



## The effect of acidification on the determination of elemental carbon, char-, and soot-elemental carbon in soils and sediments

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### ABSTRACT

We studied the influence of acid pretreatment on the effective distinction between elemental carbon (EC) and organic carbon (OC), and between char-EC and soot-EC. Though widely employed in the pretreatment of soils and sediments for EC quantification, the use of HCl, HF, and HNO<sub>3</sub> could decrease soot thermal stability as acid remains, leading to an underestimation of soot-EC by thermal methods. We compared thermal optical reflectance (TOR) measurements of EC concentrations in char reference materials and in lacustrine and marine sediments following pretreatment with various acids. The results showed that pretreatment with 2 M HCl, concentrated HNO<sub>3</sub>, 7 M HNO<sub>3</sub>, and 1 M HNO<sub>3</sub> did not result in EC oxidation. However, hot concentrated HNO<sub>3</sub> oxidized EC significantly, leading to lower concentrations of EC, char-EC and soot-EC. By comparing the removal of potentially interfering materials, which contain little fire-derived carbon, with different acid pretreatments, we recommend the HCl–HF–HCl and concentrated (not hot) HNO<sub>3</sub>–HF–HCl pretreatments for the determination of EC, char-EC, and soot-EC in soils and sediments using the TOR method.

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### 1. Introduction

Elemental carbon (EC) is a chemically heterogeneous, biologically refractory class of carbonaceous matter produced from the incomplete combustion of fossil and biomass fuels (Goldberg, 1985; Schmidt and Noack, 2000; Masiello, 2004; Andreae and Gelencsér, 2006; Koelmans et al., 2006). EC is also termed black carbon (BC). Sediment and soil studies generally use the term BC, while aerosol studies use the terms BC and EC, with BC implied to have optical properties. Clear definitions of EC and BC can be referred to Andreae and Gelencsér (2006). Because the high-temperature carbon isolated by the thermal optical reflectance (TOR) method has been conventionally termed EC (Chow et al., 1993, 2001), we expand the use of this term to include soil and sediment studies using similar method (Han et al., 2007a).

As a continuum, EC ranges from partially charred plant materials (char or charcoal) to soot particles formed from gas phases during combustion and pyrolysis (Goldberg, 1985; Hedges et al., 2000; Schmidt and Noack, 2000; Masiello, 2004). The distinction between char and soot is based mainly on physical and chemical properties, such as particle size, formation temperature, morphology, surface area, density, and carbon/hydrogen or carbon/oxygen molar ratios

(Goldberg, 1985; Fernandes et al., 2003; Elmquist et al., 2004). Char is comprised of larger particles (diameter generally 1–100 μm) formed at low temperatures, while soot consists of sub-micron particles formed at higher temperatures and always in the form of agglomerates of 0.1–1 μm (Stanmore et al., 2001; Masiello, 2004).

There is no generally accepted or universally applied method for measuring EC in natural matrices (Masiello, 2004; Hammes et al., 2007). Available methods for EC quantification in soils and sediments involve various pretreatments for differentiating between three forms of carbon, i.e. inorganic carbonates, thermally unaltered organic carbon (OC), and EC (Kuhlbusch, 1995; Lim and Cachier, 1996; Gustafsson et al., 1997, 2001). Carbonates can be removed using acids (Kennedy et al., 2005), while organic matter is differentiated from EC using chemical (Lim and Cachier, 1996; Verardo, 1997), chemothermal (CTO, Kuhlbusch, 1995; Gustafsson et al., 1997, 2001; Gelinas et al., 2001), high energy ultraviolet photo-oxidation (Skjemstad et al., 1999, 2002), and TOR methods (Han et al., 2007a). The CTO and TOR methods are based on the assumption that EC is more resistant to thermal oxidation than OC (Elmquist et al., 2004; Hammes et al., 2007; Han et al., 2007a,b). The advantages and disadvantages of the CTO method have been summarized by Nguyen et al. (2004) and Hammes et al. (2007). The TOR method, which has been widely used to quantify OC and EC in aerosol samples for more than two decades (Chow et al., 1993, 2001), was recently introduced to quantify EC in

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sediments and soils (Han et al., 2007a). TOR provides an opportunity to utilize the same method as EC quantification for different environmental matrices, and has the advantage of potentially differentiating between char-EC and soot-EC (Han et al., 2007b).

Analytical methods for EC quantification are based mainly on various measures of oxidation resistance. Artifacts occur in most EC methods, and previous studies have linked these artifacts to organic charring (overestimation), losses during solution handling (underestimation), and artificial, operationally defined EC measurement (e.g. Hammes et al., 2007). The artifacts have not been linked to the changes in EC stability in wet chemical processes as there have been no studies of the effects of various wet chemical processes on oxidation resistance of EC (Elmqvist et al., 2004), as well as on oxidation resistance of the different forms of EC, char and soot. It is therefore necessary to know how stable the different forms of EC are to acid pretreatments, toward more effectively differentiating between OC and EC, and between char and soot.

In our previous study (Han et al., 2007a) hydrochloric acid (HCl) pretreatment was used for quantifying EC concentrations in sediments and soils by the TOR method. However, this pretreatment cannot completely remove potentially interfering materials, which contain little fire-derived carbon (Hammes et al., 2007). In the present study, we: (1) tested the thermal stability of the different EC forms following different acid pretreatments; (2) investigated the influence of these acid pretreatments on char materials and marine and lake sediments; and (3) tested the effects of the acid pretreatments on removing the potentially interfering materials, and selected the most suitable pretreatment for EC quantification using the TOR method.

