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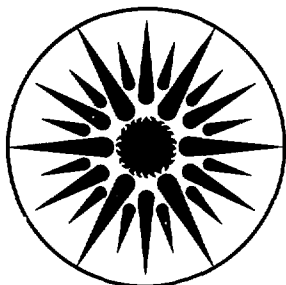
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Influence of sample composition on aerosol organic and black carbon determinations

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Abstract: In this paper we present results on characterization of filter-collected redwood (*Sequoia sempervirens*)-needle and eucalyptus smoke particles by thermal, optical, and solvent extraction methods. Our results demonstrate that organic and black carbon concentrations determined by thermal and optical methods are not only method dependent, but also critically influenced by the overall chemical composition of the samples. These conclusions are supported by the following: (1) the organic fraction of biomass smoke particles analyzed includes a component, ranging in concentration from about 6–20% of total carbon or from 16–30% of organic carbon, that is relatively non-volatile and has a combustion temperature close to that of black carbon; (2) presence of K or Na in biomass smoke samples lowers the combustion temperatures of this organic component and of black carbon, making their combustion properties indistinguishable; (3) about 20% of total organic material is nonvolatile when heated to 550°C in an inert atmosphere. Consequently, thermal methods that rely on a specific temperature to separate organic from black carbon may either underestimate or overestimate the black and organic carbon concentrations, depending on the amounts of Na and K and on the composition and concentration of organic material present in a sample. These analytical uncertainties and, under some conditions, absorption by organic material may contribute to the variability of empirically derived proportionality between light transmission through filter deposits and black carbon concentrations.

Introduction

Determining mass concentrations of major chemical species of biomass aerosols is a prerequisite for assessing the effects of biomass burning on the composition of the atmosphere and its influence on global and regional climate change. Accurate methods for chemical analyses of inorganic species are extensively used in most aerosol characterization studies. In contrast, techniques for characterizing carbonaceous material are much less accurate, and the results obtained by these methods are in many instances highly uncertain. Reasons for this situation are the chemical and physical complexity of carbonaceous (and other) aerosol material, sampling artifacts, and lack of appropriate standard materials.

At the simplest level, chemical characterization of carbonaceous aerosols involves determination of the concentration of classes of materials commonly referred to as total (TC), organic (OC), black (BC) (also known as elemental or graphitic), and carbonate carbon. Commonly used methods can be divided into two categories—thermal for total, organic and black carbon, and optical for black carbon determinations. The definitions of organic and black carbon used in conjunction with these methods are based on presumed volatilization, combustion, and optical properties of these classes of carbonaceous materials and are, therefore, operational and method dependent. These analytical problems are compounded by a lack of accepted standard materials and terminology, e. g. terms such as "black", "elemental," and "graphitic" carbon are sometimes used interchangeably. For simplicity, in this paper we will use the term "black carbon" as a synonym for both elemental and graphitic carbon.

Methods for total aerosol carbon determination rely on combusting the sample in oxygen, thereby converting all the carbon content to CO_2 . The CO_2 is quantitatively determined, either directly as CO_2 or after methanation over a suitable catalyst to CH_4 . Such a method was first applied to urban aerosols by *Mueller et al.* (1972) and different variants of this method are still presently in use.

Separation of organic and black carbon by thermal methods relies on the assumption that these components can be distinguished by their volatilization and combustion properties. These usually involve progressively heating a sample in an oxidizing or inert carrier gas and measuring the concentrations of gases evolved from the sample as a function of sample temperature. One method of evolved gas analysis used in this study is described below (*Novakov, 1981, 1982*). *Huntzicker et al.* (1982) employs

step-wise ramping of the sample temperature and two carrier gases—inert (pure He) and oxidizing (2% O₂ + 98% He mixture). This method defines OC as the sum of concentrations of species that volatilize at 350°C in a He/O₂ mixture and the fraction that volatilizes at 600°C in He. BC is defined as carbon oxidized in three temperature steps at 400, 500, and 600°C in a He/O₂ mixture. A modified version of the *Huntzicker et al.* apparatus was constructed by *Chow et al.* (1993). In this method organic carbon is defined as the sum of the carbon component evolving in a He atmosphere at four discrete temperature steps (from ~25–120°C, 120–250°C, 250–450°C, and 450–550°C). The BC component is taken as the integrated carbon concentrations released in a 2% O₂ + 98% He atmosphere at 550, 700, and 800°C. Both of these methods monitor the changes in sample darkness to correct for sample charring.

