aromatic carbon of BC. The oxidation may be performed either with strong oxidants in liquid solutions (so-called "chemical" oxidation) or in an oxidizing atmosphere (e.g., air or O_2) under controlled temperature (so-called "thermal" oxidation). This chemical/

thermal (or wet/dry) oxidation step is accompanied with various forms of treatments to remove carbonates and to minimize risk of matrix effects, such as encapsulation of organic matter by secondary minerals.

The wet chemical pretreatment-wet chemical oxidation (wet-wet) methods (e.g., Wolbach and Anders 1989; Lim and Cachier 1996; Verardo 1997; Masiello et al. 2002; Song et al. 2002) have an advantage over thermal oxidation methods: there is a lower risk of charring. However, the extensive handling of samples in liquid solutions may lead to losses of BC particles, which, due to their hydrophobic character, tend to adsorb to inner surfaces of test tubes and to the water-air interface (e.g., Gélinas et al. 2001*b*). Particularly the fine soot BC may then easily be lost during decanting and subsequent transfer of the sample solution. Another disadvantage with wet chemical oxidation is that the oxidative strength (i.e., cut-off between BC and non-BC) is more difficult to control than in thermal oxidation as it depends on many factors such as concentration of chemical oxidant, type of oxidant applied, and reaction time. Also, the wet chemical oxidation techniques may be extremely time consuming (e.g., Wolbach and Anders 1989; Masiello et al. 2002).

The wet chemical pretreatment-dry thermal oxidation (wet-dry) chemothermal methods (e.g., Kuhlbusch and Crutzen 1995; Gustafsson et al. 1997, 2001; Verardo 1997; Gélinas et al. 2001*b*; Mannino and Harvey 2004) have fundamentally the same putative problems in the wet pretreatment step as the wet-wet methods. However, temperature and gas flow can be easily monitored during combustion, which makes the subsequent thermal oxidation procedure more controllable. A disadvantage with the thermal oxidation strategy is that sediments may undergo charring at elevated temperatures if the oxygen mass transfer is not properly assured, leading to overestimation of BC. Underestimation of BC can also occur if BC particles from the less condensed end of the BC spectrum (char BC) are partly or completely oxidized during the combustion (Jonker and Koelmans 2002; Fernandes et al. 2003; Nguyen et al. 2004).

This current study further evaluates and develops perhaps the most commonly applied method for BC quantification in sediments, the chemothermal oxidation (at 375°C) CTO-375 method (Gustafsson et al. 1997, 2001; Gélinas et al. 2001*b*). This wet-dry method has been applied in a multitude of studies (the original method paper, Gustafsson et al. 1997, is cited 166 times according to the Web of Science database: <http://isi3.isiknowledge.com/portal.cgi/wos>, 21 June 2004). The CTO-375 method involves 18-h thermal oxidation at 375°C of small and well-ground samples in active airflow to oxidize organic matter, and micro-acidification *in situ* in the Ag capsules to remove the carbonates followed by quantification of the residual carbon as BC using elemental analysis. Hence, the basic CTO-375 method is a wet *in situ*-dry method and, thus, circumvents the risk of soot BC handling losses inherent to many wet *ex situ*-dry chemical methods (e.g., Gélinas et al. 2001*b*).

The CTO-375 method has been subjected to extensive testing both in the field and in the laboratory, and our knowledge of its applicability and limitations is continuously growing. Studies with real environmental matrices have provided geochemically consistent measures of BC: (1) radiocarbon dating of CTO-375 isolated BC was well separated from the radiocarbon date of the bulk total organic carbon (TOC) signal but had a radiocarbon value similar to polycyclic aromatic hydrocarbon (PAH) combustion markers (Reddy et al. 2002). (2) The environmental distribution of PAHs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are better correlated with CTO-375 estimates of BC than with TOC, both in lake sediment cores (Gustafsson et al. 1997) and geographically in surface sediments (Gustafsson and Gschwend 1997; Persson et al. 2002). (3) The solid-water and solid-air distribution of PAHs and PCDD/Fs are better explained by CTO-375 quantified BC than by bulk TOC (Gustafsson et al. 1997; Naes et al. 1998; Dachs and Eisenreich 2000; Bucheli and Gustafsson 2001; Persson et al. 2002; Cornelissen and Gustafsson 2004).

Laboratory testing with both positive standards (BC-containing material such as diesel particles and charcoal) and negative standards (potentially interfering nonpyrogenic organic matter such as melanoidin, carbohydrates, proteins and other N-containing compounds, pollen, phytoplankton, wood, kerogen, and coal of increasing degree of maturity) suggest overall good method selectivity with generally low interference/charring potential of the negative standards (Gustafsson et al. 1997, 2001; Gélinas et al. 2001*b*; Accardi-Dey 2003; Mannino and Harvey 2004). Exceptions may be certain phytoplankton and globular proteins (Gustafsson et al. 2001; Gélinas et al. 2001*b*; Accardi-Dey 2003) that indicated larger propensity to char. However, because these may be smaller components of sedimentary organic matter, this may not necessarily constitute a widespread problem. Charring has also been suggested to occur when organic matter is encapsulated within the mineral lattice and therefore physically inaccessible to molecular oxygen during thermal oxidation (Gélinas et al. 2001*b*). Gélinas et al. (2001*b*) therefore added two additional steps upstream of the basic CTO-375 method: (1) demineralization with hydrochloric (HCl) and hydrofluoric (HF) acids to prevent encapsulation effects and (2) removal of hydrolyzable organic matter (HOM; such as proteins and carbohydrate) with trifluoroacetic acid (TFA) and HCl.

