

Shipboard measurements of concentrations and properties of carbonaceous aerosols during ACE-2

By T. NOVAKOV*, TIMOTHY S. BATES and PATRICIA K. QUINN, *Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., MS-73, Berkeley, CA 94720, USA; NOAA, Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA 98115, USA*

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ABSTRACT

Mass concentrations of total, organic and black carbon were derived by analyzing the supermicron and submicron aerosol fractions of shipboard collected samples in the eastern Atlantic Ocean as part of the second Aerosol Characterization Experiment (ACE-2). These analyses were complemented by experiments intended to estimate the water-soluble fraction of the submicron carbonaceous material. Our results can be summarized as follows. Depending on the sample, between 35% and 80% of total aerosol carbon is associated with the submicron fraction. Total submicron carbon was well correlated with black carbon, a unique tracer for incomplete combustion. These correlations and the approximately constant total to black carbon ratios, suggest that the majority of submicron total carbon is of primary combustion derived origin. No systematic relationship between total submicron aerosol carbon and sulfate concentrations was found. Sulfate concentrations were, with a few exceptions, significantly higher than total carbon. Our experiments have demonstrated that water exposure removed between 36% and 72% of total carbon from the front filter, suggesting that a substantial fraction of the total submicron aerosol organic carbon is water-soluble. An unexpected result of this study is that water exposure of filter samples caused substantial removal of, nominally insoluble, submicron black carbon. Possible reasons for this observation are discussed.

1. Introduction

Atmospheric aerosol mass is composed of complex mixtures of chemical species, including sulfates, other water-soluble inorganic compounds, carbonaceous material, seasalt, and mineral particles. The optical and nucleation properties, sources, and spatial distributions of sulfate aerosols are relatively well-known. In contrast, data on the concentrations, sources, formation mechanisms, and radiative and nucleation properties of the carbonaceous component of anthropogenic and natural aerosols are much scarcer. One reason

is that characterizing carbonaceous material is more difficult because of the chemical and physical complexity of organic aerosol material and the large uncertainties caused by sampling artifacts. Analyses of aerosol samples collected during the second International Global Atmospheric Chemistry (IGAC) Program's Aerosol Characterization Experiment (ACE-2) provide an opportunity to broaden our knowledge of the concentrations and properties of carbonaceous aerosols in the ACE-2 region.

In this paper, we report results on mass concentrations of supermicron and submicron aerosol carbon material obtained by analyzing shipboard collected ACE-2 samples. For the supermicron aerosol fraction we present data on total carbon

* Corresponding author.
e-mail: TNovakov@lbl.gov

TC ($>1 \mu\text{m}$), defined as the sum of organic and black carbon. For the submicron fraction, concentration data on total TC ($<1 \mu\text{m}$), organic OC ($<1 \mu\text{m}$), and black carbon BC ($<1 \mu\text{m}$) are given. Mass concentration measurements were complemented by experiments intended to estimate the water-soluble fraction of the submicron carbonaceous material. This paper is structured as follows: we first describe the sampling and analytical methods, this is followed by measurement results, and by conclusions and discussion.

2. Sampling and analytical methods

2.1. Sampling

Aerosol samples for chemical analysis were collected aboard the RV *Vodyanitskiy* during the ACE-2 project. The experiment took place off the coasts of Portugal and North Africa from 20 June 1997 to 25 July 1997. During this time, the ship transited back and forth through the region extending from 29° to 41° north and 7° to 15° west. All references to sampling time are reported here in UTC. Dates are given as Day of Year (DOY) where noon on 1 February equals DOY 32.5.

Aerosol particles were sampled at 10 m above sea level through a heated mast. The mast extended 6 m above the aerosol measurement container and was capped with a rotating cone-shaped inlet nozzle that was positioned into the relative wind. Air was pulled through this 5 cm diameter inlet nozzle at $1 \text{ m}^3 \text{ min}^{-1}$ and down the 20 cm diameter mast. The lower 1.5 m of the mast were heated to dry the aerosol to a relative humidity (RH) of 55%. 15, 1.9 cm diameter conductive tubes extending into this heated zone were used to subsample the air stream for the various aerosol instruments at flows of 30 l min^{-1} .

Samples were collected for chemical analysis only when the wind speed was greater than 3 m s^{-1} , the wind direction was forward of the beam, and the concentration of particles greater than 15 nm in diameter indicated the sample air was free of contamination from the *Vodyanitskiy* or passing ships. One of the fifteen 1.9 cm diameter tubes, constructed of stainless steel, was used to supply ambient air to a specially designed 2-stage multijet cascade impactor (Berner et al., 1979) for collecting samples for organic analysis. The

impactor has 50% aerodynamic cutoff diameters of 1.0 and $10 \mu\text{m}$. Supermicron particles were collected on an Al foil and submicron particles on a quartz filter. The impactor also included a second, backup, quartz filter the purpose of which is to assess the magnitude of sampling artifacts commonly encountered with filter sampling of organic aerosols. The Al foils and quartz filters were combusted immediately before use at 600°C for 4 h to remove residual organic contaminants. Foils and filters were loaded and unloaded into a second impactor without air flow to serve as a sampling blank. Foils and filters were stored frozen in tightly capped glass vials until analysis to inhibit possible microbial activity.