## 2. Materials and procedures

### 2.1. Materials

Samples analyzed included positive EC reference materials, potentially interfering materials, and sediment samples. Positive EC reference materials are comprised of EC-rich materials, including char and soot, from the BC ring trial and elsewhere (Elmqvist et al., 2006; Hammes et al., 2007; Han et al., 2007a,b). The materials used were nonbriquetted mesquite char (Han et al., 2007b), *n*-hexane soot, and diesel soot (SRM-2975 and SRM-1650).

Two different types of sediments were used. One was a marine sediment from a core (112°06'E, 9°42'N) collected at a depth of 166 cm, in August 1999 from the South China Sea (Han et al., 2007a). The sample has a <sup>14</sup>C age of 41201 ± 360 years before present (Y.M. Han, unpublished data), indicating no human-induced fossil fuel influence. The other was lacustrine material from a sample of the top 2 cm of sediment in Lake Taihu (120°25'E, 31°08'N). This site is in a highly industrialized zone on the Yangze River delta in eastern China, and the sediment is thus expected to be highly influenced by human activities.

Potentially interfering materials, including urea–glucose melanoidin (from the Physical Geography Department, University of Zurich, <http://www.geo.uzh.ch/phys/bc>), Suwannee River natural organic matter (Suwannee NOM, from International Humic Substances Society, St. Paul, MN, USA), and two coals with different degrees of maturity, Pocahontas bituminous coal and Beulah-Zap lignite (from the Argonne National Laboratory, Argonne, IL, USA), were also investigated to assess their influence on EC determination following various acid pretreatments.

### 2.2. Pretreatments

In our previous study, in the first step Han et al. (2007a) used HCl for removing carbonate and some metals from sediment sam-

ples. After rinsing with de-ionized water (Millipore, Bedford, MA), hydrofluoric acid (HF) was used to remove silicates and residual metals. The residues were then dissolved in HCl. This was followed by another rinsing, and the residue was then filtered onto a 47-mm quartz filter for carbon analysis. In the present study, nitric acid (HNO<sub>3</sub>) with various strengths was also used in the first step instead of HCl, to investigate any effects this substitution may have on EC determination and on removing the potentially interfering materials.

Four sets of samples with different pretreatment procedures are as follows:

- (1) Pure soot samples: Because of their hydrophobic character, the concentrations of the pure soot particles cannot be quantitatively obtained under acid pretreatment. Thus we just assess the effects that these acids may have on the thermal stability of the soot samples by comparing the variation of their thermograms with the TOR method. *n*-hexane and two diesel soot samples (SRM-2975 and SRM-1650) were conducted without acid pretreatment, and acid pretreatment with 2 M HCl, concentrated HF, and 7 M HNO<sub>3</sub>, respectively. Without acid pretreatment, ~60 μg of samples were weighed and directly daubed onto 0.526 cm<sup>2</sup> pre-fired (3 h, 850 °C) quartz filter for carbon analyses. For acid pretreatment, in order to assess the influence of remaining acid strength on the stability of soot particles under high temperature, each acid (6 mL) was reacted with three parallel samples (each of ~0.8 mg) for 24 h in 50 mL polypropylene test tube and these samples were then treated with no rinsing, less intense (2 times), and intense (6–8 times) rinsing, respectively. Each rinse was conducted with 40 mL water. Finally the residues were filtered onto 47 mm pre-fired quartz filter (0.4 μm pore size, Whatman) and dried in an oven at 40 °C for ~6 h for further carbon analyses. Note that the carbon analyzer is made of glass, and since acids, especially HF, damage glass instruments, these acid-retained experiments could not be conducted with a large number of samples.
- (2) Char materials: Pre-weighed (~0.8 mg) nonbriquetted mesquite char materials were pretreated in 6 mL of 2 M HCl, hot (50 °C) concentrated HNO<sub>3</sub>, concentrated HNO<sub>3</sub>, 7 M HNO<sub>3</sub>, and 1 M HNO<sub>3</sub> (Verardo, 1997; Glaser et al., 1998; Middelburg et al., 1999), respectively, in 50 mL polypropylene test tubes for 24 h, and then rinsed 3 times with de-ionized water and filtered onto 47 mm pre-fired quartz filters for carbon analysis (Han et al., 2007a). Another nonbriquetted mesquite char was treated with concentrated HNO<sub>3</sub> for only 20 min (Kuhlbusch, 1995) and followed with rinse 3 times and filtered onto quartz filter for further carbon analyses.
- (3) Marine and lake sediments: Table 1 summarizes the pretreatment steps with different acids for the marine and lake sediments.
- (4) Potentially interfering materials: These materials (~0.8 mg of each) were stepwise pretreated with concentrated HNO<sub>3</sub>, HF, and HCl (identical to the number 10 step in Table 1) and finally filtered onto quartz filter for carbon analysis.

### 2.3. Carbon analysis

The DRI Model 2001 Thermal/Optical Carbon Analyzer (AtmAA Inc.) was used for the carbon analysis following the IMPROVE protocol (Chow et al., 1993, 2001, 2006; Han et al., 2007a,b). In this method, a filter sample (0.526 cm<sup>2</sup>) is heated under a stream of pure He and a mixture of a 2% O<sub>2</sub> and 98% He, while a laser is used to monitor the reflectance or transmittance of the filter throughout

**Table 1**

Acid pretreatment steps used in comparing the EC, char-EC, and soot-EC concentrations of lacustrine and marine sediments. After dried in an oven at 60 °C for ~48 h, the two sediments were ground to pass through 63 µm sieve. About ~0.15 ± 0.05 mg ground samples were weighed and put into 50 mL polypropylene test tubes. Acid pretreatment in each step was about 24 h to ensure that the reactions ran to completion. The rinse and wash with ~40 mL de-ionized water (Millipore, Bedford, MA) were conducted in each step (Han et al., 2007a). In the last step pH test paper was used to ensure that the pH value is close to 7. Then the residues were diluted in 200 mL of water and filtered through a 47 mm pre-fired quartz filter. Meanwhile 200 mL water slowly pours into the filter to wash the glass wall of the filter.