In addition to the above methods that use either continuous or step-wise increasing of the sample temperature, several simplified two-step methods have been developed. *Mueller et al.* (1982) have used a method in which a sample is placed in contact with MnO₂ which serves as the oxidizing agent. OC is defined as the carbon evolved from the sample at 550°C. BC is determined by the difference between total carbon (measured on a second sample aliquot) and organic carbon. Another two-step thermal analysis procedure was developed by *Cachier et al.* (1989). In this method a sample is first exposed to 340°C for 2 hr in pure oxygen to remove the organic material. BC is defined as the total carbon remaining on the sample after the precombustion treatment. Total carbon is determined by combustion of another aliquot of the untreated sample and the OC concentration derived by difference. *Wolff et al.* (1982) used a two-step volatilization/oxidation procedure at a constant (650°C) temperature. During the first step, the concentration of carbon-containing gases evolved in a He atmosphere is defined as OC. In the second step, the carrier gas is changed from He to O₂, and the detected CO₂ is attributed to BC.

Black carbon concentrations are routinely monitored by optical methods based on measuring the the light intensities transmitted through either precollected filters (*Rosen et al.*, 1980) or in a continuous mode through the accumulating filter deposit by an "aethalometer" (*Hansen et al.*, 1984). When BC is the principal light-absorbing species, its mass concentration (per unit filter area, in $\mu\text{g cm}^{-2}$) is given by $\text{ATN} = \sigma_{\text{BC}} \cdot \text{BC}$, where $\text{ATN} = -100 \ln(I/I_0)$, I and I_0 are the light intensities transmitted through the loaded and blank filters, and σ_{BC} is the mass absorption coefficient or cross section for BC (in $\text{m}^2 \text{g}^{-1}$). In practice, however, σ_{BC} should be viewed as an empirically derived proportionality constant rather than the absolute value of the BC absorption cross section. As discussed below, the empirical σ_{BC} values were found to be highly variable, depending on factors

such as aerosol chemical composition, presence of other light-absorbing species, and, to a large extent, the accuracy of analytical BC determinations.

In this paper we present results on the characterization of filter-collected redwood (*Sequoia sempervirens*)-needle and eucalyptus smoke particles by thermal, optical, and solvent extraction methods, with particular emphasis on determinations of BC and OC concentrations. As we show below, BC and OC concentrations of biomass smoke particles determined solely by any thermal method may significantly underestimate or overestimate the actual BC and OC concentrations. The derived concentrations are not only method dependent but also critically influenced by the chemical composition of the samples, particularly the amounts of Na and K and certain organic materials present in these samples.

We first describe sample generation and collection, the methods by which these samples were analyzed, and summarize our results that demonstrate the effects of sample chemical composition on the derived BC and OC concentrations. Finally, we discuss the implications of our results on the application of commonly used methods for the characterization of carbonaceous material in biomass smoke samples.

Experimental

Smoke particles used in this work were generated by burning redwood needles and eucalyptus bark. Approximately 10 g of redwood needles and 25 g of bark supported on a metal screen were burned in air under both flaming and smoldering conditions. Smoke particles from these fires were sampled after dilution with ambient air through a water-cooled duct and collected on 47-mm diameter pre-fired quartz filters. The details of smoke generation are shown in Table 1.

Smoke samples were characterized by a thermal and an optical method. The thermal method used in this study—Evolved Gas Analysis (EGA) (Novakov, 1981, 1982)—is based on an approach originally introduced by Malissa *et al.* (1976). EGA involves progressive heating of a sample (a punch of 1 cm² or less taken from the quartz filter) from room temperature to about 600°C at a rate of 12.5°C min⁻¹ in an oxidizing (O₂) or a neutral (N₂) atmosphere. In the oxidizing mode, the carbon-containing gases and vapors evolving from the sample as a result of volatilization, decomposition, and combustion of the carbonaceous material are converted to CO₂ over a MnO₂ catalyst maintained at ~800°C and are detected by a nondispersive infrared (NDIR) analyzer. When the analysis is done with purified, oxygen-free N₂ as the carrier gas, the hot MnO₂ acts as the oxygen donor, converting the volatilized gases and vapors to CO₂, thus

enabling use of the same NDIR detector in both modes of operation. The plot of the rate of evolution of CO_2 vs. temperature gives the "thermogram" of carbonaceous material evolved from the sample. The area under the thermogram is proportional to the TC content of the sample. Carbon thermograms show a structure, often in the form of well-defined peaks, indicative of the classes of sample materials with different volatilization, decomposition, and combustion properties. The carbon concentrations corresponding to these classes of materials can be obtained from the areas under these peaks.

Samples were analyzed by EGA as collected (original state) and after removal of their organic and water-soluble content. For this purpose replicate aliquots in the form of circular punches with areas $\leq 1 \text{ cm}^2$ were taken from exposed 47-mm diameter quartz filters and extracted with acetone and deionized water. To remove the organic material, the sample punches were immersed in acetone for about 4 hr. Water exposures were done in the same manner for time periods ranging from 20 min to several days. After extraction the sample punches were dried in air at room temperature and analyzed.

