

Intercomparison of Measurement Techniques for Black or Elemental Carbon Under Urban Background Conditions in Wintertime: Influence of Biomass Combustion

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A generally accepted method to measure black carbon (BC) or elemental carbon (EC) still does not exist. An earlier study in the Vienna area comparing practically all measurement methods in use in Europe gave comparable BC and EC concentrations under summer conditions (Hitzenberger et al., 2006a). Under summer conditions, Diesel traffic is the major source for EC or BC in Vienna. Under winter conditions, space heating (also with biomass as fuel) is another important source (Caseiro et al., 2007). The present study compares the response of thermal methods (a modified Cachier method, Cachier et al., 1989; a thermal-optical method, Schmid et al., 2001; and two thermal-optical (TOT) methods using Sunset instruments, Birch and Cary, 1996 and Schauer et al., 2003) and optical methods (a light transmission method, Hansen et al., 1984; the integrating sphere method, Hitzenberger et al., 1996; and the multiangle absorption photometer MAAP, Petzold and Schönlinner, 2004). Significant differences were found between the TOT methods on the one hand and all other methods on the other. The TOT methods yielded EC concentrations that were lower by 44 and 17% than the average of all measured concentrations (including the TOT data). The largest discrepancy was found when the contribution of brown carbon (measured with the integrating sphere method) was largest.

1. Introduction

Black carbon (BC) or elemental carbon (EC), which is produced by incomplete combustion of carbonaceous fuels, is an important component of the atmospheric aerosol because of its light absorbing characteristics (1) and possible

health effects (2). Despite intensive efforts over the last three decades, no widely accepted standard measurement method exists.

Over the years, numerous method intercomparison studies were performed (see review in ref 3 and intercomparison studies in refs 4–6). Usually, thermal methods differ little in total carbon (TC) concentrations. The major problem is the OC (organic carbon)/EC split. EC (measured with thermal methods) or BC (measured with optical methods) can differ in intercomparisons by factors of three or four depending on aerosol characteristics.

In recent years, humic like substances (HULIS) were found in atmospheric aerosols (7, 8). This organic material weakly absorbs visible light with stronger absorption at short wavelengths. HULIS are therefore often called “brown” carbon (9), although brown carbon seems to include also other compounds (33). Brown carbon originates mainly from biomass fires (10) and chemical reactions in the atmosphere (11, 12). Samples containing biomass smoke present more analytical difficulties than, e.g., traffic emissions because Na and K can lower the combustion temperature of EC (13). HULIS, however, are thermally rather stable, so they evolve at higher temperatures than other OC (9, 10) leading to interferences with the EC signal.

The study by Hitzenberger et al. (14) compared practically all methods for EC and BC determination in use in Europe under summer conditions in the urban area of Vienna. No significant differences were found, so at least under the conditions of the study (urban background aerosol, strong Diesel traffic source) all methods performed equally well. We decided to perform another study under wintertime conditions, when space heating contributes an important fraction to the EC or BC aerosol in Vienna (15).

The goal of the present study was to investigate whether the different source contributions in wintertime influence the relative performance of the measurement methods. The newly developed extension of the integrating sphere technique to separate black and brown carbon is used to examine the effect of brown carbon on the comparability of the optical and thermal methods. We show here that the presence of specific wintertime sources, such as domestic heating, leads to the occurrence of brown particulate material that can interfere considerably with current EC/OC or BC determination techniques.

2. Experimental Section

2.1. Site Description. Measurements were performed during the heating season from February 7 to March 15, 2006, at the roof laboratory of the Physics building of the University of Vienna, Austria, at 35 m above ground under late winter conditions. Daily average temperatures ranged from -7.7 to 6.2 °C, and average humidities were between 56.5 and 90.5%. During this period, winds were mostly from the north to west sector.

The sampling site ($48^{\circ}13'17''$ N, $16^{\circ}21'19''$ E) is situated in central Vienna (population 1.8 million) in a densely built upon area heavily impacted by traffic. The site, however, does not receive direct traffic emissions because it is separated from the nearest road by ca. 100 m of interconnected buildings and courtyards. The street directly below is used mainly for parking. Roof heights in this part of the city are rather homogeneous. Sampling was performed during the heating season, but only little direct influence from nearby chimneys is expected, because most of the buildings in the area are heated by district heating or natural gas.