Number	Pretreatment step	Abbreviate
1	(a) 2 N HCl; (b) concentrated HF; and (c) 2 N HCl	HCl-HF-HCl
2	(a) 2 N HCl; (b) concentrated HF; and (c) 2 N HCl. Supernatants return	HCl-HF-HCl, SR <sup>a</sup>
3	6 N HCl + concentrated HF	HCl + HF
4	6 N HCl + concentrated HF. Supernatants return	HCl + HF, SR <sup>a</sup>
5	(a) Hot concentrated HNO <sub>3</sub> ; (b) concentrated HF; and (c) 2 N HCl	Hot HNO <sub>3</sub> -HF-HCl
6	(a) Concentrated HNO <sub>3</sub> ; (b) concentrated HF; and (c) 2 N HCl	HNO <sub>3</sub> -HF-HCl
7	(a) Concentrated HNO <sub>3</sub> ; (b) concentrated HF; and (c) 2 N HCl. Supernatants return	HNO <sub>3</sub> -HF-HCl, SR <sup>a</sup>
8	7 N HNO <sub>3</sub> + concentrated HF.	HNO <sub>3</sub> + HF
9	7 N HNO <sub>3</sub> + concentrated HF. Supernatants return	HNO <sub>3</sub> + HF, SR <sup>a</sup>
10	(a) 7 N HNO <sub>3</sub> ; (b) concentrated HF; and (c) 2 N HCl	7 N HNO <sub>3</sub> -HF-HCl
11	(a) 1 N HNO <sub>3</sub> ; (b) concentrated HF; and (c) 2 N HCl	1 N HNO <sub>3</sub> -HF-HCl

<sup>a</sup> Supernatants return (SR) means that the supernatant liquids from each step were collected together with 500 mL polypropylene vessels and diluted to 500 mL. Then the supernatants were filtered with pre-fired quartz filters, and 400 mL water was used to wash the acid and the wall of the filter. The filters were also dried at 60 °C for 4 h in an oven. Supernatants carbon analyses were also conducted with 0.526 cm<sup>2</sup> filter. The results were added to those of the residue, and are presented as the measured results.

the analysis. OC is evolved in a pure He environment as the sample is heated stepwise to 120, 250, 450 and 550 °C, producing four OC fractions (OC1, OC2, OC3, and OC4). The analysis is then switched to a He/O<sub>2</sub> mixture, and the oven temperature is raised from 550 to 700 and then 800 °C, producing three EC fractions (EC1, EC2, and EC3). As O<sub>2</sub> enters the oven, pyrolyzed/charred OC (POC) that is produced in the pure He environment becomes oxidized, and a concurrent increase in filter reflectance/transmittance occurs. Correction for the charring effect is accomplished by identifying the time at which the filter reflectance/transmittance returns to its initial value. This point is defined as the split between the OC and EC. The sum of the OC and EC is total carbon (TC).

That carbon abundances in these fractions differ by carbon sources has long been observed in aerosol studies (e.g. Chow et al., 2004) and was used for the source apportionment (Cao et al., 2005). However, the potential differentiation of char-EC and soot-EC using the TOR method has not been exploited. Recently, Han et al. (2007a) found that EC measured by the CTO method, which was generally referred to as soot-EC by many researchers (Gelinas et al., 2001; Gustafsson et al., 2001; Elmquist et al., 2006), always occurred in EC2 and EC3 as measured by the TOR method. Further studies (Han et al., 2007b) revealed that char materials always peaked at EC1, while pure soot samples always peaked at EC2 and EC3. Han et al. (2007b) thus postulated that the TOR method can differentiate between char-EC and soot-EC by use of its stepwise thermal oxidation procedure. Char-EC is defined as EC1 – POC and soot-EC is EC2 + EC3. This differentiation has been applied in a recent aerosol study (Han et al., 2008).

All reported EC quantifications for the four sets of samples were from triplicate measurements. High homogeneity of the samples in the filters has been reported by Han et al. (2007a).