2.2. Analytical methods

Carbonaceous submicron aerosol material is principally composed of an organic component, commonly referred to as "organic carbon" (OC), and a light absorbing component referred to as "black carbon" (BC). "Total carbon" (TC) designates the sum of OC and BC. Carbonate carbon from mineral dust is usually confined to larger particles and is not considered here. Total carbon content in a sample and be accurately determined by any of the combustion methods. Accurate determination of BC by thermal and optical methods is a nontrivial problem. Uncertainties in BC and OC determinations by the commonly used methods have been demonstrated by an intercomparison study (Shah and Rau, 1990) which showed that most methods agree for TC but significantly differ for OC and BC determinations. While the measurement of total carbon on the filter is analytically straight forward, the uncertainties associated with positive and negative sampling artifacts are substantial and cannot be rigorously calculated from the measurements conducted during ACE-2. Our attempt to correct for the positive sampling artifact is discussed below.

The definitions of OC and BC used in conjunction with thermal methods are based on presumed volatilization and combustion properties of these classes of carbonaceous materials and are operational and method dependent. Uncertainties in black carbon determinations by thermal methods are caused, in large part, by some of the organic materials present in the sample. These may either burn at temperatures close to that of BC, or may

pyrolyze during heating producing a charred material having a combustion temperature similar to that of actual BC. Therefore, we refer to the BC determined solely by combustion methods as the apparent black carbon BC(app). Because the organic component is the main interfering material, its removal prior to BC analyses is an obvious option for a more accurate BC determination (Novakov and Corrigan, 1995). The details of these procedures adopted in this study are described below.

Application of optical transmission measurements to BC estimation is based on empirical results that assume the attenuation of visible light by the filter deposit is proportional to the surface concentration of black carbon. The accuracy of optically determined black carbon concentrations critically depends on the choice of the proportionality constant σ . Results from a number of field experiments show that σ values may differ by a factor of 5 (Lioussé et al., 1993; Niessner and Petzold, 1995). Because these values are derived from calibrations against independently determined BC concentrations, uncertainties in BC determination could be a major cause of the observed variability in the σ values. Furthermore, theoretical considerations suggest that σ may depend on whether the BC is internally or externally mixed with non-absorbing species such as sulfates.

The disposition of filter samples for EGA analyses was as follows. One half of each filter sample (and the corresponding backup filter) was analyzed to characterize the carbonaceous aerosol in its original state. The other halves of filter samples were divided into 2 parts. One of these aliquots was first treated with acetone prior to analysis, and the other aliquot was used for measurements involving water extraction as described below. The extraction procedures consisted of immersing separate filter aliquots in 30 ml acetone for about 30 min and in 80 ml of de-ionized water for 30 min, both without agitation. This procedure efficiently removes most of the organic material but leaves BC intact (Novakov and Corrigan, 1995). This allows for an interference-free BC determination and eliminates the need for thermogram peak deconvolution. Experiments were also conducted to investigate the effect of water exposure on the carbonaceous aerosol material.

Mass concentrations of these carbon compon-

ents collected on impactor foils and on quartz filters were determined by a thermal — evolved gas analysis — (EGA) method (Novakov, 1981) and, following the rationale outlined above, supplemented by analyses of solvent extracted samples. In EGA an aliquot of the filter or impactor foil sample is progressively heated at a rate of $12.5^{\circ}\text{C min}^{-1}$ in an oxygen atmosphere from 50°C to 600°C . The carbon-containing gases evolving from the sample as a result of volatilization, decomposition and combustion of the carbonaceous material are converted to CO_2 over a catalyst. The resulting CO_2 concentrations are measured by a non-dispersive infrared analyzer. A plot of the rate of carbon evolution versus temperature constitutes the “thermogram” of the sample. The area under the thermogram is equal to the total carbon content of the sample. This method is quantitative for TC within about 10% with a reproducibility of 3–5% (Dod et al., 1979; Gundel et al., 1984).

Both the original and the extracted quartz filters were also characterized by an optical transmission method similar to that described by Rosen et al. (1980). This method compares the transmission of white light through a loaded filter relative to that of the blank filter. The relationship between the optical attenuation, ATN, and the BC concentration (per unit filter area) is given by $\text{ATN} = \sigma\text{BC}$, 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 is a proportionality constant. Because of the uncertainties in the σ values (as discussed above) we used ATN measurements solely to monitor the possible loss of BC from the filter samples during exposure to solvents and not to quantify the BC concentrations.