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TABLE 1. Description of Methods, Their Codes, Filters and Other Characteristics^a

method	code	filter type	upper cut size	wavelength
light transmission	LTM	Pallflex Tissuquartz 2500QAT-UP	10 μm	"white"
multiangle absorption photometer	MAAP	glass fiber Schleicher Schuell GF 10		630 nm
integrating sphere	IS	MSI polycarbonate, 0.2 μm pore size	80 μm	550 nm
thermal-optical	TOM-TU	Pallflex Tissuquartz 2500QAT-UP	10 μm	Charring corr.:671 nm
two-step thermal	Cachier	Pallflex Tissuquartz 2500QAT-UP	10 μm	n a.
thermal-optical, NIOSH protocol	TOT-NIOSH	Whatman QM-A Quartz fiber	10 μm	670 nm
thermal-optical, alternate 3 protocol	TOT-A3	Whatman QM-A Quartz fiber	10 μm	670 nm

^a n.a., nonapplicable.

Diesel traffic is an important source of EC or BC in Vienna, as all heavy duty vehicles and a large fraction of passenger cars have diesel engines. In 2006, 51.5% of passenger cars used diesel fuel (Statistik Austria, 2007, personal communication), which contributed 57% to the total automotive fuels sold in Austria (OMV, 2007, personal communication). In wintertime, space heating also contributes to the carbonaceous aerosol. In the AQUELLA study (16, 17) biomass burning was found to contribute 10% to PM10 in Vienna, and 15% of PM10 emitted by biomass combustion was found to be EC. Wood chips or pellets are a widely used fuel in the surroundings of Vienna, so wood burning is a large source for the Vienna aerosol even though it is not important in Vienna itself (only 2.8% of total heating energy; City of Vienna, Climate Protection Coordination, personal communication).

2.2. Sampling Schedule. Sampling times for the filter based methods were 24 h with sample change nominally at 14:00 CET (i.e., 13:00 UTC). Because of different programming of one of the automatic sample changers, one set of filters (used for analysis with the TOT methods) was changed at 11:30 CET instead. The multi-angle absorption photometer (MAAP) measured continuously with a time resolution of 1 min, so the data of this instrument were used to correct for the temporal offset of the sample changer. For the comparison with the off-line samples, the quasi continuous BC concentrations collected by the MAAP were converted to 24 h averages as performed previously (14).

Three filter samplers were operated in parallel. Two were fitted with PM10 heads, whereas one (collecting samples on polycarbonate filters for the integrating sphere (IS) method) had an open-face upside down filter holder. The MAAP instrument sampled through a horizontal 1.5 m vacuum tube without sampling head. As little BC (2.6%, (18)) is found in the size fraction $> 2 \mu\text{m}$ at our site, the upper cut size of the samplers is unimportant.

2.3. Analysis Methods for EC or BC. Table 1 shows all methods, their specific properties, the codes used in the figures and discussion as well as the filter materials. The codes are identical to the summer study where applicable. In the winter study, the VDI method and the aethalometer were not available for logistical reasons. The TOT methods had not been available during the summer study.

2.3.1. Thermal Methods. Elemental carbon (EC) was determined both with a two-step method (Cachier method), and three thermal-optical methods with different temperature protocols. For all thermal methods, prefired filters were used. The filters used for the Cachier and TOM-TU method had been heated for 4 h at a temperature of 450 °C to remove adsorbed carbonaceous material. After preheating, these filters were cooled in an H₂O-atmosphere. The filters used for both TOT methods had been prefired for 24 h at 550 °C. All filters were kept at -18 °C except during handling, transport, and sampling.

In the two-step method (19), aliquots of loaded filters are heated for 2 h in a pure O₂ stream at 340 °C to remove organic carbon (OC). In the subsequent step, EC and carbonates are oxidized at 1000 °C (C_{step1}). Carbonates were determined (20)

by heating aliquots of the filters for 1 h in a pure O₂ stream at 460 °C; in this preheating step OC and EC are removed and the remaining carbonates are combusted at 1000 °C (C_{step2}). Carbonate-corrected EC is calculated as the difference of the carbon-fractions obtained after the two preheating steps: $\text{EC} = C_{\text{step1}} - C_{\text{step2}}$.