Acting in the opposite direction, other laboratory spiking studies have suggested that the CTO-375 method underestimates the BC concentration and that the survivability of condensed carbon standards was related to their size, with smaller particles being less stable and char-BC being less stable than soot BC (Accardi-Dey 2003; Nguyen et al. 2004). Similarly, in a BC analysis intercomparison (Currie et al. 2002), the CTO-375 method measured a lower BC concentration for the analyzed reference material (NIST SRM-1649a) than all other employed methods. This suggests that the CTO-375 method is less prone to charring (or incomplete

oxidation of non-BC organic matter) than other methods but, besides oxidizing organic matter, also may remove some of the less condensed BC particles.

The geochemical importance of BC, combined with the putative overestimation caused by charring or underestimation due to BC oxidation, necessitates further testing and development of the chemothermal oxidation approach to BC quantification. The specific aspects addressed in this paper are (1) thorough testing of the two pretreatment steps proposed by Gélinas et al. (2001*b*) upstream of the basic CTO-375 method, by using a soot BC standard in both *ex situ* and *in situ* systems and (2) exploration of a novel BC standard additions approach to derive accurate estimates of the native BC concentrations in both freshwater and marine sediments.

Materials and procedures

Sampling sites and characteristics of the two test sediments—Two different types of sediments were used in this study. The first type represents marine shelf sediments, which here were underlying oxic bottom water, with a top of 1 to 2 cm oxic. It was collected in the Kosterfjord (58°53' N, 11°06' E), a sub area of the Skagerrak on the Swedish West Coast, with a Kayak corer and the upper 10 cm were combined to a bulk sample. The Kosterfjord area is away from large urban regions so the BC concentration is expected to be low. The following concentrations were determined for the bulk sample: total carbon (TC; inorganic and organic carbon) = 26 mg C/g dry weight (gdw), TOC (containing both black carbon and organic carbon) = 14 mg C/gdw, and total nitrogen (TN) = 1.4 mg N/gdw and pyrene = 0.47 nmol/gdw.

The second sediment was collected in Lake Ketelmeer, the Netherlands, a sedimentation basin of Rhine River. This site (52°36' N, 5°45' E) has densely populated shorelines and industrialized zones upstream so the BC concentration in this anoxic sediment is expected to be high (Cornelissen and Gustafsson 2004). The following concentrations were determined for the bulk sample: TC = 76 mg C/gdw, TOC = 59 mg C/gdw, TN = 2.6 mg N/gdw, and pyrene = 35 nmol/gdw.

The CTO-375 method—The CTO-375 method has been widely used to quantify BC in sediment matrices. Briefly, the sediment is oven-dried at 60°C and ground to fine powder with a ball grinder. Aliquots of 5 to 10 mg of the sediment powder were weighed into precombusted Ag capsules (5 × 9 mm, Säntis Analytical). Thereafter, samples were combusted in a tube furnace (375°C, 18 h) under constant airflow of 200 mL min⁻¹ (Gustafsson et al. 2001). After the samples cooled, they were wetted with distilled water before inorganic carbonates were removed by micro-acidification (1 M HCl; total volume of 75 µL) directly into the Ag capsule. In the original CTO-375 method (Gustafsson et al. 1997), the micro-acidification was performed after the thermal combustion but the order was changed (Gustafsson et al. 2001) to release any encapsulated organic matter before thermal combustion to minimize charring effects. In this study, the micro-acidification is again per-