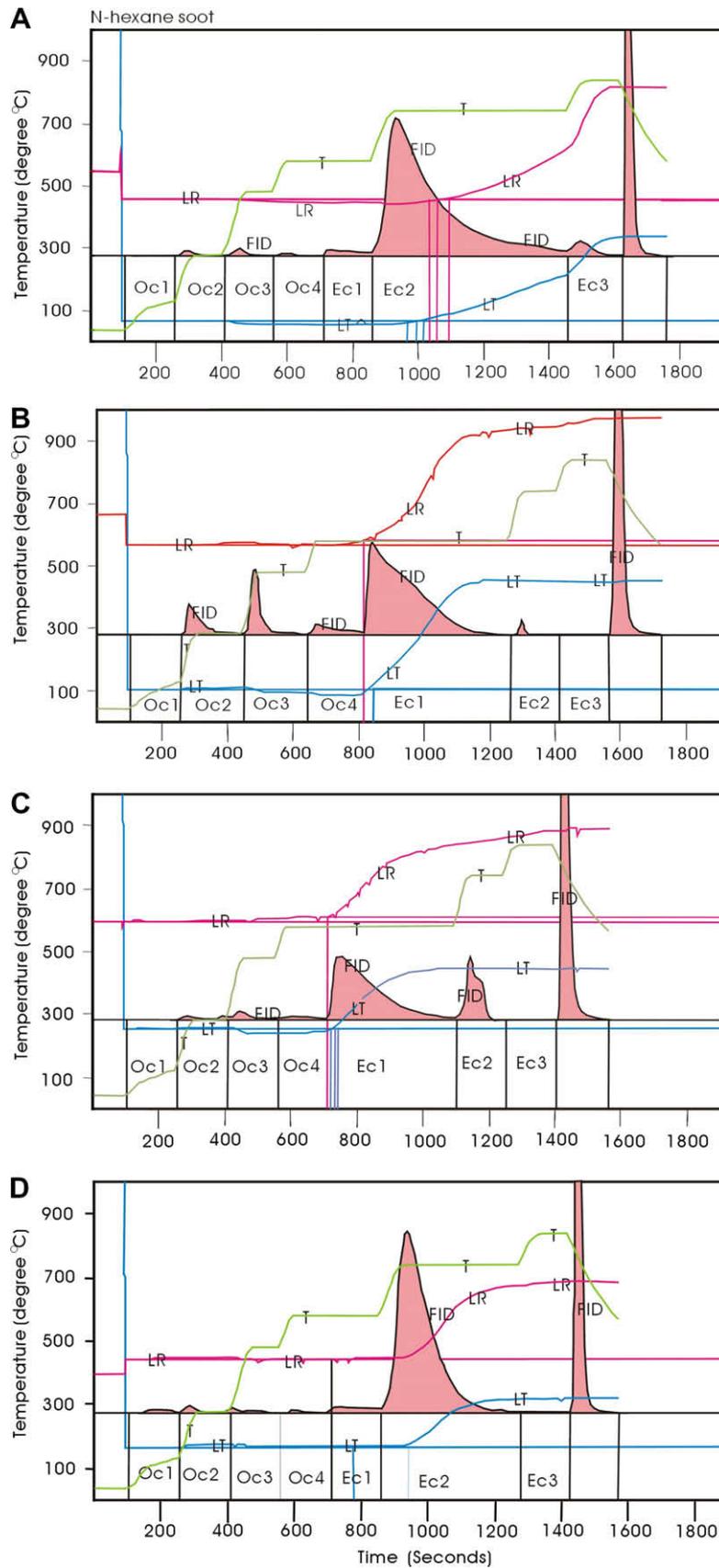
### 3. Results and discussion

#### 3.1. The influence of acidification on the thermal stability of soot materials

Fig. 1 shows the variations of the thermograms of *n*-hexane soot samples without acid pretreatment and pretreated with HCl in situ, less intense rinsing, and repeated rinsing, respectively. The soot samples with no-acid pretreatment peaked at EC2 (Fig. 1A), while the peak shifted completely to EC1 when soot samples were pretreated with HCl in situ (Fig. 1B). However, the thermogram peaks gradually shifted from EC1 to EC2 with increased rinsing (Fig. 1C and D). The results indicated that the activation energy of soot increased under high temperature as acid intensity decreased.

There is a similar pattern for different soot materials (*n*-hexane and diesel) with different acid pretreatments (HCl, HF, and HNO<sub>3</sub>; not shown). However, for soot samples pretreated with HNO<sub>3</sub> in situ, the EC2 peak only partially moved to EC1 (not shown), which was a little different to HCl pretreated soot samples for which the EC2 peak completely moved to EC1. Many researchers (e.g. Nguyen et al., 2004; Han et al., 2007a) have found that the CTO method partly oxidizes soot-EC, leading to an underestimation of soot-EC. In HCl pretreatment condition, the underestimation was even greater (Gustafsson et al., 2001). For example, Gustafsson et al. (2001) found a decrease of soot-EC concentrations using the CTO method when the sample pretreatment changed from without HCl pretreatment (Gustafsson et al., 1997) to HCl pretreatment in situ (Gustafsson et al., 2001). They attributed the decreased soot-EC concentrations to decreased charring of nonpyrogenic organic matter and the release of some encompassed organic matter during HCl pretreatment (Gustafsson et al., 2001). Accardi-Dey (2003) proposed decreasing the oxidation time to 14 h for the CTO method, while Elmquist et al. (2004) recommended lowering the temperature of the CTO method from 375 to 360 °C. No studies have yet connected the decrease in soot-EC concentrations with the influence of acids on thermal stability. Apart from the possible influences of charring and of encapsulated organic matter suggested by Gustafsson et al. (2001) and Elmquist et al. (2004), our results revealed that acid remaining may be the most significant factor influencing sedimentary EC quantification.

Previously, Han et al. (2007a) found little variation in total EC concentrations of pure char and soot materials using the TOR method with and without acid pretreatment. With no-acid pretreatment, char materials were oxidized during EC1, while soot materials were oxidized in EC2 and EC3 (Han et al., 2007b). However, in the present study, soot was also significantly oxidized during EC1 with acid remaining, indicating the decrease in thermal stability of soot materials. This may be associated with soot structure. Although soot particles vary with the type of source fuels and the conditions of combustion (Bond and Bergstrom, 2006), they are primarily comprised of two different nanostructures with an inner core and a highly ordered outer shell (Ishiguro et al., 1997), while char materials lack this shell structure (Ishiguro et al., 1997). The outer shell with very high order may have higher activation energy than char, which would protect soot particles from oxidation. However, the surface of soot particles contains various polar organic functional groups and organics, such as hydroxyl, dicarboxylic acids, oxygenated polyaromatic hydrocarbons, and aliphatic compounds (Akhter et al., 1985; Stanmore et al., 2001; Gelencsér, 2004; Braun et al., 2006). Any soot particle can be regarded as a complex three-dimensional organic polymer with the ability to transfer electrons, rather than merely an amorphous form of EC (Gelencsér, 2004). The raw soot material is non-porous in nature and the presence of soluble organics adsorbed on its surface or