Analyses of filter and impactor samples give the mass loading of TC, OC and BC present in the samples. Volumetric mass concentrations, particularly of TC and OC, may not be always derived from their mass loading unless corrections for sampling artifacts are made. The reason being that the sampled air contains organic material in both the particle and gas phase. During filter sample collection, gaseous organic species may adsorb onto filter material and thus increase the organic content of the filter deposit (“positive” artifact). A positive artifact is most pronounced with filter sampling because of high surface area of the filter matrix. Positive artifacts should be less

pronounced with impactor samples because of the low surface area of the sampling substrates (such as aluminum foils used in this study) and the fact that with impactor stages the air is not drawn through the sampling substrate.

To approximately correct for the positive artifact we used 2 quartz filters in series as suggested by Fitz (1990). This approach assumes that the front filter efficiently retains all particles and that organic gases are adsorbed roughly equally on both front and back filters. Consequently, if positive artifacts dominate then the organic aerosol concentration is determined from the difference between the OC loadings on the front and back filters and the sampled air volume. This technique has been intercompared in a polluted urban location with a number of other techniques and found to be largely consistent with them (Hering et al., 1990). It should be noted, however, that the same intercomparison study has shown that no technique for aerosol carbon mass can yet be considered ideal.

Positive artifacts, however, may not be the only source of uncertainty in deriving the aerosol carbon. Some of the semivolatile organic aerosol species may desorb from the particulate phase during sampling. This "negative" artifact is especially pronounced when relatively unpolluted air is sampled, when it may result in significant underestimation of the particulate OC concentration (Eatough et al., 1993, 1996). Negative artifact has been demonstrated with filter sampling but it may, possibly, also affect impactor foil samples.

3. Results

3.1. Total aerosol carbon

The primary analytical data used to derive total carbon associated with supermicron TC ($>1 \mu\text{m}$) and submicron TC ($<1 \mu\text{m}$) concentrations were obtained by EGA analyses of impactor foils and front and backup filter samples (examples of thermograms are shown in Fig.1). Total carbon loadings determined on impactor foils TC(I), front filters TC(F), and back filters TC(B) for all samples (expressed in $\mu\text{g C}$ per filter or foil) are shown in Table 1. Total carbon loadings on blank impactor foils were less than $2 \mu\text{g}$ and about $5 \mu\text{g}$ on blank filters with 40% in the most volatile

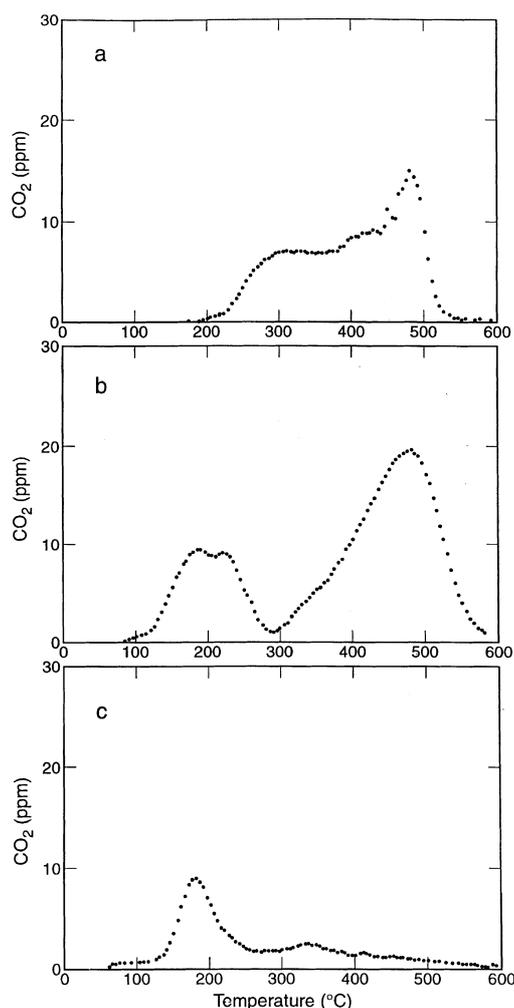


Fig. 1. Examples of EGA thermograms of (a) supermicron particles collected on impactor foils, (b) submicron particles collected on front filter and (c) adsorbed gas-phase species collected on backup filter (sample set 12).

region. These loadings are considerably lower than those of exposed foils and filters (Table 1).

Volumetric mass concentrations of aerosol carbon (in $\mu\text{g m}^{-3}$) can be directly calculated from the air volumes and the carbon loadings (Table 1) only if the latter are unaffected by sampling artifacts. As mentioned above samples collected on impactor foils are less likely to be affected, at least by positive artifacts, than filter samples. Consequently, the mass concentrations of total

Table 1. Sample numbers, sampling start and end, total carbon mass loadings determined on impactor foils TC(I), front TC(F) and backup filters TC(B), and air volumes used for sample collections