The thermal-optical method TOM-TU (4) exposes aliquots of loaded filters to constantly increasing temperatures (20 °C/min) up to a maximum temperature of 800 °C in a pure O₂ stream. A MnO₂ catalyst (at 700 °C) converts all the evolved carbonaceous gases to CO₂, which is detected by a NDIR detector. Charring of organic material is accounted for by monitoring the signal of a laser beam transmitted through the sample (wavelength: 671 nm). All CO₂ detected after the transmitted light signal has reached its initial value is attributed to EC.

The other thermal-optical method (TOT) is based on a two-phase thermal analysis. Charring is monitored by recording the signal of a laser beam (wavelength: 670 nm) transmitted through the sample. In the first phase, filter aliquots are heated in a pure He atmosphere, while in the second phase the atmosphere consists of 98% He and 2% O₂. Two different Sunset instruments with different temperature protocols were used. In the TOT-NIOSH method (21), the temperature in the first phase is raised up to 870 °C, whereas in the TOT-alternate 3 (TOT-A3) method (22) the temperature is raised only up to 550 °C; the latter temperature program is similar to that of the DRI method (23). The thermally desorbed (first phase) or combusted (second phase) carbonaceous products are oxidized to CO₂ with a MnO₂ catalyst (at 870 °C), the CO₂ is reduced to CH₄ in a Ni-firebrick methanator (at 500 °C), and the CH₄ is measured with a flame ionization detector (FID). The FID signal is attributed to EC after the transmitted laser signal has reached its initial value.

2.3.2. Optical Methods. Black carbon (BC) was determined with three optical methods: the multiangle absorption photometer (MAAP), a light transmission photometer (LTM), and the integrating sphere method (IS).

In principle, the optical methods can measure only a signal that is proportional to the absorption properties of the sample. To obtain BC concentrations, the signals have to be converted either using a calibration curve obtained with a carbon black standard (the IS method) or by applying specific absorption coefficients (the MAAP method) or instrument factors (the LTM method) for EC aerosols. These coefficients or factors were originally obtained with thermal methods for traffic-derived EC samples. All optical methods are therefore indirectly based either on traffic aerosol or on an EC standard. Moreover, the usual optical methods attribute all light absorption by aerosol particles to BC. The presence of other light absorbing material will lead to an overestimation of BC concentrations.

In the MAAP instrument (24) a filter sample is illuminated by a LED (effective wavelength: 630 nm (25)). Simultaneous measurements of transmitted and backscattered light at several detection angles in both forward and back hemispheres are used to calculate the absorption coefficient σ_a of

TABLE 2. Ratios of Averages^a

method	ratio to average summer	ratio to average, winter, IS old calibration	ratio to average, winter (only methods used in both studies, new IS calibration)	ratio to average, winter, new IS calibration
VDI	0.936			
Cachier	1.083	1.00	0.978	1.13
TOM-TU	1.020	1.04	1.024	1.19
MAAP	0.911	1.2	1.224	1.42
IS	1.120	1.3	0.825	0.95
LTM	0.910	0.96	0.949	1.10
AET	0.979			
TOT-NIOSH		0.46		0.52
TOT A3		0.68		0.78

^a Campaign averages for each method are divided by the grand average of all data collected during the campaign. For the grand average of the winter data in column 3, only data obtained with methods used also in the summer study were included. All data for the summer study were published by Hitzenberger et al. (2006a). To better compare the winter and summer studies, ratios were also calculated using the IS calibration curve used in the summer study ("old calibration").

the deposited aerosol with radiative transfer techniques. A conversion factor of 6.5 m²/g was used to obtain BC concentrations from σ_a . No further correction of aerosol light scattering or filter loading effects is needed (26).

The light transmission photometer (LTM) uses a white light source and a silicon photodiode detector to measure light transmitted through a loaded and a clean reference filter. The attenuation signal is converted to BC concentration using an instrument factor of 19 m²/g (this setup corresponds to an "off-line" aethalometer (27)).