**Fig. 1.** Comparison of the thermograms of *n*-hexane soot samples. (A) Non-acid pretreatment, with one peak at EC2. (B) HCl pretreatment in situ, and therefore no rinsing, with one peak at EC1. (C) Less intense rinsing (2 times) after HCl pretreatment, with two peaks at EC1 and EC2. (D) Intense (6–8 times) rinsing after HCl pretreatment, with one main peak at EC2. The last peak from each thermogram is a methane standard calibration. Shaded areas represent the FID response to evolved carbon. LR – light reflectance, LT – light transmittance, T – temperature, FID – flame ionization detector. There is a similar pattern for different soot materials (*n*-hexane and diesel) with different acid pretreatments (HCl, HF, and HNO<sub>3</sub>).

**Table 2**

The effects of different acidifications on mesquite char (concentrations are expressed as average  $\pm$  standard deviation of triplicate measurements). Mesquite char was ground to pass through 63  $\mu\text{m}$  sieve.  $\sim 0.8$  mg samples were weighed and followed with these acid pretreatments mentioned in the table for 24 h. Finally the residues were washed three times, filtered onto pre-fired quartz filter, and dried at 40  $^{\circ}\text{C}$  for 8 h in an oven for carbon analyses using the TOR method. More than 96% EC are comprised of EC1 – POC (char-EC).

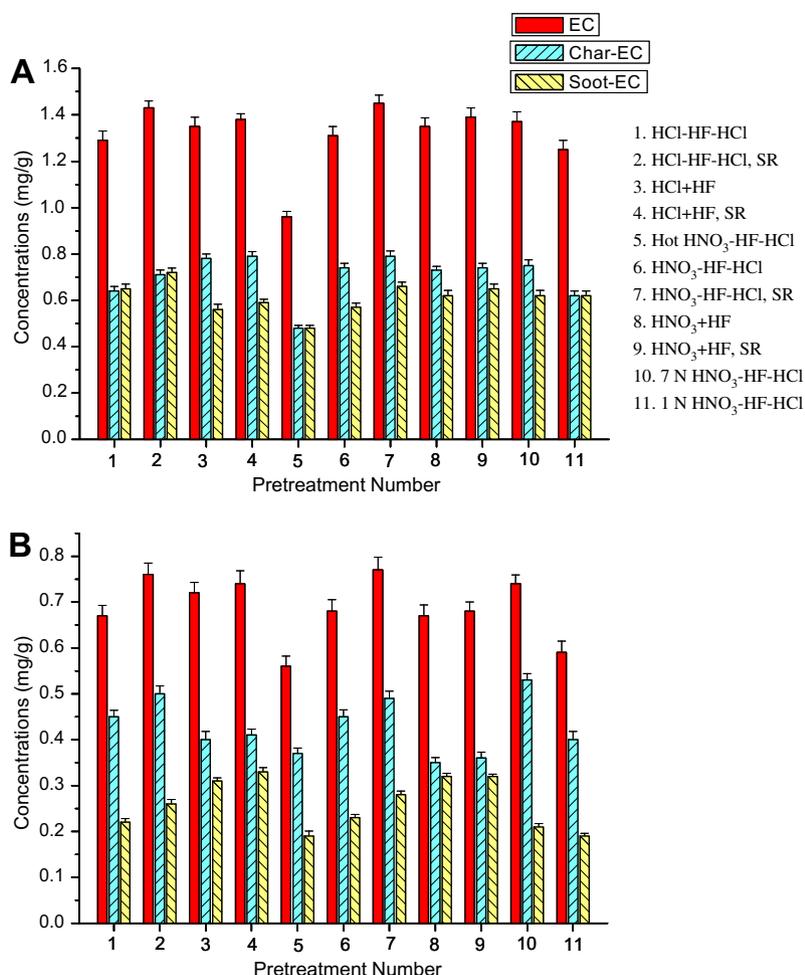
Pretreatment	TC ( $\text{mg g}^{-1}$ d.w.)	OC ( $\text{mg g}^{-1}$ d.w.)	EC ( $\text{mg g}^{-1}$ d.w.)
<i>Mesquite char</i>			
1. No acid pretreatment	675 $\pm$ 15	333 $\pm$ 10	342 $\pm$ 18
2. 2 N HCl acid	566 $\pm$ 18	221 $\pm$ 16	346 $\pm$ 18
3. Hot concentrated HNO <sub>3</sub>	238 $\pm$ 12	87 $\pm$ 11	151 $\pm$ 14
4. Concentrated HNO <sub>3</sub>	446 $\pm$ 21	88 $\pm$ 10	359 $\pm$ 16
5. Concentrated HNO <sub>3</sub> for 20 min	455 $\pm$ 14	110.4 $\pm$ 9	345 $\pm$ 17
6. 7 N HNO <sub>3</sub>	465 $\pm$ 16	130 $\pm$ 11	336 $\pm$ 20
7. 1 N HNO <sub>3</sub>	534 $\pm$ 22	159 $\pm$ 14	375 $\pm$ 17

between the particles does not significantly affect the textural properties of soot particulates. When  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{NO}_3^-$  ions were added, they can act as extractions to remove some unburned species adsorbed on soot (Collura et al., 2005), such as hydrocarbons, aromatics and organosilicons, which are the main components of soluble organics. This process can also modify (or decrease) the high order of the outer shell of raw soot particles, leading to the de-

crease in activation energy of the reaction between oxygen and soot particles under high-temperature treatment. The thermal treatment would also increase the surface areas of soot particulates when soluble organics were removed (Collura et al., 2005). Thus, HCl, HF, and HNO<sub>3</sub> can promote the oxidation of soot particles at high temperatures (Fig. 1A and B).