Sample no.	Sampling start–end ^{a)}	µg C per sample			Air volume (m ³)
		TC(I)	TC(F)	TC(B)	
1	174.5–176.7	32	104	33	48
3	181.4–184.2	NA	54	31	105
4	184.3–187.2	47	149	31	109
5	187.3–188.2	35	168	26	38
6	188.3–189.2	29	58	20	38
7	190.6–193.2	64	98	23	102
8	193.2–194.2	20	45	14	38
9	194.3–195.5	41	75	18	49
10	158.8–198.0	90	73	25	85
11	199.2–199.7	20	45	9	17
12	200.1–203.8	44	75	24	47
13	201.3–203.8	54	103	28	88

^{a)} Times are in UTC. Dates are given as Day of Year (DOY) where noon on 1 February equals DOY 32. NA: not analyzed.

supermicron aerosol carbon TC (> 1 µm) could be calculated from TC(I) and the sampled air volume assuming that negative artifacts can be neglected. TC (> 1 µm) concentration derived in this manner are listed in Table 2.

Table 2. Mass concentrations of supermicron total carbon TC (>1 µ) particles, and submicron total TC (<1 µ), black BC (<1 µ), organic carbon OC (<1 µ), and sulfate; also shown are %s of total, and black carbon mass removed by water

Sample no.	µg C m ⁻³					Water removed fraction (%)		
	TC (> 1 µ)	TC (< 1 µ)	BC (< 1 µ)	OC (< 1 µ)	SO ₄ ²⁻	TC	BC ^{a)} (EGA)	BC ^{b)} (ATN)
1	0.7	1.5	0.6	0.9	4.7	58	60	
3	NA	0.2	0.1	0.1	1.6	36	<4.0	12
4	0.4	1.1	0.3	0.8	2.5	53	5	
5	1.0	3.9	1.1	2.8	3.9	70	64	
6	0.8	1.0	0.4	0.6	4.2	64	70	83
7	0.6	0.7	0.2	0.5	4.8	72	52	
8	0.5	0.8	0.3	0.5	6.1	50	52	≈80
9	0.8	1.2	0.4	0.8	9.6	59	50	67
10	1.1	0.6	0.3	0.3	6.3	53	45	54
11	1.2	2.2	0.8	1.4	6.2	58	53	83
12	0.9	1.1	0.3	0.8	6.1	49	23	72
13	0.6	0.9	0.3	0.6	5.6	72	57	

^{a)} From EGA analysis.

^{b)} From ATN measurements.

NA: not analyzed.

Total submicron aerosol carbon concentrations TC (<1 µm) can be derived from TC(F) loading only if a correction for sampling artifacts is made. To accurately account for sampling artifacts refined denuder-based methods, such as those devised by Eatough et al. (1993, 1996), should be used. These, however, were not available in the present study. Instead we had to use an approximate approach based on TC(F) and TC(B) concentration differences, as mentioned above. That this approach is applicable to the samples analyzed in this study can be argued by the data in Table 1 and by the examples of thermograms shown in Fig. 1 as discussed below.

As it is seen from Fig. 1 the shapes and structures of thermograms of the impactor foil and the front and backup filters (corresponding to sample set 12) are different and reflect the differences in the composition of carbonaceous material collected on the 3 sampling substrates. The thermogram of the front quartz (submicron) filter shows 2 low temperature peaks at ~180°C and ~230°C and a larger and wider structure extending to 600°C. (The latter contains BC as discussed below.) Most of the carbon on the backup quartz filter is confined to a single peak at ~180°C coinciding with the most volatile peak seen with the front filter. In contrast, the impactor foil

thermogram shows a broad structure extending from $\sim 200^{\circ}\text{C}$ to above 500°C , with a peak at $\sim 480^{\circ}\text{C}$ most likely due to BC. Noticeably absent, however, are any low temperature peaks such as those seen with filter samples. This comparison suggests that the species giving rise to the 180°C peak, seen with both front and back filters, are gas phase organic species adsorbed on the quartz filter matrix. (Particles are not expected to penetrate the front filter.) Absence of volatile species in the foil thermogram is consistent with this suggestion because adsorption of gaseous organics is not favored on the low surface area impactor foil.

Assuming that positive artifacts dominate and all the carbon on the backup filter is caused by such artifacts, then the difference in the carbon loading on the front and back filters can be used to derive an approximate measure of total submicron aerosol carbon. A condition for the validity of this assumption is that both front and back filters are similarly saturated with adsorbed species. That this condition may be satisfied is suggested by comparing TC(F) and TC(B) loadings shown in Table 1. The spread in TC(B) values is much smaller than the spread in TC(F) values. With the exception of sample 11, collected with the lowest air volume, TC(B) values range from about 14 to $33\ \mu\text{g}$ and TC(F) loadings range between about 45 to $168\ \mu\text{g}$. TC ($<1\ \mu\text{m}$) concentrations derived in the manner described are listed in Table 2. We note, however, that if negative artifacts are significant then TC ($<1\ \mu\text{m}$) and possibly TC ($>1\ \mu\text{m}$) would be underestimated. The present data, however, do not allow for the quantification of this underestimation.