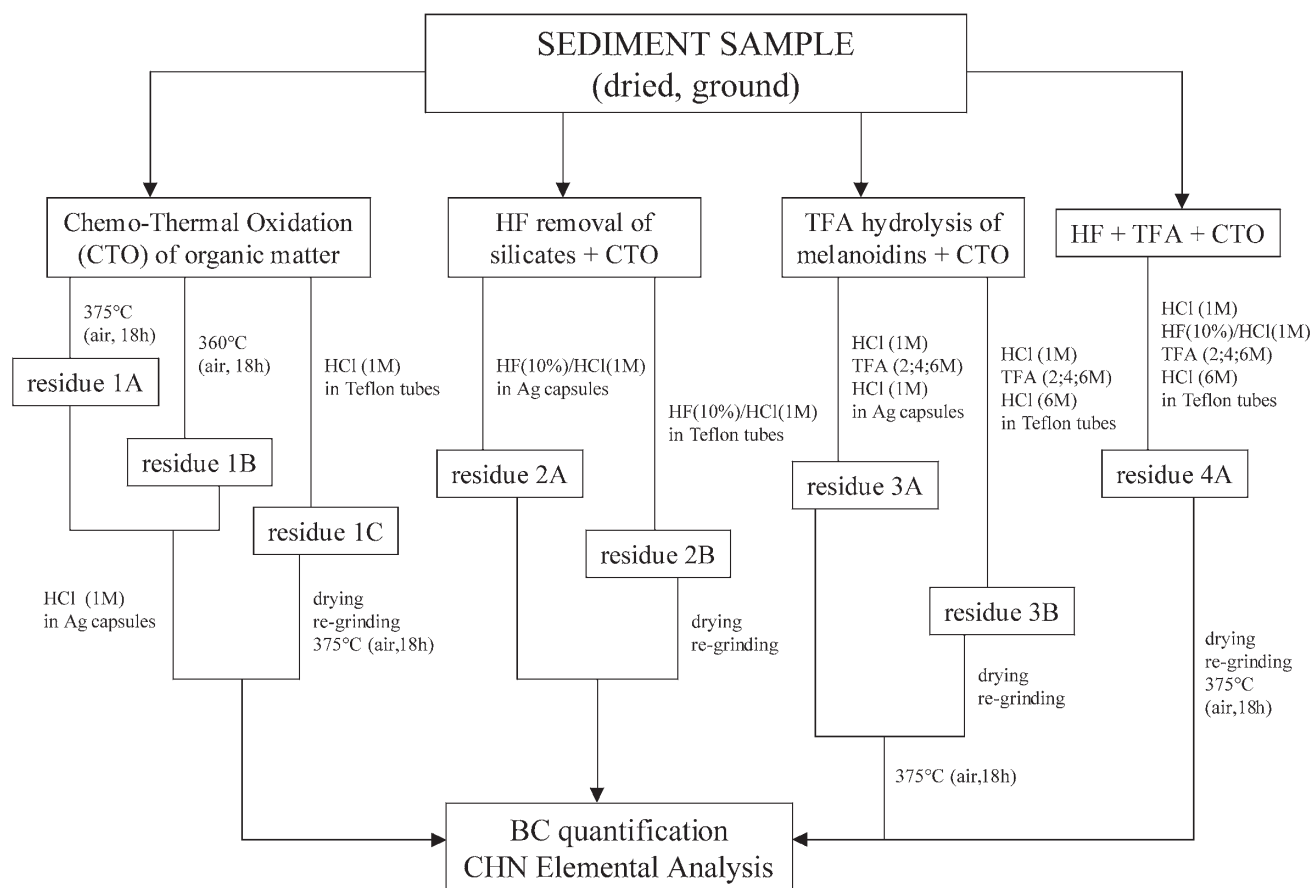


Fig. 1. A schematic of different methods tested in this study for BC quantification in sediments. The three pretreatments CTO, HF dissolution of silicates, and TFA removal of melanoidin-like material, or a combination of pretreatments (HF + TFA + CTO), were performed on both a marine sediment (Kosterfjord) and a freshwater sediment (Lake Ketelmeer) in situ in Ag capsules or ex situ in Teflon tubes. Residual carbon was quantified with elemental analysis as BC.

formed after the thermal combustion because we and others (Mannino and Harvey 2004) have found that micro-acidification prior to combustion may lead to “cake formation,” which potentially limits the oxygen mass transfer in the sediment. The residual BC is measured with an isotope ratio mass spectrometer (Europa Hydra 20/20) (residue 1A; Fig. 1). For comparison, the CTO-375 method was also performed ex situ in Teflon tubes (residue 1C; Fig. 1). Here, 10 mL of 1 M HCl was added to about 1 g sediment weighed into 50 mL Teflon centrifuge tubes (NALGENE Labware, Teflon-fluorinated-ethylene-propylene with closures of Tefzel-ethylene-tetrafluoroethylene). After 60 min at room temperature, the samples were washed (30 mL distilled water) and centrifuged (3000 rpm, 10 min) before the supernatant was discharged. This washing step was repeated twice before the samples were dried (60°C, 24 h) and reweighed. The dry sediment was ground with mortar and pestle to fine powder and sub-samples (triplicates) were combusted (375°C, 18 h) and analyzed for BC.

HF demineralization—Large-scale ex situ method. Hydrofluoric acid (HF) is used to dissolve silicate minerals and release any encapsulated organic matter from the mineral matrix. The

ex situ demineralization performed in Teflon tubes largely follows the protocol described by Gélinas et al. (2001a). About 1 g sediment sample (dried, ground) was weighed into 50-mL Teflon centrifuge tubes and 10 mL 1 M HCl was added. The tubes were left standing at room temperature for 60 min before washing the residue with distilled water (about 30 mL), centrifuging (3000 rpm for 15 min), and discharging the supernatant. After three rinses, 10 mL HF (10% v/v; 5.6 M) and HCl (1 M) mixture was added. The samples were shaken slowly overnight and, the next day, were washed once with about 30 mL distilled water and centrifuged. The supernatant was then discharged, a new 10 mL portion of the HF/HCl solution was added, and the samples were once again placed on the shaker. After a total reaction time of 24 h between HF/HCl and sediment, the samples were rinsed three times with distilled water, dried (60°C, about 24 h), and reweighed. Sub-samples were analyzed for BC (residue 2B; Fig. 1).

Micro-scale in situ method. The hydrophobic character of BC particles makes them adsorb to the water surface and the inner walls of test tubes. Pretreatments performed in test tubes with repeated clean up of the sample create many possibilities