In the integrating sphere method (IS; 28, 29), the decrease of light flux in the sphere (at 550 nm) caused by absorbing materials is converted to $\mu\text{g BC}$ (denoted here as BC-IS) using a calibration curve obtained with a commercial carbon black (Elftex 124, Cabot Corp.). The BC concentration measured with the IS method is therefore equivalent to the concentration of the test substance which would give the same IS signal. In this study, two different kinds of sample were analyzed. The IS data were obtained from polycarbonate filters dissolved in chloroform, whereas the IS-TOM and IS-TOT data were measured from small punches of the quartz fiber filters used for the TOM and TOT analyses which were immersed in an acetone/isopropanol/water mixture. In both cases, the decrease in light flux was measured relative to a blank filter dissolved or immersed in the respective liquid. BC data measured from the quartz and polycarbonate filters were well correlated (Supporting Information 1; $r^2 = 0.67$ for IS-TOT and $r^2 = 0.86$ for IS-TOM; if one outlier each is removed, $r^2 = 0.84$ and 0.88). The regression lines of BC concentrations (in $\mu\text{g}/\text{m}^3$) are IS-TOT = $1.11 \times \text{BC-IS} - 0.13$ and IS-TOM = $1.38 \times \text{BC-IS} - 0.52$. The main difference between the two filters is the filter material (see Table 1). The photometer was redesigned to extend the wavelength range and had, therefore, to be recalibrated. In the new calibration curve, the focus was on the lower concentrations of BC found in recent years. For comparison purposes, Table 2 contains also a column where calculations were performed using the old calibration curve. All other IS data were obtained with the new calibration curve.

2.3.3. Estimation of Brown Carbon. Originally, the basic assumption for converting the IS photometer signal to BC concentrations is that BC is the only light absorbing substance in the atmospheric aerosol, as airborne humic-like material

(HULIS) was generally recognized only in recent years. In a separate study (30), a procedure to estimate brown carbon concentrations was developed. Calibration curves were obtained at four wavelengths (405, 450, 550, and 650 nm) both for Elftex 124 (as a proxy for fresh combustion BC) and for a humic acid standard (humic acid sodium salt, Acros Organics, no. 68131-04-4) as a proxy for "brown carbon". Using the different wavelength dependence of the calibration curves, an iterative procedure was applied to estimate the concentrations of brown and black carbon. The resulting (reduced) concentration of black carbon is labeled "BC-black" in contrast to BC, which stands for BC obtained in the usual way. The concentration of brown carbon is called "BC-brown". We performed this separation for all filter types. Figure 3 contains the results obtained from the TOT filters. Again, any BC-brown concentration is actually the concentration of the humic acid standard causing the same absorption signal as the actual atmospheric brown carbon, whose optical properties are highly variable (8). The C content of brown carbon can be calculated from BC-brown by dividing by 1.8 (31).

3. Results and Discussion

3.1. EC and BC Method Intercomparison. Figure 1 shows all data except BC-black and BC-brown. The general trend of EC or BC concentrations is similar, but significant differences exist between the methods, which are more severe than during the summer study (14). The MAAP method yielded the highest BC concentrations (Figure 1a). The differences within the thermal methods (Figure 1b) were quite large. No comparison in terms of thermal methods between winter and summer is possible because the TOT methods had not been previously available.

As there is no standard method, no data set can be labeled as the "correct data set". The data obtained from each method were, therefore, averaged over the whole campaign and compared to the grand average of all data measured with all methods (Figure 2). Contrary to the results of the summer study, the differences between the method averages are well visible in winter.

The TOT-NIOSH method yielded the lowest campaign average ($1.36 \mu\text{g}/\text{m}^3$), whereas the MAAP method gave the highest average ($3.71 \mu\text{g}/\text{m}^3$). The data obtained with the optical methods are all rather close to the average (except the MAAP data), and the thermal methods also lie close to the average except the two TOT methods. Table 2 gives the ratios of the method averages to the grand average of all data of the campaign for both winter and summer studies. The IS-TOT and IS-TOM data (ratio to average 1.01 and 0.90) are not included in this table, as they had not been measured previously. To better compare the studies, an additional column is given in Table 2 where the wintertime ratios are calculated only for those methods that had been used in both studies.