3.2. Black carbon

The difficulty of BC determination by thermal properties alone is illustrated by thermograms (sample set 5) shown in Fig. 2. The high temperature thermogram region of the front filter is broad and apparently composed of several individual peaks some of which undoubtedly are due to black carbon. It is clear that taking the entire high temperature feature as the representation of BC will seriously overestimate its concentration. As can be seen from Fig. 2a, the BC, or more appropriately the BC(app) if defined in this manner, will account for most of the carbonaceous material and the sample would contain essentially

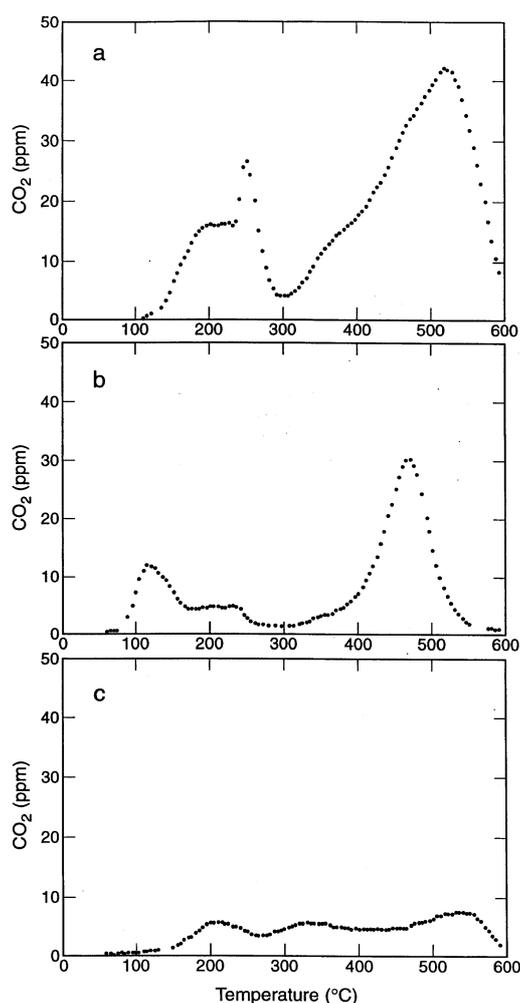


Fig. 2. Thermograms of (a) untreated, (b) acetone and (c) water exposed filter aliquots (sample set 5) taken from the same front quartz filter.

no OC, which is a very unlikely possibility. Alternatively, the complexity of the high temperature region is caused by a mixture of BC and interfering organic materials such as the pyrolysis products (i.e. charred material) and high molecular weight organics (i.e. tarry materials) both having combustion temperatures close to those of true black carbon. Consequently, removal of most of the organic material from the sample prior to analysis, for example by exposure to acetone, should give a more accurate measure of BC (Novakov and Corrigan, 1995). The effect of

acetone exposure on thermograms is illustrated by Figs. 2a,b, where thermograms of the untreated and the acetone exposed aliquot taken from the same front quartz filter (sample 5) are shown. As expected acetone removed most of the organics and revealed a well defined Gaussian BC peak at $\sim 480^\circ\text{C}$. The small peak at the lowest temperature is due to residual solvent.

That acetone exposure does not physically remove BC from the sample was shown by optical attenuation measurements performed on the samples before and after acetone exposure. Ratios of optical attenuation (ATN) on all samples before and after acetone exposure ranged from 0.94 to 1.16 with an average of 1.04 ± 0.08 . These results show that no appreciable loss of BC occurs upon acetone exposure. The slight decrease in optical transmission of 4% could be due, in part, to the removal of high molecular weight slightly absorbing organic material. Furthermore, the filter backing used for sample collection consisted of a perforated disk. As a consequence the deposit on the filters appeared in a similar pattern of dots, making the precise alignment in the ATN apparatus difficult, and thus the ATN results less accurate. We note, however, that all EGA measurements were normalized to the number of dots on the sample analyzed.

Submicron BC ($<1 \mu\text{m}$) concentrations determined in this manner are given in Table 2, where OC ($<1 \mu\text{m}$) concentrations derived from TC ($<1 \mu\text{m}$)-BC ($<1 \mu\text{m}$) differences are also shown.

3.3. Effect of water exposure on OC and BC

The original purpose of EGA measurements of water exposed filter samples was to estimate the water soluble fraction of organic aerosol component. We have arbitrarily chosen a water volume of 80 ml to simplify the analytical procedure. We realize water solubility is a relative term and do not mean to imply that the water soluble fraction measured here would be equal to the water soluble fraction at the liquid water content of humid air or a cloud droplet.

The approach was to compare the thermograms and total carbon content of identical aliquots of untreated and water exposed front filter samples. A thermogram obtained with a water exposed filter (sample 5) is shown in Fig. 2c. Comparison of the areas under the thermograms of untreated

(Fig. 2a) and water exposed samples show that water exposure resulted in the loss of about 70% of the original total carbon. The results of such measurements performed on all samples and summarized in Table 2 show that depending on the sample, between 36% and 72% of TC loading on the front filters is apparently water soluble. These results are not unexpected in view of the fact that some of the organic aerosol species are known to be water soluble (Saxena and Hildemann, 1996), and contribute to cloud condensation nuclei (Novakov and Penner, 1993; Rivera-Carpio et al., 1996).