### 3.2. The influence of acidification on char materials

HNO<sub>3</sub> is frequently used to remove carbonates when quantifying EC in sediments and soils (e.g. Kuhlbusch, 1995; Lim and Cachier, 1996; Verardo, 1997; Gustafsson et al., 1997, 2001; Han et al., 2007a), though no studies have investigated whether HNO<sub>3</sub> itself oxidizes char-EC. Kuhlbusch (1995) pretreated samples using concentrated HNO<sub>3</sub> for only 10–20 min to prevent the oxidation of EC, while Verardo (1997) applied hot (50  $^{\circ}\text{C}$ ) concentrated HNO<sub>3</sub> to isolate OC from EC, and defined the retained carbon as char-EC. Glaser et al. (1998) used HNO<sub>3</sub> heated to a higher temperature (170  $^{\circ}\text{C}$ ) to isolate condensed benzenepolycarboxylic acids as specific markers for EC. Table 2 summarizes the TC, OC, and EC mass concentrations by dry weight (d.w.) of nonbriquetted mesquite char after pretreatment in different acids for 24 h, and for another pretreatment using concentrated HNO<sub>3</sub> for only 20 min (Number 5 in Table 2, Kuhlbusch, 1995). The results show that



**Fig. 2.** Comparison of EC, char-EC and soot-EC concentrations in (A) lake sediment and (B) marine sediment using different acid pretreatments. Char-EC = EC1 – POC; Soot-EC = EC2 + EC3. Pretreatment numbers correspond to those in Table 1. The error bars are standard deviations from triplicate measurements. SR (supernatants return) means that the supernatant liquids from each step were collected with 500 mL polypropylene vessels and filtered with pre-fired quartz filters, and that carbon analyses of the supernatants was also conducted. The supernatant carbon analysis results were added to those of the residue, and are presented as the measured results.

the char-EC concentrations of the samples pretreated with 2 M HCl, concentrated HNO<sub>3</sub>, 7 M HNO<sub>3</sub>, 1 M HNO<sub>3</sub> were similar to those without acid pretreatment (Han et al., 2007a,b). This suggests that HCl and unheated HNO<sub>3</sub> have little influence on char-EC concentrations, regardless of whether the pretreatment time is 20 min or 24 h. However, the char material pretreated in hot concentrated HNO<sub>3</sub> had EC concentration far lower than the other pretreated samples, only accounting for 44% EC of the samples without acid pretreatment. Even its TC concentration is slightly lower than the EC concentrations of the other measurements (Table 2). Our results indicate that the hot concentrated HNO<sub>3</sub> pretreatment (Verardo, 1997) not only oxidizes char-EC, but also retains organic matter (Table 2).

### 3.3. Comparison of EC, char-EC, and soot-EC with different acid pretreatments

Fig. 2 shows the variations of EC, char-EC and soot-EC concentrations of lacustrine (Fig. 2A) and marine (Fig. 2B) sediments using the different acid pretreatments (Table 1). In lake sediment, EC concentrations ranged from 0.92 to 1.45 mg g<sup>-1</sup> d.w., char-EC from 0.48 to 0.79 mg g<sup>-1</sup> d.w., and soot-EC from 0.48 to 0.72 mg g<sup>-1</sup> d.w.; for each, the lowest values were for the samples pretreated with heated HNO<sub>3</sub> (pretreatment 5 in Fig. 2A). The results indicated that the hot HNO<sub>3</sub> pretreatment probably oxidized both char-EC and soot-EC. The TC concentrations after hot HNO<sub>3</sub> pretreatment were of similar magnitude to, but about 2–3 times higher than, the EC concentrations following other acid pretreatments (Fig. 2). Excluding the sample pretreated in hot HNO<sub>3</sub>, the EC concentrations varied between 1.25 and 1.45 mg g<sup>-1</sup> d.w., char-EC between 0.64 and 0.79 mg g<sup>-1</sup> d.w., and soot-EC between 0.62 and

0.72 mg g<sup>-1</sup> d.w. When the losses to the supernatant liquids (Table 3) were incorporated, the differences between EC, char-EC and soot-EC with different acid pretreatments were even smaller. The relative standard deviation of the four acid pretreatments with losses of the supernatant liquids being incorporated were 2.3%, 5.2%, and 8.1%, for EC, char-EC, and soot-EC, respectively. The marine sediment also showed the same pattern of narrow EC, char-EC and soot-EC variations except for the sample pretreated in hot HNO<sub>3</sub> (Fig. 2). This confirms the conclusion (see Section 3.2) that HCl and unheated HNO<sub>3</sub> have little influence on EC concentrations, while hot concentrated HNO<sub>3</sub> may oxidize char-EC and soot-EC.

The losses of EC, char-EC, and soot-EC into the supernatant liquids during the various acid pretreatments were also assessed. Table 3 summarizes the differences between the residue TC, OC, EC, char-EC, and soot-EC of the sample, and those with their supernatant liquids returned (supernatants were reanalyzed and added). The supernatants contain up to 10% and up to 11.7% of the EC from lacustrine and marine sediments, respectively. However, these supernatant-returned samples after different acid pretreatments had similar EC results, indicating that returning the supernatants could offset most of the loss from supernatant discharges.