A comparison of total carbon (TC) concentrations measured by the thermal analysers, showed an excellent agreement. For the TC concentrations obtained with the NIOSH temperature protocol, the regression line was $\text{TC}(\text{TOT}) = 1.034 \times \text{TC}(\text{Cachier})$ and for those obtained with the A3 protocol, $\text{TC}(\text{A3}) = 0.979 \times \text{TC}(\text{Cachier})$. In both cases, $r^2 = 0.91$. The differences between the thermal methods were obviously not caused by aerosol inhomogenities or sampling uncertainties.

3.2. Influence of Brown Carbon. Based on the data in Section 3.1 only, one could conclude that all methods agree fairly well except for the TOT methods. Figure 1b, however, has an interesting feature. On some days (or time periods spanning several days) the thermal methods agree rather well, but during other periods the differences are very marked. The days with the marked differences are days with low

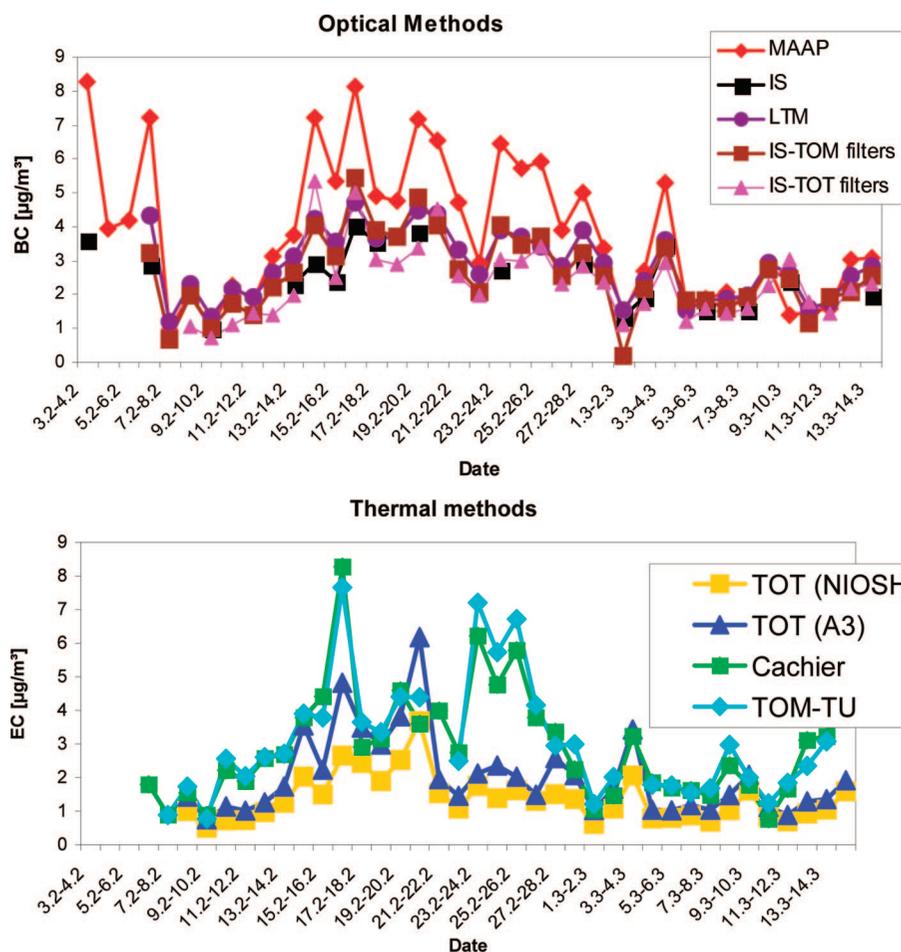


FIGURE 1. (a) (above): BC concentrations obtained with optical methods. For the integrating sphere technique, concentrations obtained from dissolved polycarbonate filters (IS) and the quartz fibre filters used for the TOM-TU (IS-TOM filters) and the TOT (IS-TOT filters) techniques are given. No correction for "brown carbon" was made in the IS concentrations. (b) (below): EC concentrations obtained with thermal methods. For the method codes, see Table 1.