Both the original and the extracted samples were also characterized by an optical transmission method similar to that described by *Rosen et al.* (1980) and *Gundel et al.* (1984). The purpose of these measurements was not to accurately determine the absorption coefficients but rather to monitor the possible physical loss of BC from the samples during the extraction and to provide an estimate of BC concentration. Aliquots of collected filter samples extracted in 20 ml deionized water after 30-min sonication were analyzed for anions and cations by ion chromatography (Dionex 2020 1).

Results

The main features of the EGA thermograms of several smoke particle samples (recorded with O_2 as the carrier gas) are illustrated by the examples shown in Fig. 1a. Significant differences among these thermograms are obvious. The thermogram of sample #10 consists of a single peak at about 380°C . In contrast, the thermograms of samples #6 and #3 are more complex, showing features extending to about 100°C , in addition to the pronounced high temperature peaks. Thermal analyses of urban and source samples combined with simultaneous measurement of optical transmission through the sample collected on a quartz filter showed that the loss of optical absorption (or sample blackness) occurred simultaneously with the appearance of the high temperature thermogram peak appearing at 450°C to almost 600°C (*Rosen et al.*, 1982). The aerosol carbon component giving rise to this peak was therefore termed "black carbon" (*Novakov*, 1981, 1982). This high temperature peak could be used to derive the BC concentration,

assuming that this peak results from the combustion of BC alone. The carbon concentrations corresponding to the remainder of the thermogram could be assigned to organic carbon.

For the purpose of this discussion, we refer to the carbon concentration derived from the high temperature EGA peak of untreated (as collected) filter samples as the “apparent black carbon” (BC_{app}). A more accurate measure of the actual black carbon (BC_{act}) concentration can be obtained by analyzing samples from which most of the organic material has been removed by solvent (e.g. acetone) extraction. As BC is not soluble in organic solvents, the removal of OC from the sample should minimize its possible interference with BC peak assignment.

Thermograms of acetone-extracted samples are shown in Fig. 1b. The thermograms of the original (untreated) and the acetone-extracted sample #10 appear to be similar, indicating that the BC_{app} and BC_{act} concentrations are equivalent. That this sample is composed almost entirely of BC and has minimal OC is evident from the fact that the TC content of the acetone-extracted sample is only about 4% lower than that of the original sample (Table 2). A different situation is seen for samples with a larger organic content, such as samples #6 and #3. The high temperature thermogram peak (BC_{act}) of the acetone-extracted sample #6 is considerably smaller than the BC_{app} peak of the untreated sample. Even more drastic differences between BC_{app} and BC_{act} are seen for samples composed predominantly of organic material: one such example is sample #3, for which the BC_{app} is about 6 times greater than the BC_{act} concentration. In Table 2 we also show the ATN values determined from untreated and acetone-extracted samples. The fact that the ATN values before and after extraction are similar (average ATN ratio 0.98 ± 0.13) shows that essentially no BC was removed from the samples during this treatment. (The ATN value of sample #10 is anomalously low because of the uneven sample coverage.) The results described so far indicate that a fraction of soluble organic material contributes to the BC_{app} peak in the untreated smoke particle samples.

The approximate constancy of absorption cross sections (average value = $19.8 \pm 5.0 \text{ m}^2 \text{ g}^{-1}$) estimated from ATN values of untreated samples and BC_{act} concentrations (Table 2) demonstrates that black carbon (defined as BC_{act}) is the species principally responsible for light absorption of the filter-collected material. The contribution of organic species in biomass smoke to light absorption can be roughly estimated from the data shown in Table 2. The ATN values and OC concentrations for the two samples (yellow and brown in color) with 98.5% organic content (acetone soluble) are 23.8 and 55.3, and 118 and $443 \mu\text{g cm}^{-2}$ respectively, resulting in apparent mass absorption cross sections of the total organic material in these samples of 0.20 and $0.12 \text{ m}^2 \text{ g}^{-1}$. The contribution of

this material to the light absorption per unit mass of carbon is therefore about two orders of magnitude lower than that of black carbon.