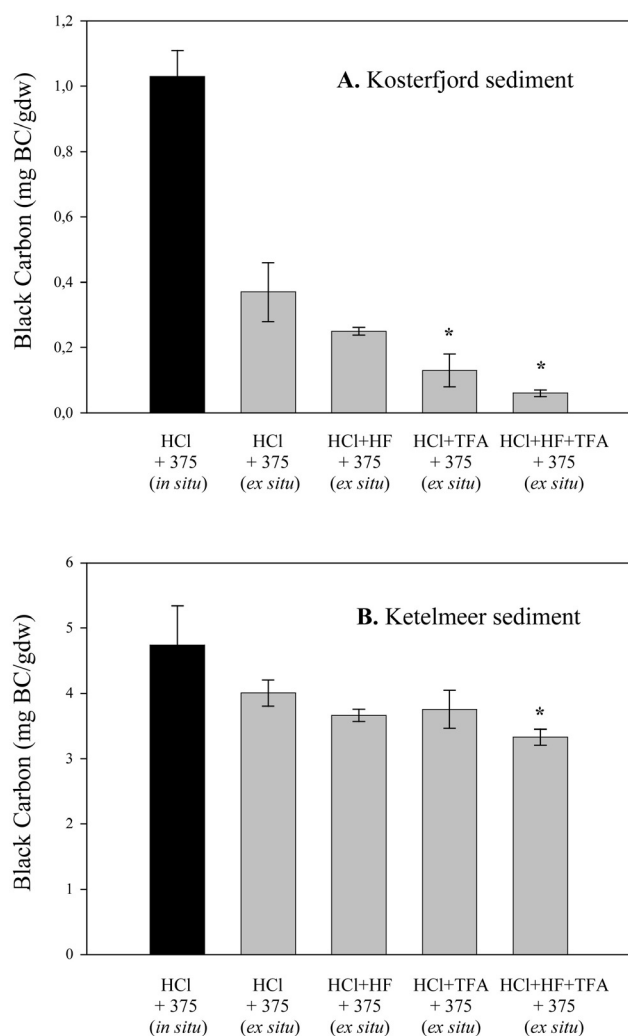


Fig. 2. The resulting estimates of BC concentration for the Kosterfjord (A) and Lake Ketelmeer (B) sediments when different wet chemical methods were performed in Teflon tubes. The basic HCl + 375 treatment is illustrated for both ex situ in Teflon tubes (gray bars) and in situ in Ag capsules (black bar; the standard CTO-375 method), for comparison. Error bars represent one standard deviation of at least triplicate measurements. The asterisk denotes the pretreatments that are statistically separated ($P < 0.05$) from the HCl + 375 method performed ex situ in Teflon tubes for each type of sediment.

for the BC to be lost. So, to minimize the BC losses, an alternative technique was attempted where the HF/HCl was added directly to the sediment in the Ag capsules. About 10 mg sediment sample (dried, ground) was weighed into Ag capsules and placed on a specially made Teflon plate; 100 μ L of the HF/HCl solution was added before a lid was put on and parafilm wrapped around to decrease any vapor loss. The Teflon plate was then placed in a fume hood overnight. Then, new 50 μ L portions of the HF/HCl mixture were added to each sample, the lid was closed, and parafilm was wrapped around it. Total reaction time between HF/HCl and sediment was 24 h and the

mass ratio of the HF/HCl mixture and sediment was kept at 15 to 20. To clean the sediment from acids, the Teflon tray with samples were placed on a hot plate and warmed to evaporate the liquid. Small portions of distilled water were added with a Pasteur pipette. When some of the liquid had evaporated, a new portion of water was added with a total amount of 10 to 15 water drops to each capsule. The samples were dried (60°C, 24 h) before combustion at 375°C, and the residual carbon was treated as coming from BC (residue 2A; Fig. 1).

Removal of hydrolysable organic matter using trifluoroacetic acid—Large-scale ex situ method. It was tested whether trifluoroacetic acid (TFA) additions had any influence on the CTO-375-measured BC concentration. Two different types of treatments were applied to the sediments: (1) HCl and TFA (residue 3B in Fig. 1; Fig. 2), and (2) with all three acids (residue 4A; Fig. 1). The first ex situ treatment involved HCl pretreatment (described earlier) and an additional step of TFA, following G elinas et al. (2001b). After the HCl step, the samples were purged with N₂(g) for 5 min and then 5 mL 2 M TFA was added during continuous supply of N₂(g). The centrifuge tubes were closed, placed in an oven (100°C, 3 h), and thereafter the sediments were washed with about 30 mL distilled water before the 2 M TFA step was repeated. To be certain that all HOM were oxidized during the TFA treatment, additions of 4 M TFA (reaction time of 18 h) and 6 M TFA (reaction time 20 h) were also performed, respectively, under continuous N₂(g) supply. After the last TFA addition, the residual HOM was removed with 5 mL 6 M HCl (110°C, 24 h), washed with distilled water three times, dried (60°C, 24 h), reweighed, and ground to fine powder. Sub-samples were combusted (375°C, 18 h) before analysis of BC.

The second ex situ treatment had, in addition to the above described TFA method, an extra step with additions of HF/HCl. The samples were first treated with 1 M HCl. Then, two consecutive additions of the HF/HCl mixture were performed, as described earlier. After 24 h of total reaction time between HF/HCl and sediment, the samples were washed three times with distilled water and thereafter the TFA method described above was performed following drying (60°C, 24 h), weighing, and grinding of the residue to fine powder. Sub-samples (triplicates) were combusted at 375°C and analyzed for BC.

Micro-scale in situ method. It was also desired to test whether HOM can be removed efficiently with in situ additions directly to small sample sizes in Ag capsules to minimize transfer and handling losses of BC. The ex situ TFA steps described earlier had to be adapted for the small volume of an Ag capsule. Also, a pilot study showed that the capsules became very brittle, and next to impossible to handle if 6 M HCl was used, as suggested for ex situ treatment (G elinas et al. 2001b). For this reason, 1 M HCl was used in the Ag capsule as also proposed by Nieuwenhuize et al. (1994).

About 10 mg sediment (dried, ground) was weighed into Ag capsules and wetted with 25 μ L distilled water before addition of 25 μ L 1 M HCl. After 30 min, another portion of