### 3.4. Testing potentially interfering materials

The potentially interfering material impacts on EC determination have been reported by Hammes et al. (2007) for various methods. Recently, Han et al. (2007a) also tested the impact with the TOR method using HCl pretreatment (Table 4), and revealed that Suwannee River natural organic matter (Suwannee NOM) and Beulah-Zap lignite were generally removed, while urea-glucose melanoidin and Pocahontas bituminous coal could not be com-

**Table 3**

Losses of EC, char-EC and soot-EC in sediments from discharges into the supernatant liquids (concentrations are the average of triplicate measurements, and the standard deviations are shown in Fig. 2).

Pretreatment	TC (mg g <sup>-1</sup> d.w.)	OC (mg g <sup>-1</sup> d.w.)	EC (mg g <sup>-1</sup> d.w.)	Char-EC <sup>a</sup> (mg g <sup>-1</sup> d.w.)	Soot-EC <sup>b</sup> (mg g <sup>-1</sup> d.w.)
<i>TS, lacustrine sediment sample</i>					
HCl-HF-HCl	7.79	6.50	1.29	0.64	0.65
HCl-HF-HCl SR <sup>c</sup>	9.73	8.30	1.43	0.71	0.72
Recovery (%) <sup>d</sup>	80.1	78.3	90.9	90.2	90.3
HCl + HF	6.92	5.57	1.35	0.78	0.56
HCl + HF SR <sup>c</sup>	7.21	5.83	1.38	0.79	0.59
Recovery (%) <sup>d</sup>	96.0	95.5	97.8	98.7	95.0
HNO <sub>3</sub> -HF-HCl	5.34	4.03	1.31	0.74	0.57
HNO <sub>3</sub> -HF-HCl SR <sup>c</sup>	7.29	5.85	1.45	0.79	0.66
Recovery (%) <sup>d</sup>	73.2	68.9	90.3	93.7	86.7
HNO <sub>3</sub> + HF	6.15	4.8	1.35	0.73	0.62
HNO <sub>3</sub> + HF SR <sup>c</sup>	6.46	5.07	1.39	0.74	0.65
Recovery (%) <sup>d</sup>	95.2	94.7	97.1	98.7	95.3
<i>NS99, marine sediment sample</i>					
HCl-HF-HCl	3.76	3.09	0.67	0.45	0.22
HCl-HF-HCl SR <sup>c</sup>	4.72	3.96	0.76	0.5	0.26
Recovery (%) <sup>d</sup>	79.7	78.1	88.3	90.2	84.8
HCl + HF	3.6	2.88	0.72	0.4	0.31
HCl + HF SR <sup>c</sup>	3.77	3.04	0.74	0.41	0.33
Recovery (%) <sup>d</sup>	95.5	94.7	97.3	97.6	94
HNO <sub>3</sub> -HF-HCl	3.07	2.39	0.68	0.45	0.23
HNO <sub>3</sub> -HF-HCl SR <sup>c</sup>	3.58	2.81	0.77	0.49	0.28
Recovery (%) <sup>d</sup>	85.8	85.1	88.5	91.8	82.4
HNO <sub>3</sub> + HF	3.33	2.66	0.67	0.35	0.32
HNO <sub>3</sub> + HF SR <sup>c</sup>	3.5	2.81	0.68	0.36	0.32
Recovery (%) <sup>d</sup>	95.1	94.7	98.5	97.3	100

<sup>a</sup> Char-EC = EC1 – POC.

<sup>b</sup> Soot-EC = EC2 + EC3.

<sup>c</sup> Supernatants return (SR) means that the supernatant liquids from each step were collected and filtered with quartz filters, and that carbon analysis of the supernatants was also conducted. The supernatant carbon analysis results were added to those of the residue, and are presented as the measured results.

<sup>d</sup> Recovery represents the concentrations of the different species divided by the corresponding concentrations with supernatant return.

**Table 4**  
The TOR results of potentially interfering materials after using different acid pretreatments (concentrations are expressed as average  $\pm$  standard deviation of triplicate measurements). The non-acid treatment represents the TOR results of non pretreated, pre-weighed samples; HCl treatment represents the HCl–HF–HCl pretreatment; HNO<sub>3</sub> treatment represents the concentrated HNO<sub>3</sub>–HF–HCl pretreatment. Samples were ground to pass through 63  $\mu$ m sieve.  $\sim$ 0.8 mg samples were weighed and followed with the acid pretreatment mentioned above. Finally the residues were filtered onto pre-fired quartz filter and dried in an oven at 60 °C for 4 h for carbon analyses.