A further insight into the thermal properties of biomass smoke particles is provided by the thermograms of water-exposed samples, examples of which are shown in Fig. 1c. These thermograms show that removal of water-soluble material results in a substantial increase in the BC_{app} peak temperatures over those seen in untreated samples. Water exposure of sample #10 (4.2% acetone-extractable organic content) resulted in a 130°C increase of the BC peak temperature above that of the untreated sample. Water treatment also resulted in a noticeable change in the BC peak shape but not in its area. Water treatment of sample #6 (63% acetone extractable) reduced the total carbon content from 131 $\mu\text{g cm}^{-2}$ to 83 $\mu\text{g cm}^{-2}$ (or by 37%) and caused the single BC_{app} peak seen in the thermogram of the untreated sample to separate into two distinct peaks at ~430°C and ~515°C. The carbon concentration corresponding to these two peaks accounts for 77% of the BC_{app} concentration of the untreated sample. We note that the carbon concentration represented by the 515°C peak ($\approx 26 \mu\text{g cm}^{-2}$) agrees with the BC concentration determined from the acetone-extracted sample, suggesting that this component is due to the combustion of black carbon; while the peak at 430°C appears to be due to the water-insoluble component of a relatively oxidation-resistant organic component. Water treatment of sample #3 (86% organic) reduced the total carbon content by 35% (from 658 $\mu\text{g cm}^{-2}$ to 233 $\mu\text{g cm}^{-2}$). Exposure to water reduced the apparent BC concentration by ~20%, increased the BC_{app} temperature by ~80°C, and changed the shape of this peak.

We attribute the changes in the thermograms to removal of water-soluble organic and inorganic species from the smoke samples. (Concentrations of water-soluble carbon, K^+ , Na^+ , Cl^- , and SO_4^{2-} are listed in Table 3.) The most abundant water-soluble inorganic species present in our samples were found to be K^+ and, to a lesser degree, Na^+ . These metals are common constituents of biomass smoke particles and are also known combustion catalysts. Consequently, when these metals are present in a sample, the BC_{app} temperature is lower than in the water-extracted sample, in which these species are absent. We note that Na was shown to lower the combustion temperatures of laboratory-generated (Lin and Friedlander, 1988) and urban (Grosjean et al., 1994) carbonaceous particles.

When catalytic species are present, all combustible material (including both the actual BC and the organic species that appear as a part of BC_{app}) will be rapidly oxidized when the temperature reaches a threshold value until it is consumed. This will result in a narrow, well-defined single thermogram peak. Conversely, in the absence of these catalysts, the high temperature thermogram should give an indication of the presence of

species with differing combustion temperatures as indicated from the difference in BC_{app} peak shapes seen in water-exposed and untreated samples.

The EGA analyses described so far were all done by using O_2 as the carrier gas. Additional information about the nature of the organic material was obtained from the thermograms measured with both O_2 and N_2 as the carrier gas. The results for a predominantly organic (98.5% extractable) sample (#11) are shown in Fig.2. A comparison of the N_2 thermogram with the one obtained in an O_2 atmosphere shows that the low temperature regions of both thermograms are identical. In contrast, the peak at about 320 °C is only partially reproduced in the N_2 mode. The BC_{app} prominent in the oxygen thermogram is virtually absent in the nitrogen thermogram. This comparison clearly shows that the lowest temperature peak is derived entirely from volatile species, while the species responsible for BC_{app} and, to a lesser degree, for the 320°C peak are nonvolatile under our experimental conditions. The nonvolatile carbonaceous material can be recovered by re-analyzing in O_2 the residue remaining in the sample after the run in N_2 . The oxygen thermogram of this residue (shown by dashed line in Fig.2) consists of a peak at the same temperature, with about the same concentration as the BC_{app} in the oxygen thermogram of the original sample.

The distinct BC_{app} peak at $\sim 425^\circ\text{C}$ ($BC_{app} = 81.2 \mu\text{g cm}^{-2}$) seen in O_2 thermogram shown in Fig. 2 must be derived from organic material because this sample is composed of $\approx 99\%$ acetone-soluble organic material, with BC_{act} below detection (Table 2). Organic carbon can contribute to BC_{app} in two ways. The first possibility is that the sample contains an organic component having a combustion temperature corresponding to the observed BC_{app} peak. The second possibility is that the material giving rise to the BC_{app} peak is a product of pyrolysis (or charring) of lower-volatility organic species that combust at temperatures similar to BC. We estimated the contribution of the pyrolyzed organic carbon to BC_{app} from the ATN values of the original sample and the sample preheated (in O_2) to 345°C, corresponding to the onset of the BC_{app} peak. The ATN values before and after heating were found to be 55.3 and 130 respectively. This increase in ATN values shows that some charring of the sample in an O_2 atmosphere did occur. The contribution of this material to BC_{app} is small, approximately equal to $ATN/\sigma \approx 130/20 \approx 6.5 \mu\text{g cm}^{-2}$, or about 8% of BC_{app} . The ATN value at the end of the nitrogen run was found to be 286, which corresponds to an estimated pyrolysis contribution of $\approx 14 \mu\text{g cm}^{-2}$, or about 18% of the total residual carbon concentration ($80.0 \mu\text{m cm}^{-2}$). The results of these analyses demonstrate that most of the carbon corresponding to BC_{app} in predominantly organic smoke samples is not derived from pyrolysis but from relatively non-volatile organic species.