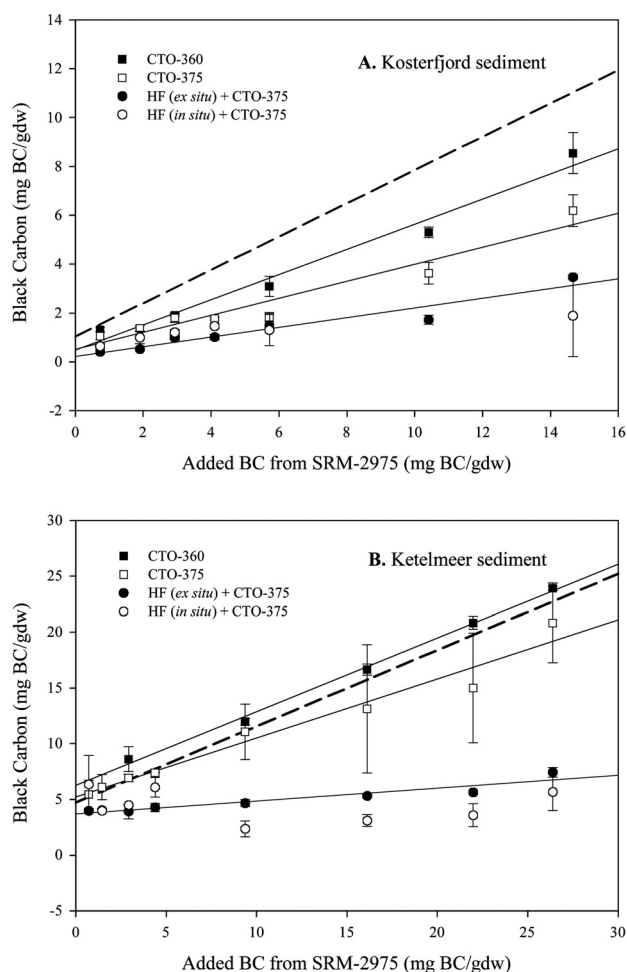


Fig. 3. Standard addition curves of SRM-2975 soot BC added to sediment from the Kosterfjord (A) and Lake Ketelmeer (B). Solid lines represent linear regression for the CTO-360, the CTO-375, and HF + CTO-375 (Teflon tubes), and regression statistics are presented in Table 1. Dashed line represents predicted BC from additions of SRM-2975, based on a BC concentration of the pure standard of 68.2% ± 0.9% (Gustafsson et al. 2001). Error bars show one standard deviation of triplicate measurements.

50 μ L HCl was added, reacted for 30 min, and thereafter another 50 μ L of 2 M TFA was added. The samples were placed in an oven at 60°C. Originally, a temperature of 100°C was used but this was decreased to 60°C to prevent TFA vaporization from the sample too quickly. After 30 min, a second portion of 100 μ L TFA (2 M) was added to the samples (60°C, 30 min). Then, 100 μ L TFA (4 M) and thereafter 100 μ L TFA (6 M) additions were performed in the same way, but the reaction time was increased to 60 min for each step. To remove HOM, 50 μ L HCl (1 M) was added, and the samples were placed in oven (60°C, 30 min). Thereafter, the samples were left to dry in a fume hood (48 h) covered with aluminum foil and then combusted (375°C, 18 h). The remaining carbon was measured and treated as coming from the BC compartment (residue 3A; Fig. 1).

The results from the TFA additions were compared with the results obtained from control samples (triplicates). Here, distilled water was used instead of TFA but otherwise the protocol was identical.

Standard additions of diesel soot—To test whether the method of standard additions could be used to derive sedimentary BC concentration, a standard reference material SRM-2975 (forklift diesel soot from the National Institute of Standards and Technology, Gaithersburg, Md., U.S.A.) was added in incremental amounts to each of the two test sediments. The properties of this reference material are extensively described in the NIST certificate and in Gustafsson et al. (2001). The BC standard and sediment was first mixed with a spatula and then ground with an agate mortar and pestle until no lumps or aggregates were visible. Sub-samples of the mixtures were taken for the CTO-375, CTO-360, and the large-scale and micro-scale HF demineralization techniques.

The SRM-2975 was added to a series of the Kosterfjord sediment yielding the following initial standard BC concentrations: 0.73, 1.9, 2.9, 4.1, 5.7, 10.4, and 14.6 mg BC/gdw. The standard BC concentrations resulting after additions of SRM-2975 in the Ketelmeer sediments were: 0.73, 1.5, 2.9, 4.4, 9.4, 16.1, 22.0, and 26.4 mg BC/gdw. The BC concentration of the original sediment is derived from the y intercept in a plot of measured BC concentration (y axis) compared with added amount of BC from standard to the sample (x axis). The dashed line in Fig. 3 represents the predicted total concentration of BC resulting from SRM-2975 additions to a starting BC concentration of 1.0 mg BC/gdw for the Kosterfjord and 4.7 mg BC/gdw for Lake Ketelmeer. In this study, a BC concentration of 68.2% ± 0.9% was applied for SRM-2975, which has been reported for “pure” SRM-2975 (Gustafsson et al. 2001). Nguyen and coworkers (2004) reported a similar BC concentration for this same material (63% ± 4.1%).

Test of inorganic matrix effects: additions of silica, copper oxide, and chloride—The physical aggregation state of the BC may affect its stability toward oxidation. Furthermore, natural sediments may contain different catalysts that can enhance the oxidation of BC particles during combustion. It has also been shown that chloride ions may increase the oxidation further by acting as a “wetting agent” between the BC aggregate and the catalyst (Mul et al. 1995; Neeft et al. 1996; Wang and Haynes 2003). A material was prepared by adding SRM-2975 to silica (Merck, 60 μ m, precombusted at 600°C) and carefully homogenizing in an agate ball grinder (20 min). The predicted BC concentration for this material, based on “native” SRM-2975 of 68% BC, was calculated to 23 ± 0.03 mg BC/gdw.

Eight other materials were prepared in crucibles by adding incremental amounts of sodium chloride (NaCl, analytical grade) to copper oxide (>97% CuO). About 50 mL distilled water was added to each sample; thereafter they were dried in oven (105°C, about 24 h) and well ground in an agate mortar. The CuO + NaCl materials were then mixed in a series with the silica + SRM-2975 material yielding the following NaCl

concentrations: 0, 2.6, 7.0, 9.3, 10.9, 11.8, 14.2, 14.9 wt% and about 25 wt% CuO. Sub-samples were weighed into Ag capsules and subjected to the CTO-375 method.