An unexpected result of these analyses is that water exposure appears to significantly affect the black carbon loading. As seen in Fig. 2 water exposure affected the entire thermogram temperature region, including the highest temperature peak which, as shown above, contains the BC. The peak at about 550°C seen with the water exposed sample represents the apparent black carbon, BC(app), due both to BC and, possibly, some thermally stable organic matter not removed by water exposure. (The shift of the apparent black carbon peak relative to the BC peak in the acetone extracted sample is caused by the removal of water-soluble catalysts, such as Na and K containing compounds, that promote combustion (Lin and Friedlander, 1988; Novakov and Corrigan, 1995). A comparison of BC(app) area and the BC peak observed in the thermogram of the acetone extracted sample (Fig. 2) shows that water exposure resulted in about 64% loss of apparent black carbon. (Both BC areas were determined by a Gaussian peak fit assuming a symmetrical peak shape.) The apparent BC loss for all samples determined in this manner by EGA is shown in Table 2.

During the analyses of the first batch of 5 samples, it became obvious that most water exposed samples showed distinctly less coloration than the corresponding untreated and acetone exposed samples. Because BC is the principal light absorbing aerosol species and mainly responsible for the deposit coloration, the observed decrease in sample coloration indicated BC removal. Consequently, the remaining original and water exposed samples were also analyzed by optical attenuation (transmission) measurements. The reduction in ATN values upon water exposure is an alternative qualitative measure of BC loss. BC

losses estimated from ATN measurements are shown in Table 2. Black carbon losses estimated from ATN changes are generally larger than those estimated from EGA analyses. This discrepancy is not unexpected because BC(app) is not necessarily a true measure of BC, and ATN derived BC may be subject to unknown effect of sample composition. A more accurate analytical procedure would require application of acetone extraction to water exposed samples. Limited sample material, however, prevented us from doing this and other possible experiments to quantify the BC loss. Therefore, data on BC losses derived both by EGA and ATN should be viewed as semi-quantitative estimates.

4. Discussion and conclusions

In the following we discuss our results on: (1) the partitioning of total carbon between supermicron and submicron particles; (2) relationships between submicron total and black carbon and sulfate concentrations obtained in this study, and compare these with previously obtained data over the anthropogenically influenced western Atlantic Ocean during the Tropospheric Aerosol Radiative Forcing Experiment (TARFOX) (Hobbs et al. 1996); and (3) removal of total and black carbon from filters upon water exposure. Table 2 summarizes the pertinent data obtained in this study.

Before proceeding with the data discussion we emphasize that the ACE-2 *Vodyanitskiy* carbon aerosol data set must be considered as a regional representation of concentrations during this time period as sampling intervals did not correspond to a single air mass back trajectory. Hence, multiple air mass sources could have contributed to one carbon aerosol sample.

The data show that total carbon in supermicron particles, TC ($>1\ \mu\text{m}$), is at times comparable to submicron total carbon, TC ($<1\ \mu\text{m}$). Depending on the sample, between 35% and 80% of total (sub- and supermicron) carbon is associated with the submicron fraction. Here we report only the TC ($>1\ \mu\text{m}$) concentrations because supermicron BC was not determined. It should be noted, however, that the shapes and structure of the thermograms of the supermicron and submicron samples

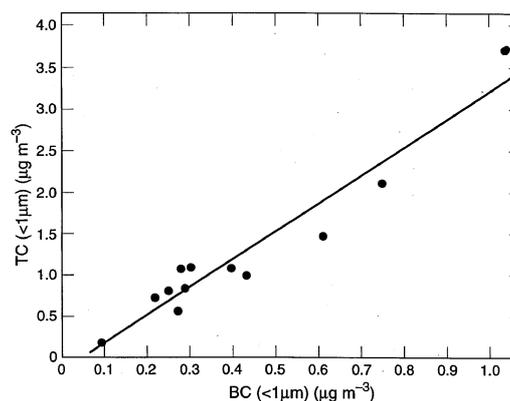


Fig. 3. Plot of total submicron aerosol carbon, corrected for positive artifacts, TC ($<1\ \mu\text{m}$) versus black carbon BC ($<1\ \mu\text{m}$) concentrations.

are distinctly different reflecting the compositional differences of the 2 fractions (Fig. 1).

Black carbon, a unique indicator of incomplete combustion, was detected in all samples collected during the cruise. In Fig. 3 total submicron carbon concentrations TC ($<1\ \mu\text{m}$) are plotted versus the BC concentrations (Table 2). Linear regression of these data resulted in relation $\text{TC} (<1\ \mu\text{m}) = 3.37 (\text{BC}) - 0.14$, with a correlation coefficient $r^2 = 0.94$. High correlation coefficients and the low intercept suggest that most of the aerosol carbon is combustion derived.