Discussion

The results presented above have several implications for determining black and organic aerosol carbon by both thermal and optical methods. Before proceeding to discuss these implications, it is instructive to review the degree of disagreement in OC and BC determinations by commonly used methods. These disagreements are illustrated by the results of the recent Carbonaceous Species Methods Comparison Study (*Shah and Rau, 1990*). In this intercomparison study, ambient urban samples, source samples, and, of particular relevance to biomass burning aerosols, two ambient samples heavily influenced by residential wood burning, were prepared and distributed to a number of laboratories for analyses by a variety of thermal methods.

The intercomparison results show that most methods can accurately measure total carbon (within 5% of the common average). Organic and black carbon determinations of urban ambient samples showed respectively 6–9% and 28–31% variations from common averages (% variation taken as $100 \times \text{avg./std. dev.}$).

The discrepancies between OC and BC concentrations for the two wood smoke samples obtained by nine thermal methods were significantly greater. The operational definitions used by different methods and the analytical results for these samples, compiled from *Shah and Rau* (1990), are summarized in Table 4. These data show that the total carbon concentrations (the sum of OC and BC concentrations) range from 65 to 101 $\mu\text{g cm}^{-2}$ and from 228 to 469 $\mu\text{g cm}^{-2}$ for the two sample sets. If the TC concentrations obtained by method 2 are excluded as being obviously too low, the remaining TC values agree within about 13–17% (concentration ranges 86–101 $\mu\text{g TC cm}^{-2}$ and 328–469 $\mu\text{g TC cm}^{-2}$).

Differences in OC and especially in BC determinations are, however, much larger. OC concentrations differ by about 50% (concentration ranges 62–93 $\mu\text{g OC cm}^{-2}$ and 253–392 $\mu\text{g OC cm}^{-2}$). The reported BC concentrations range from 3.8–36 $\mu\text{g BC cm}^{-2}$ and from 79–1.6 $\mu\text{g BC cm}^{-2}$ for the two samples, resulting in 10- to 50-fold differences among individual determinations. Consequently, the OC/BC ratios differ by up to two orders of magnitude (OC/BC ranges 1.7–23 and 3.2–228). Furthermore, OC/BC ratios differ significantly, even when obtained by seemingly similar analytical procedures. For example, the OC/BC ratios obtained by two-step procedures (methods 1 through 4) differ by a factor of about 5, and methods that account for sample charring (methods 5 through 7) by factors of 5.7 to 8.5.

Implicit in methods 1–8 is the assumption that all organic material is removed from samples by volatilization in an inert atmosphere (He) at temperatures ranging from 525 to 950°C. Our results, however, show that a substantial organic fraction of biomass smoke particles is nonvolatile when heated in an inert atmosphere to about 550°C in a manner similar to those used in methods 5 and 6. Consequently, OC would be underestimated if this fraction were not included in the reported OC concentration. Furthermore, our results indicate that only a part of this nonvolatile material is due to pyrolysis and therefore not necessarily accounted for in methods that rely on monitoring the sample darkness during analysis. The residual material remaining after heating in an inert atmosphere could be oxidized in the subsequent combustion step and thus erroneously assigned to BC. The magnitude of the resulting error in BC will depend on the relative concentrations of OC (and its relatively nonvolatile component) and actual BC. Obviously, even a relatively small underestimation of OC would result in a large overestimation of BC for samples with the high OC/BC ratios common in biomass smoke particles.

Because the combustion temperatures of both apparent and actual BC are strongly influenced by catalytically active metals such as Na and K, no single temperature can be defined that distinguishes black and organic carbon in samples that contain these species. Methods that rely on thermal pretreatment of samples in oxygen at a fixed temperature to remove the organic material (for example, method 9 in Table 4) could be more accurate when applied to samples that contain an appreciable fraction of black carbon and are relatively free of these catalytic materials. However, when K and Na are part of the sample, the black carbon will readily be oxidized at this temperature because of the lowered combustion threshold. This could result in underestimating the black carbon concentration not only in biomass smoke samples, but also (because of the catalytic effect of Na) in marine aerosol samples.