Assessment

Evaluation of HCl-HF-TFA pretreatments—Ex situ approaches. Ex situ HCl treatment suggested a BC concentration for the Kosterfjord of 0.37 ± 0.09 mg BC/gdw (Fig. 2; residue 1C shown in Fig. 1) that was much lower than the standard CTO-375 HCl treatment performed in situ in Ag capsules (1.0 ± 0.08 mg BC/gdw; Fig. 2 residue 1A in Fig. 1). The concentration decreased further to 0.25 ± 0.01 mg BC/gdw (Fig. 2; residue 2B in Fig. 1) when both HCl and HF were added. For the HCl + TFA pretreatment the obtained value was 0.13 ± 0.05 mg BC/gdw and decreased to 0.06 ± 0.01 mg BC/gdw, when all three acids (HCl + HF + TFA) were used ex situ on the sediment (Fig. 2; residue 4A in Fig. 1).

The BC concentration in the Ketelmeer sediments was measured to 4.0 ± 0.2 mg BC/gdw when only HCl was added to the sediment ex situ (residue 1C), and it decreased to 3.7 ± 0.1 mg BC/gdw when both HCl and HF were applied (Fig. 2). A similar BC concentration was detected when HCl and TFA were used (3.8 ± 0.1 mg BC/gdw), but the concentration decreased to 3.3 ± 0.1 mg BC/gdw when all three acids were used ex situ. Noticeable is that the HCl + HF + TFA treatment produced dark aggregates for both types of sediments, which tended to associate with the air interface. These aggregates were difficult to separate from the solution during centrifugation, and it was usually apparent that a major part of them was lost during washing. This could be one explanation for the lower BC concentrations measured in these ex situ pretreated samples.

Is the lower BC concentration measured from the ex situ HCl + HF and the HCl + HF + TFA pretreatments evidence for removal of non-BC organic material that otherwise would have been charred, or is it simply an artifact from BC losses during the repeated washing of the sample? G elinas and coworkers (2001b) argue that the HF treatment is very important to release organic matter trapped inside mineral capsules or within the lattice of biogenic or clay minerals. Encapsulation of organic matter may be produced by flocculation of clay particles, adsorption of mineral particles around organic particles, or formation of stable aggregates (Baldock and Skjemstad 2000). If this organic matter is also a quantitatively significant portion of the total organic matter and is not released and oxidized during the thermal treatment, it could lead to an overestimation of the BC concentration of the sediment (G elinas et al. 2001b). However, just by shifting the employed CTO-375 method from micro-scale in situ pretreatments in Ag capsules, to large-scale ex situ pretreatments in Teflon tubes, the latter with several washing and transfer steps, the BC concentration decreased substantially (Fig. 2). The Ketelmeer sediment apparently lost about 15% of its native BC concentration while the BC in the Kosterfjord decreased nearly 50% because of ex situ handling around the HCl step.

Micro-scale pretreatments in Ag capsules—To avoid the evident handling losses of BC particles associated with ex situ approaches, it was attempted to perform the HF digestion and the TFA treatments directly on samples in situ in Ag capsules. It is imperative that further pretreatment development of the original CTO-375 method is focused on microchemistry in situ in Ag capsules. Only the Ketelmeer sediments were used for this microchemistry experiment due to its higher BC content. The attempt to use TFA in situ was unfortunately unsuccessful. The apparent BC concentration increased after TFA usage, which probably reflects difficulties in removing the organic acid during the in situ washing of the content in the Ag capsules. To not rupture the Ag capsules, the HCl concentration had to be lowered, from 6M HCl in the original method (Allard et al. 1998; G elinas et al. 2001b) to 1 M HCl. This apparently led to ineffective removal of the TFA and thus the BC concentration was overestimated.

When the HF digestion of the silicates was performed directly in situ in Ag capsules, the BC concentration decreased to 2.7 ± 0.3 mg BC/gdw. This lowering of concentration could come from release of encapsulated organic matter. It could also stem from dissolution of BC particles during HF removal. In contrast to the ex situ method where repeated washing steps are used to remove HF, the in situ samples with HF solution in Ag capsules had to be heated to about 180°C to try to evaporate the HF solution. This heating might have led to an alteration of the BC. Ishiguro et al. (1997) noticed that the inner core of diesel soot particles was dissolved when subjected to another acid (HNO₃) under heating. So, while the ex situ demineralization method may undergo substantial losses of BC particles during washing and handling, the explored in situ HF method also appears to have its problems with underestimation of the BC concentration due to other types of losses during the clean-up stage.

The standard additions approach—The method of standard addition is particularly useful for analyzing complex samples, which can have substantial matrix effects (Skoog et al. 1998). This is true when analyzing BC in sediments. The sediment from the Kosterfjord has a low native BC concentration, which was measured with the CTO-375 method to 1.0 ± 0.08 mg BC/gdw. The standard addition experiment with the Kosterfjord sediment gave a BC concentration of 0.50 ± 0.30 mg BC/gdw ($r^2 = 0.94$) for the CTO-375 method (Fig. 3A and Table 1). When the HF digestion technique was performed in Teflon tubes (residue 2B), a concentration of 0.22 ± 0.19 mg BC/gdw was derived for the Kosterfjord sediment ($r^2 = 0.93$). The third method applied, HF digestion performed in situ in Ag capsules (residue 2A), gave erratic results, likely reflecting BC-abrasive artifact of the heated acid as described above. The somewhat lower slopes for the sediment-amended BC standard compared with those predicted from the direct CTO-375 measurement of BC in the pure standard, suggests that 375°C may add too much thermal energy when a natural sediment matrix is also present (see further section 'Possible enhanced

Table 1. The regression data from the SRM-2975 diesel soot standard addition experiments

	Intercept	Slope	r^2	P
Kosterfjord sediment				
CTO-360	0.48 ± 0.4	0.51 ± 0.05	0.98	0.0017
CTO-375	0.50 ± 0.3	0.35 ± 0.04	0.94	0.00036
HF + CTO-375 (ex situ)	0.22 ± 0.2	0.20 ± 0.03	0.93	0.00055
HF + CTO-375 (in situ)	*	*	0.21	0.30
Lake Ketelmeer sediment				
CTO-360	6.2 ± 0.4	0.66 ± 0.02	0.99	0.000085
CTO-375	5.2 ± 0.6	0.53 ± 0.04	0.96	0.000016
HF + CTO-375 (ex situ)	3.7 ± 0.2	0.11 ± 0.02	0.90	0.00030
HF + CTO-375 (in situ)	—	—	0.04	0.63

The native BC concentrations in the original sediments are estimated from the intercept value.