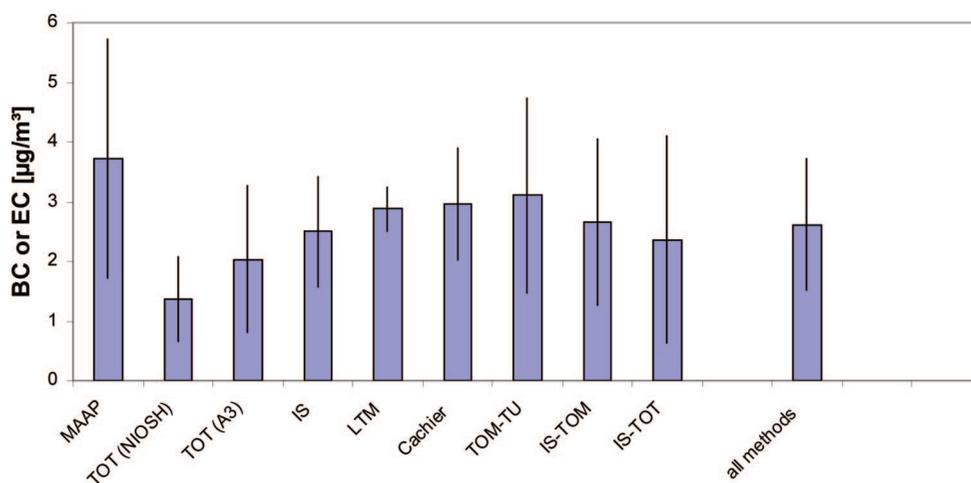


FIGURE 2. All data; campaign averaged for each method and grand average (right bar). The data for the IS method were obtained with the new calibration curve, but were not corrected for the influence of brown carbon. The vertical lines are one standard deviation of the campaign averages. obtained by the different methods. For the grand average, the bars indicate the standard deviation of the averages.

temperatures (from February 23 to 27, e.g., 24 h average temperatures dropped to $-4\text{ }^{\circ}\text{C}$, whereas from March 4 to 8, the maximum daily average temperature was $8.3\text{ }^{\circ}\text{C}$). During cold episodes, the source strength of space heating increases. Using conventional BC or EC measurement techniques, however, the changes in carbonaceous aerosol characteristics cannot be traced.

The picture changes when the separation of black and brown carbon [(30)] is performed. Figure 3 shows again the EC data obtained by the thermal methods, but this time BC-brown and BC-black are also included. On the days with the largest discrepancies, the BC-black is better comparable to the TOT data than to the other thermal methods. On these days, both the concentration and the contribution of brown

Thermal methods and "BC-black"

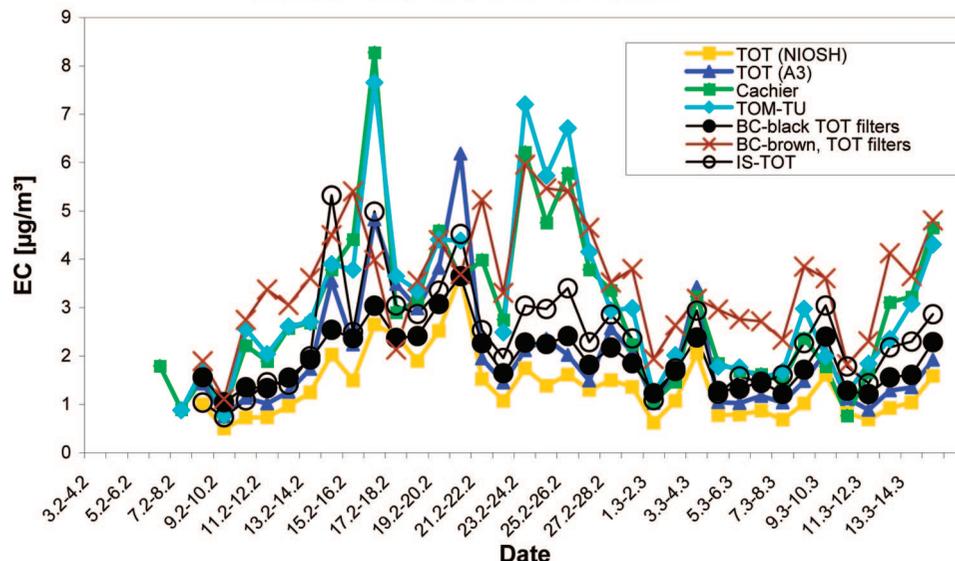


FIGURE 3. EC concentrations obtained with the thermal methods compared to BC ("BC- black", full circles) obtained from the IS method after removal of the influence of "brown" carbon ("BC-brown", crosses). Uncorrected IS BC data ("IS-TOT") are also given (open circles). All BC data were obtained from the filters used for the TOT analyses.