BC concentrations are routinely estimated from the empirical relationship $ATN = \sigma_{BC} BC$. However, the accuracy of such measurements using a single σ_{BC} value could be questionable because of the large variability in σ_{BC} values derived by different investigators (see *Lioussse et al.*, 1993). There is evidence that the ATN vs. BC proportionality may depend on the kind of aerosol, composition (i.e. chemical and physical) even when the same transmission measurements and procedures for BC determination are used. For example, *Niessner and Petzold* (1994) obtained σ_{BC} that varied from about $5 \text{ m}^2 \text{ g}^{-1}$ for rural aerosols to $18 \text{ m}^2 \text{ g}^{-1}$ for urban aerosols. *Lioussse et al.* (1993) derived σ_{BC} values that were similarly variable depending on the sampling location. The lowest value of $5 \text{ m}^2 \text{ g}^{-1}$ was obtained in remote areas, and the highest

value of $20 \text{ m}^2 \text{ g}^{-1}$ was measured in the African Savannah regions. A significant part of this variability, particularly for samples with high organic content, is undoubtedly caused by errors in BC determinations, as illustrated by the large differences in apparent σ_{BC} that would be obtained if BC_{app} concentrations instead of BC_{act} were used (Table 2).

Conclusions

The results of our experiments can be summarized as follows: (1) the organic fraction of biomass smoke particles analyzed includes a component ($\text{BC}_{\text{app}} - \text{BC}_{\text{act}}$), ranging in concentration from about 6–20% of total carbon or from 16–30% of acetone-extractable organic carbon, that is relatively nonvolatile and has a combustion temperature close to that of black carbon; (2) combustion temperatures of this organic component and of black carbon in biomass smoke samples are significantly lowered when these contain K or Na; (3) when these metals are present in a sample, the combustion temperatures of both the black carbon and this organic material are indistinguishable; (4) about 20% of total organic material is nonvolatile when heated to 550°C in an inert atmosphere; (5) the contribution of colored organic material to the light absorption cross section of filter deposits is about two orders of magnitude smaller than that of black carbon; (6) the water-soluble fraction of biomass smoke samples includes a substantial organic component.

Because the combustion temperatures of both apparent and actual BC are strongly influenced by catalytically active metals such as Na and K, no single temperature can be defined that distinguishes black and organic carbon in samples that contain these species, even when aerosols with similar OC and BC content are sampled. Using a single temperature to separate BC from OC could result in an underestimation of the BC concentration not only in biomass smoke samples, but also (because of the catalytic effect of Na) in marine aerosol samples.

The assumption that all organic material is removed from samples by volatilization in an inert atmosphere may not be valid. The residual material remaining after heating in an inert atmosphere could erroneously be assigned to BC. The magnitude of the resulting error in BC will depend on the relative concentrations of OC (and its relatively nonvolatile component) and actual BC. Even a relatively small underestimation of OC would result in a large overestimation of BC for samples with high OC/BC ratios common in biomass smoke particles.

Estimating BC concentrations from the empirical relationship $\text{ATN} = \sigma_{\text{BC}} \text{BC}$ could be questionable because of the large variability in σ_{BC} values derived by different

investigators (*Lioussé et al.*, 1993; *Niessner and Petzold*, 1994). A significant part of this variability, particularly for samples with high organic content, is undoubtedly caused by errors in BC determinations by thermal methods. Contribution of BC to light absorption per unit mass is about two orders of magnitude larger than combustion-generated (colored) organic material. The light attenuation caused by these species could be erroneously attributed to BC for biomass smoke samples with high OC/BC ratios. For comparison, the contribution of mineral dust to light absorption cross sections has been estimated to be 2-3 orders of magnitude smaller than BC (*Schnell et al.*, 1995).

In summary, the results and discussion presented above demonstrates that OC and BC concentrations determined by thermal and optical methods are not only method dependent but also critically influenced by the overall chemical composition of the samples. Therefore, only a combined approach using different methods can give actual black carbon and organic concentrations.

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Table 1. Fuels and combustion conditions

Sample	Fuel	Amount (g)	Burn time (min)	Flame ^a
redwood needles				
2	dry	5	1	F
3	dry + green	2.5	1	S
4	dry+green	2.5	1.2	S
5	green	5	1	S + F
eucalyptus				
6		12	1	F
9		25	1.5	S
10		50	0.5	F
11		25	1	S

^a F - flaming; S - smoldering

Table 2. Total carbon (TC), apparent black carbon (BC_{app}) and actual black carbon (BC_{act}) concentrations (all in $\mu\text{g cm}^{-2}$). Also shown, acetone extractable carbon mass fraction (C_{extr}), ATN, and σ_{BC} values (in $\text{m}^2 \text{g}^{-1}$) estimated from BC_{act} concentrations.

Sample	TC	C _{extr} (%)	BC _{app}	BC _{act}	ATN ^a	ATN ratio ^b	σ_{BC}
10	58.3	4.2	40.0	36.2	≥ 376	0.95	≥ 10.4
12	30.8	54.0	14.2	9.2	203	0.77	22.1
6	130.8	63.3	48.0	22.1	460	1.16	20.8
2	619	75.3	153	20.0	408	1.08	20.4
4	5580	80.9	1060	21.7	356	1.03	16.4
3	658	86.2	91.0	14.8	390	1.00	26.3
9	118	98.4	15.8	bd ^c	23.8	3.90	—
11	443	98.5	81.2	bd	55.3	1.86	—

^a Measured on untreated filters.