*Represents no statistically significant correlation between added SRM-2975 and measured BC.

BC oxidation due to presence of ambient metal oxides'). Therefore, a slightly modified chemothermal oxidation method was also attempted with the combustion temperature lowered to 360°C. This CTO-360 method gave a larger slope (see subsequent paragraph) and a BC concentration of 0.48 ± 0.41 mg BC/gdw ($r^2 = 0.98$ in Table 1) that was comparable with the direct CTO-375 results for pure standard.

The Ketelmeer sediment naturally has a much higher and heterogeneous native BC concentration, which has been measured with the CTO-375 method for different batches to vary between 4.7 and 7.2 mg BC/gdw (Cornelissen and Gustafsson 2004 and this study). The CTO-375 method, operated with a SRM-2975 standard addition approach, here revealed a sedimentary BC concentration of 5.2 ± 0.6 mg BC/gdw ($r^2 = 0.96$; Fig. 3B and Table 1) and 3.7 ± 0.2 mg BC/gdw ($r^2 = 0.90$) when using the ex situ addition of HF to digest the silicate minerals. The HF digestion performed in Ag capsules (residue 2A) also gave erratic results here, and no correlation between measured BC and added amount of standard could be determined. When the temperature was lowered to 360°C, the BC concentration increased to 6.2 ± 0.4 mg BC/gdw, and the slopes were almost identical for the standard addition CTO-360 approach and the prediction from the analysis of pure SRM-2975 (Gustafsson et al. 2001), indicating that 360°C provided sufficient thermal oxidation energy to remove amorphous organic matter (OM), while retaining soot BC in this sediment matrix.

When comparing the slopes of the different standard additions with the dashed line (Fig. 3), which represents prediction from pure BC analysis (Gustafsson et al. 2001), the CTO-375 technique with SRM-2975 mixed with sediments yielded 51% of BC from pure SRM-2975 measurements for the Kosterfjord sediment and about 78% return when mixed with the Lake Ketelmeer sediment. The values for the HF digestion technique performed ex situ in Teflon tubes were even lower with 29% for the Kosterfjord and 17% for the Ketelmeer, respectively. When the combustion temperature was lowered to 360°C, 76% of BC from SRM-2975 was measured for the Kosterfjord sediment and

97% for the Lake Ketelmeer. One reason why not all added BC is measured could be that when the SRM-2975 is diluted with sediment, it is smeared out onto particles. Then a larger surface area of the BC aggregate can be exposed to oxygen during combustion compared with when the standard reference material was analyzed in pure condition (Gustafsson et al. 2001). Yet, another possibility is that some sediment minerals act to catalyze the BC combustion so a lowering of the combustion temperature was necessary to compensate for these smearing and catalytic effects. The constantly lower BC concentration measured after HF digestion probably comes from BC particles being lost during handling and washing of the sediment during treatment, as explained above and in Gélinas et al. (2001b).

Possible enhanced BC oxidation due to presence of ambient metal oxides—A lowering of the combustion temperature from 375°C to 360°C resulted in acceptable recoveries of the sediment-amended BC reference material in the standard addition experiment. This could imply that the sediment contains one or more catalysts that speed up the oxidation of the diesel soot particles. Many studies are focused on finding good catalysts that are active at low temperatures (150 to 400°C) to decrease pollutant emissions from diesel engines. Transition metal oxides with low melting points, alkali metals, and alkaline earth metals have been found to be effective promoters especially when they are in "tight" contact with the carbon surface (Neri et al. 1997; Stanmore et al. 2001; Wang and Haynes 2003). Effective transition metal oxides are CuO, V₂O₅, TiO₂, and Cr₂O₃ while Fe₂O₃ and γ -Al₂O₃ only have a catalytic effect at low temperatures. Cesium has been found to be the most effective alkali metal catalyst followed by K and Na (Wang and Haynes 2003). Chloride favors the contact between catalyst and soot so impregnation of oxides with chloride salts can significantly improve the catalytic activity for soot oxidation (Wang and Haynes 2003).

A test was performed to investigate the possibility of a smearing effect by diluting standard SRM-2975 with silica. The predicted BC concentration of the silica + SRM-2975 material was calculated to 23.0 ± 0.03 mg BC/gdw (Fig. 4). When measuring the BC concentration in the same material