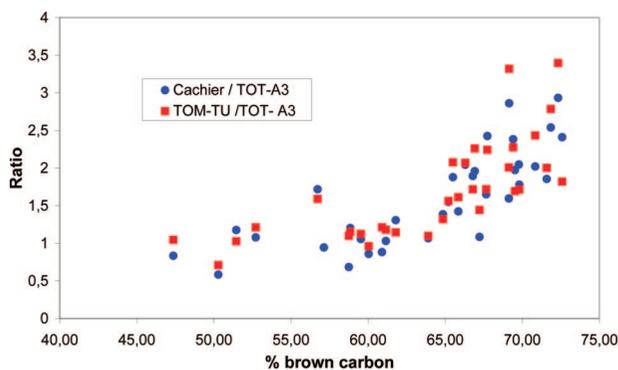


FIGURE 4. Ratios of the Cachier and the TOM-TU methods to the TOT-A3 method as a function of the percentage of brown carbon in total light absorbing carbon (determined with the IS method).

carbon to the absorption signal were high. The ratio of brown carbon to black carbon was between 2.2 and 2.6 in the period February 23–27 (compared to 1.9 during the period March 3–10). This period was also the coldest of the whole campaign, so we do expect influence from space heating. Despite the small contribution of biomass to the total heating energy sector in Vienna (2.8%), the background aerosol advected to the urban area is more influenced by biomass combustion. On the days with higher temperatures and lower influence of brown carbon, the TOT methods and the other thermal methods are much better comparable (within factors of less than 2).

The discrepancy between the thermal methods is linked to the percentage of brown carbon in total light absorbing carbon (i.e., brown/(black + brown) measured with the IS method). Figure 4 shows the ratios of the Cachier and the TOM-TU methods to the TOT-A3 as functions of % brown carbon. The ratios increase strongly with increasing brown carbon content of the aerosol. Further work is needed to investigate these trends.

At the time of the summer study, the separation of brown and black BC had not been developed, so no data are available for the comparison. Data obtained in another study show, however, that the contribution of HULIS to summertime Central European boundary layer aerosols is lower than in wintertime (32).

The results of the winter study seem to indicate that practically all usually employed methods except the TOT methods overestimate EC or BC concentrations if the aerosol contains appreciable amounts of brown carbon. The TOT-NIOSH and TOT-A3 methods, on the other hand, yield the lowest EC concentrations at all times. This feature is most pronounced for the TOT-NIOSH method, which gives EC concentrations that are 33% lower than BC-black concentrations, maybe due to a high temperature setting in the last heating step in He. The BC-black concentrations could be seen as more realistic representations of traffic and oil combustion derived BC, but again there is the question of calibration: carbon black as standard for traffic BC and humic acid as standard for brown carbon. If real world brown carbon has different wavelength dependent absorption properties, the separation procedure gives BC-black concentrations that could be too low or too high. At this point, it is only safe to conclude that the TOT methods are less sensitive to the presence of brown carbon than the other methods (including the original uncorrected IS method), but whether this conclusion is sufficient as a basis for selecting any method to monitor air quality criteria is quite doubtful. Substantial research efforts are needed to fully characterize the thermal methods for samples containing aerosol produced by biomass combustion. A pragmatic way of dealing at least with historic data would be what we recommended in the summer study (14): use a conversion table based on regression analyses (Supporting Information 3) to compare BC or EC data measured with different methods under wintertime conditions in urban areas with similar source conditions.

Acknowledgments

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Supporting Information Available

Table S1 shows exact steps in the temperature protocols of the Sunset instruments used for the TOT-NIOSH and TOT-

A3 methods, Table S3 shows Parameters of linear correlations between methods A and B, and Figure S1 shows Comparison of BC concentrations obtained with the IS method from the quartz filters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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