^b Ratio to ATN measured on acetone-extracted filters.

^c bd - below detection limit.

Table 3. Water-soluble mass fractions relative to total carbon concentration in untreated samples.

Sample	C	K ⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻
2	0.17	0.01	0.002	0.02	0.009
3	0.35	0.06	0.009	0.08	0.026
4	0.33	0.02	0.001	0.03	0.002
5	0.30	0.08	0.007	0.10	0.004
6	0.37	0.10	0.031	0.13	0.038
9	0.79	0.04	0.019	0.18	0.010
10	0.17	0.30	0.100	0.29	0.113
11	0.76	0.01	0.001	0.03	0.001

Table 4. Methods and results of OC and BC concentration ($\mu\text{g cm}^{-2}$) determinations in wood smoke influenced ambient samples, compiled from *Shah and Rau (1990)*.

Method ^a	Operational Definitions		Sample #1			Sample #2		
	OC	BC	OC	BC	OC/BC	OC	BC	OC/BC
1	600° C, He	750° C, 2% O ₂	88.3	10.4	8.5	374.5	21.7	17.2
2	600° C, He	TC - OC	47	16	2.9	195	33	5.9
3	600° C, He	650° C, 2% O ₂	86.1	5.3	16.2	257.6	77.6	3.3
4	950° C, He	950° C, 2% O ₂	82.4	21.8	3.8	390.5	78.7	5.0
5	610° C, He	750° C, 10% O ₂	71.8	26.6	2.7	299.2	94.7	3.2
6	550° C, He	650° - 800° C, 2% O ₂	62.5	35.8	1.7	253.5	74.8	3.4
7	700° C, He	900° C, 2% O ₂	82.7	8.4	9.8	320.5	11.7	27.4
8	525° C, He(MnO ₂)	850° C, He(MnO ₂)	86.1	3.8	22.6	364.7	1.6	228
9	400° C, O ₂	700° C, O ₂	92.9	6.5	14.3	392.1	11.9	32.9

^a Laboratories: 1) Environmental Monitoring Services, Inc., 2) Oregon Department of Environmental Quality, 3) US EPA, 4) General Motors Research Laboratory, 5) Oregon Graduate Institute, 6) Desert Research Institute, 7) Sunset Laboratory, 8) Environmental Research and Technology, 9) Global Geochemistry Corporation.

Figure captions

Figure 1. Thermograms of untreated (a), acetone-extracted (b) and water-extracted (c) samples. ΔT denotes the temperature shifts between untreated and water-extracted samples.

Figure 2. Thermograms of sample #11 measured with O_2 (dotted line) and N_2 (solid line) as the carrier gas. Thermogram (measured with O_2) of the residue remaining after the N_2 run (dashed line).