The average submicron BC/TC ratio derived from our data is 0.35 ± 0.07 . For comparison, a mean submicron BC/TC ratio of 0.43 was measured at Aveiro on the coast of Portugal (Nunes and Pio, 1993). Measurements of Kuhlbusch et al. (1998) BC/TC ratios for central Europe of 0.36–0.38 agree with our value. The fact that these ratios are comparable (considering that different sampling and analytical procedures were used) is consistent with the notion that the carbonaceous aerosol collected during the *Vodyanitskiy* cruise is dominated by continental combustion sources. Substantial secondary organic and non-combustion derived organic aerosols material result in lower BC/TC ratios than expected for primary combustion particles (Turpin and Huntzicker, 1995). The lack of substantial deviations of these ratios measured from the average suggests that the majority of submicron total carbon in the cruise region was of primary origin. Our data alone, however, are insufficient to quantify the

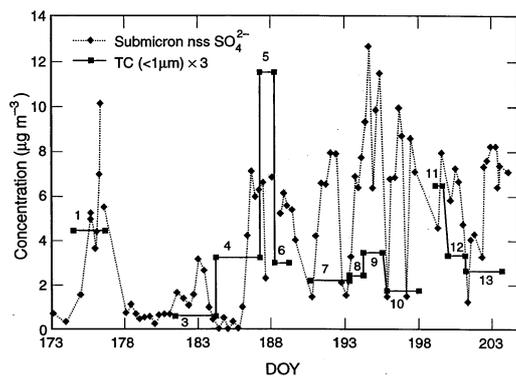


Fig. 4. Time series of submicron nss sulfate and TC ($<1 \mu\text{m}$) concentrations. Dates are given as Day of Year (DOY) where noon on 1 February equals DOY 32.5. Sampling times are in UTC. Numbers correspond to carbon sample number.

contribution of secondary organics to total submicron aerosol carbon.

An accurate comparison of aerosol sulfate and carbon concentrations must take into account the different sampling times involved. The samples for carbon analyses were collected over much longer time periods than the sulfate samples so that the carbon samples average multiple air masses. Variability in the measured TC and SO_4^{2-} concentrations for the $<1 \mu\text{m}$ aerosol fraction is shown in Fig. 4.

Submicron aerosol carbon concentrations were measured at 2 land-based sites during ACE-2, Sagres located on the southwest tip of Portugal and Punto del Hidalgo located on Tenerife. The average submicron OC concentration measured on the ship during polluted conditions ($0.89 \mu\text{g m}^{-3}$) was very similar to the average polluted value measured at Sagres ($0.75 \pm 0.32 \mu\text{g m}^{-3}$) and Punto del Hidalgo ($0.52 \pm 0.27 \mu\text{g m}^{-3}$). A comparison of marine values is not possible as a purely marine sample was not collected onboard the ship.

It is instructive to compare the aerosol carbon and sulfate concentrations from the eastern Atlantic obtained in this study with the aircraft measurements over the western Atlantic during TARFOX, conducted off the Virginia coast of the United States in July 1996 (Novakov et al., 1997; Hegg et al., 1997). The SO_4^{2-} concentration measured during the cruise (Table 2) ranged from 1.6 to $9.6 \mu\text{g m}^{-3}$, with an average of $5.1 \pm 2.0 \mu\text{g m}^{-3}$.

During TARFOX the SO_4^{2-} concentration averaged over 30 flights was $5.7 \pm 5.9 \mu\text{g m}^{-3}$, covering the range from 0.1 to $19.5 \mu\text{g m}^{-3}$. Although the average SO_4^{2-} concentrations from the 2 experiments were comparable the maximum values in TARFOX were about $2\times$ higher than found in this study. The average submicron TC concentration measured during the cruise was $1.3 \pm 0.9 \mu\text{g m}^{-3}$, ranging from 0.2 to $3.9 \mu\text{g m}^{-3}$. In contrast, the average TARFOX total carbon was $4.9 \pm 2.8 \mu\text{g m}^{-3}$ (range 0.6 to $9.9 \mu\text{g m}^{-3}$) or 3.8 times higher during TARFOX than found in the present study. The average $\text{SO}_4^{2-}/\text{TC}$ ratio of 5.3 ± 2.9 for ACE-2 (using TC $<1 \mu\text{m}$) is about $5\times$ higher than the ratio of 1.0 ± 0.6 averaged for all TARFOX flights.