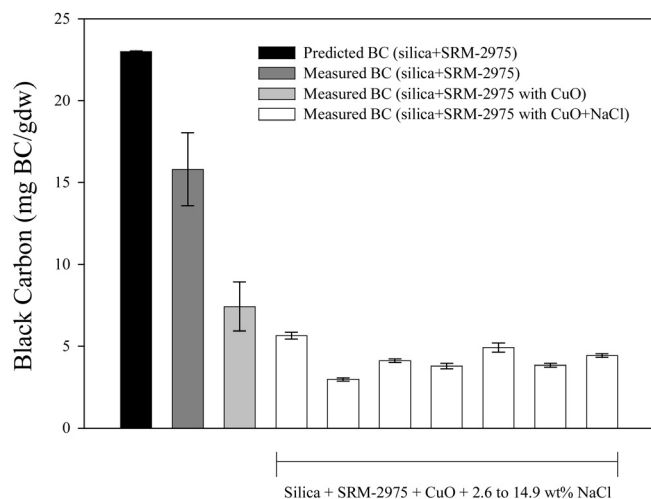


Fig. 4. Evaluation of catalytic matrix effects. The results for combustion of soot BC standard mixed with silica, copper oxide, and incremental amounts of sodium chloride. The black bar displays the predicted BC of the prepared silica + SRM-2975 material calculated with a BC concentration for the pure standard of $68.2\% \pm 0.9\%$ (Gustafsson et al. 2001), and the dark gray bar shows the measured BC when mixed with silica. The light gray bar shows measured BC with additions of both silica and CuO, whereas the white bars represent measured BC with additions of silica, CuO, and incremental amounts of NaCl. The NaCl mass concentrations were from left to right: 0%, 2.6%, 7.0%, 9.3%, 10.9%, 11.8%, 14.2%, and 14.9%. Error bars show one standard deviation of triplicate measurements.

after the CTO-375 method, the value was 15.8 ± 2.2 mg BC/gdw. This lower measured BC concentration compared with the predicted value is believed to be caused by increased BC availability for oxidation when smeared onto silica surfaces. The “smearing effect” reveals a 31% lowering of the BC concentration in this material. The addition of CuO to the silica + SRM-2975 enhanced the oxidation of BC particles by an additional 37%, yielding matrix BC concentration of 7.4 ± 1.5 mg BC/gdw (Fig. 4). The presence of chloride in the sample further increased the oxidation and the measured BC in the silica + SRM-2975 + CuO + NaCl system was on average 4.3 ± 0.4 mg BC/gdw. Increasing NaCl concentration above 2.6 wt% does not seem to have an effect on the results, but the presence of chloride ions here enhanced the oxidation with an average value of 14%.

The somewhat lower recovery of added SRM-2975 BC from the Kosterfjord than from the Lake Ketelmeer (76% versus 97% at CTO-375) may stem from such a “chloride” effect. The Kosterfjord sediment has porewater with salinity above 30 while the Lake Ketelmeer is a freshwater sediment.

Discussion

Black carbon is a significant constituent both in aquatic and terrestrial environments, and it is therefore of great importance to deduce reliable methods for its quantification. Evaluation of different methods is difficult due to a lack of reference

materials with certified BC concentrations. Suggested method artifacts include BC oxidation, char formation from natural organic matter due to pyrolysis during combustion, and loss of hydrophobic BC particles in wet chemical ex situ treatments. These effects are not uniform for all sediment types and thus incorrect assumptions on the BC concentration can be made.

The broadly used CTO-375 method was here reevaluated and the largest effect on measured BC concentration was simply between performing the wet chemistry ex situ in Teflon tubes or in situ in Ag capsule, the latter also used for combustion and elemental analysis. By performing the CTO-375 HCl pretreatment ex situ in Teflon tubes, a decrease in BC concentration was detected for both the Ketelmeer sediment and the Kosterfjord sediment with 15% and 50% loss of BC, respectively. This indicates that soot BC particles were lost during ex situ washing and handling of the sediments, as opposed to “added” by charring in the in situ CTO-375 method. Therefore, it was attempted to instead perform the two acid pretreatments (HF and TFA) in situ in Ag capsules to minimize the physical losses. Unfortunately, none of these microchemistry attempts were successful. The TFA method performed in situ in Ag capsules overestimated BC concentrations due to difficulties in completely removing the organic acid before combustion. The thermal removal of the HF from the Ag capsules appears to oxidize the BC component and thus lead to an underestimation.

The most promising alteration of the standard CTO-375 method was to spike the sediments with diesel soot standard (SRM-2975) in a traditional standard addition approach. The resulting linear standard addition curves also made it possible to evaluate how much of the added BC that was really quantified with each method. The wet chemical pretreatment performed ex situ in Teflon tubes detected only between 17% and 29% of added BC from SRM-2975 for the two sediments, respectively, while the CTO-375 method detected 51% and 78%, respectively. Again, this large difference probably comes from physical losses of standard material during the ex situ (Teflon tubes) handling of the samples. A lowering of the temperature to 360°C allowed recovery of all added BC with the CTO method for the Ketelmeer sediments. The lower temperature of 360°C is not believed to leave any residual non-BC, according to the thermogram results obtained by Gustafsson et al. (2001), where almost all interfering organic material was oxidized at that temperature even in the absence of mineral oxides. While the CTO-360 method also gave the best results for the Kosterfjord, a further decrease of combustion temperature may be needed due to ambient mineral catalysts existing within the sediment matrix, which increases the oxidation of the BC particles at a given temperature. The impact that metals and metal oxides ambient in the sediment may have on the measured BC concentration was clearly demonstrated with the test of CuO doped with NaCl performed in this study. We emphasize that the standard addition approach yields information specifically on the sediment concentrations of the type of BC that is spiked into the sediments (i.e., here diesel soot BC).

Different types of BC standards may preferentially be used for quantifying less recalcitrant parts of the BC spectrum.

Comments and recommendations

The results of this study lead to three major recommendations: (1) The ex situ wet chemical pretreatments should be avoided as the many transfer and handling steps may lead to large losses and thus underestimation of BC, (2) further testing of more extensive in situ pretreatment methods in Ag capsules may be explored using other approaches than the ones tested in this study, (3) the method of standard additions of various well-characterized BC material to natural sediments may be further explored as a promising alternative to current techniques. Future work should also investigate the effect of various native components of the sediment matrix on the physical BC aggregation state and the catalytic efficiency of these components on BC oxidation. Guided by diagnostic information from experiments with serial additions of various BC standards, it may prove rewarding to systematically test other combustion temperatures.

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