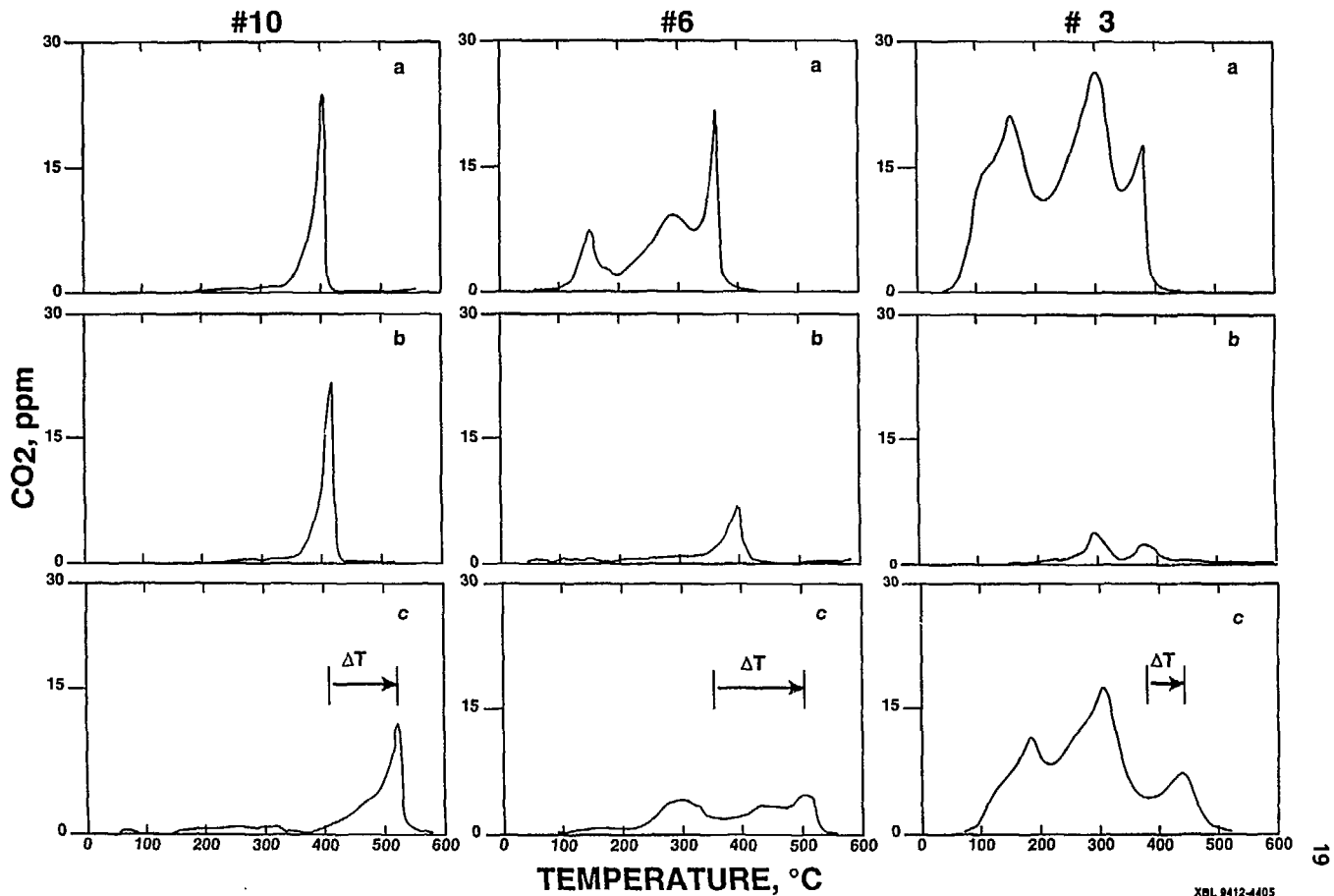
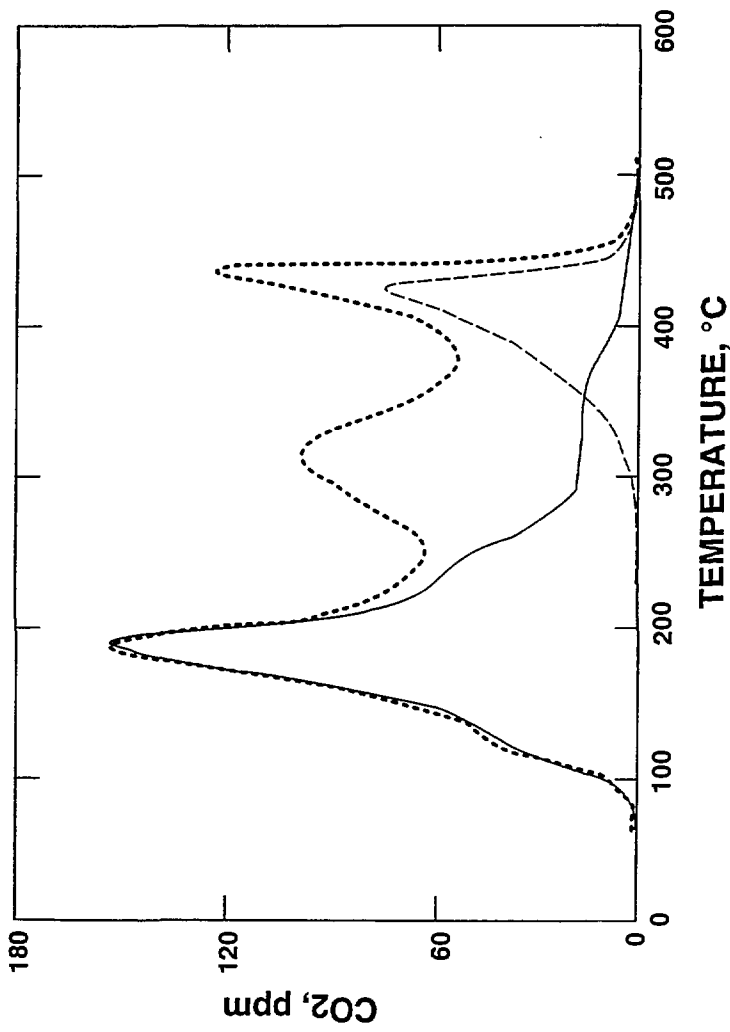


Fig. 1



XBL 9412-4406

Fig. 2