Negative EC materials	Pre-treat	Measured TC (mg g <sup>-1</sup> d.w.)	Measured OC (mg g <sup>-1</sup> d.w.)	Measured "EC" (mg g <sup>-1</sup> d.w.)	Measured "char-EC" <sup>d</sup> (mg g <sup>-1</sup> d.w.)	Measured "soot-EC" <sup>e</sup> (mg g <sup>-1</sup> d.w.)
Suwannee River NOM	Non-acid <sup>a</sup>	438 $\pm$ 11	385 $\pm$ 17	53 $\pm$ 14	46 $\pm$ 13	7 $\pm$ 1
	HCl <sup>b</sup>	261 $\pm$ 18	242 $\pm$ 20	19 $\pm$ 3	6 $\pm$ 1	14 $\pm$ 2
	HNO <sub>3</sub>	189 $\pm$ 14	180 $\pm$ 12	9 $\pm$ 2	9 $\pm$ 1	3 $\pm$ 1
Urea–glucose melanoidin	Non-acid <sup>a</sup>	580 $\pm$ 24	264 $\pm$ 23	315 $\pm$ 18	250 $\pm$ 20	65 $\pm$ 11
	HCl <sup>b</sup>	615 $\pm$ 66	338 $\pm$ 57	228 $\pm$ 9	243 $\pm$ 12	35 $\pm$ 8
	HNO <sub>3</sub> <sup>c</sup>	71 $\pm$ 6	61 $\pm$ 5	10 $\pm$ 1	2 $\pm$ 0	8 $\pm$ 1
Beulah–Zap lignite coal	Non-acid <sup>a</sup>	552 $\pm$ 11	405 $\pm$ 11	147 $\pm$ 12	146 $\pm$ 12	1 $\pm$ 0
	HCl <sup>b</sup>	400 $\pm$ 42	303 $\pm$ 26	96 $\pm$ 16	89 $\pm$ 16	7 $\pm$ 1
	HNO <sub>3</sub>	189 $\pm$ 21	97 $\pm$ 12	92 $\pm$ 8	88 $\pm$ 8	4 $\pm$ 0
Pocahontas bituminous coal	Non-acid <sup>a</sup>	855 $\pm$ 16	180 $\pm$ 16	675 $\pm$ 11	380 $\pm$ 15	295 $\pm$ 16
	HCl <sup>b</sup>	687 $\pm$ 46	170 $\pm$ 28	517 $\pm$ 33	246 $\pm$ 22	253 $\pm$ 18
	HNO <sub>3</sub>	488 $\pm$ 42	56 $\pm$ 8	431 $\pm$ 40	338 $\pm$ 38	98 $\pm$ 10

<sup>a</sup> Non-acid and <sup>b</sup> HCl treatment (TC, OC, and "EC" results are taken from Han et al., 2007a).

<sup>c</sup> The HNO<sub>3</sub> treatment for melanoidin was conducted only with the concentrated HNO<sub>3</sub> step, with no subsequent HF and HCl pretreatment steps because the material was completely dissolved in the HNO<sub>3</sub>. The carbon analysis was thus conducted using the filtered supernatants.

<sup>d</sup> Measured "char-EC" = EC1 – POC.

<sup>e</sup> Measure "soot-EC" = EC2 + EC3.

pletely removed using HCl. Although Verardo (1997) demonstrated that pretreatment in heated HNO<sub>3</sub> can remove the majority of bituminous coal, our results have shown that this pretreatment can also oxidize EC (see Sections 3.2 and 3.3), making it an undesirable pretreatment to quantify EC. In the present study, we tested the concentrated HNO<sub>3</sub> pretreatment for the removal of potentially interfering materials and the results were presented in Table 4. In HCl and without acid treatment tests, urea–glucose melanoidin showed significant influence on EC determination, while HNO<sub>3</sub> pretreatment removed almost all urea–glucose melanoidin and only bituminous coal influenced EC determination. The different acid pretreatments indicated that HNO<sub>3</sub> are more suitable for the removal of the potentially interfering materials.

Han et al. (2007a) reported only the influence of potentially interfering materials on the total EC determination, while the present study also demonstrated the influence of these materials on char-EC and soot-EC determination (Table 4). The HNO<sub>3</sub> treatment removed almost all these potentially interfering materials for soot-EC determination, and only a small amount of bituminous coal (9.8% by mass) remains. As for the influence on char-EC determination, although large amounts of bituminous coal were retained in the HNO<sub>3</sub> treatment, the other potentially interfering materials were almost completely removed. To the best of our knowledge, there is no available method that can quantify the entire continuum of EC while both removing all of the potentially interfering materials and with no EC losses.

#### 4. Conclusions

Acid pretreatment is widely used to separate OC and EC in sediments and soils, but the effect of acidification on this separation is not fully known. The present study showed that, although concentrated HNO<sub>3</sub> did not oxidize EC, hot concentrated HNO<sub>3</sub> significantly oxidized EC, including char-EC and soot-EC. We suggest that hot concentrated HNO<sub>3</sub> is not suitable for the separation of EC and OC. HCl, HF, and HNO<sub>3</sub> pretreatments can decrease soot thermal stability under high temperature, suggesting that acids remaining from the pretreatment processes would lead to underestimation of soot-EC using thermal methods. This may be associated with various polar organic functional groups and organics on the surface of soot particles that may easily be replaced with Cl<sup>-</sup>,

F<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> ions, and thus increase the chemical–thermal reactivity of the particles. This point may be also relevant for EC quantification in aerosols, in which large amounts of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions are present. The discharges of EC in the supernatant liquids were large, so the return of the supernatants was necessary for high precision determinations of EC, and this may offset most of the losses. The relative standard deviation of the lacustrine sediment between pretreatments with the supernatant liquids incorporated were 2.3%, 5.2%, and 8.1%, for EC, char-EC, and soot-EC, respectively. The concentrated HNO<sub>3</sub> pretreatment removed almost all of the potentially interfering materials for soot-EC determination. Considering that: (1) the comparison between HCl and HNO<sub>3</sub> pretreatments revealed little difference in EC, char-EC, and soot-EC concentrations for these positive reference materials and marine and lacustrine sediments; and (2) EC, char-EC, and soot-EC concentrations using the HCl pretreatment were the most comparable to the measurements on samples without acid pretreatment, such as carbonaceous aerosols, we recommend both concentrated HNO<sub>3</sub>–HF–HCl and HCl–HF–HCl pretreatments for EC, char-EC, and soot-EC quantification using the TOR method.

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