This comparison, however, may not be justified for 2 reasons. First, The ACE-2 concentrations were derived from shipboard (surface) collected samples, while the TARFOX data were obtained with samples collected at different altitudes. Second, in contrast to ACE-2 experiment when both submicron and supermicron aerosol samples were obtained, the TARFOX aerosol intake system collected particles with diameters smaller than $\sim 5 \mu\text{m}$. Therefore, a more meaningful approach is to compare the $\text{SO}_4^{2-}/\text{TC}$ ratios by using the sum of submicron and supermicron TC for ACE-2 and the TARFOX ratios corresponding to the lowest sampling altitudes ($<0.3 \text{ km}$). We note that Quinn et al. (this issue) have shown that the nss SO_4^{2-} contribution to the supermicron size range is small. The $\text{SO}_4^{2-}/\text{TC}$ ratios defined in this manner are 2.9 ± 1.3 (range 0.8–4.8) for ACE-2 and 1.6 ± 0.7 (range 0.5–2.3) for TARFOX. With these assumptions the ACE-2 ratio is 1.8 times higher than the TARFOX ratio. For comparison the $\text{SO}_4^{2-}/\text{TC}$ ratio for TARFOX samples taken at altitudes above 2.5 km is reduced to 0.6 ± 0.3 , consistent with the altitude dependence of sulfate and carbon mass fraction observed in that experiment.

The lower values of $\text{SO}_4^{2-}/\text{TC}$ ratio for TARFOX suggest that the aerosol over the western Atlantic is enriched in TC relatively to that found during ACE-2. A possible explanation is suggested by the corresponding TC/BC ratios. The average BC/TC ratio determined in this study was 0.35 which is considerably higher than the BC/TC ratio of 0.1 estimated from the TARFOX data. (We note, however, that the TARFOX black

carbon fraction was inferred from TC concentrations and concurrently measured aerosol absorption coefficients.) This TARFOX ratio is roughly consistent with ground based measurements in rural areas of the eastern US which gave the BC/TC ratio for the PM_{2.5} aerosol of about 0.15 (Malm et al., 1994). These low ratios suggest that a significant contribution of organic material over the eastern Atlantic may, at least in part, be of biogenic or secondary anthropogenic origin.

Finally, we turn to a discussion of our results on the removal of TC and BC from filter samples upon contact with water. Our experiments demonstrate that between 36% and 72% of total carbon is removed from the front filter as the result of water exposure (Table 2). This result is not unexpected because the complex aerosol organic material does contain a water-soluble fraction. An unexpected result obtained in this study pertains to the effect of water exposure on black carbon. Water exposure of filter samples caused substantial removal of submicron BC from front filters. The fraction of BC removed ranged from about 5 to 70% and 12 to 80%, estimated from EGA analyses and optical measurements, respectively (Table 2). These findings are unexpected because BC is not water soluble. In contrast to ACE-2 samples, water exposure of source dominated aerosol samples (collected in a highway tunnel and at a suburban traffic influenced site), affected the OC fraction but not the BC. Because of the inherent BC insolubility its removal must involve an indirect process.

At this time we cannot offer an exact explanation of this phenomenon. It may be that BC removal depends on whether fresh or aged aerosol is sampled. In addition, the physico-chemical properties of both the aerosol particles and the filter deposit will be different depending on whether the BC is externally or internally mixed with water-soluble species such as sulfate. In an external mixture, carbonaceous particles will exist separate from water-soluble species. If BC particles in such samples strongly adhere to each other and to the filter matrix, then water exposure will not dislodge the BC from the filter. However, aged aerosol may be largely composed of internal

carbon-sulfate mixtures, especially when the sulfate is the dominant species. Transmission electron microscopy measurements during ASTEX-MAGE and ACE-2 confirm that BC particles over the Atlantic Ocean generally occur within sulfates (Posfai et al., 1999).

Rapid dissolution of sulfate may dislodge the small BC particles occluded within the larger sulfate-carbon agglomerate. Consequently, a fraction of the BC will be introduced into the water in the form of a suspension. The removed fraction should vary depending on the relative amounts of BC and sulfate and their state of mixing. Indeed, the smallest BC loss occurred in samples having the lowest SO₄²⁻ concentrations (samples 3 and 4). Finally, the possibility that nominally hydrophobic BC may be rendered hydrophilic by chemical reactions occurring during atmospheric transport cannot be excluded. A better understanding of the BC loss indicated by our experiments warrants more study. It is clear that a mechanism similar to that affecting BC could also influence the organic aerosol component. However, as the data show 36 to 53% of TC was removed from the 2 samples (3 and 4) which showed the smallest BC loss. Therefore, a substantial part of the TC or, more accurately, its OC component, appears to be intrinsically water soluble. The solubility of carbonaceous aerosol particles may influence their transport and removal.

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REFERENCES

- Berner, A., Lurzer, C., Pohl, F., Preining, O. and Wagner, P. 1979. The size distribution of the urban aerosol in Vienna. *Sci. Tot. Environ.* **13**, 245–261.
- Dod, R. L., Rosen, H. and Novakov, T. 1979. Lawrence Berkeley Laboratory Report LBL-8696.
- Eatough, D. J., Wadsworth, A., Eatough, D. A., Crawford, J. W., Hansen L. D. and Lewis, E. L. 1993. A multiple-system, multi-channel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere. *Atmos. Environ.* **27A**, 1213–1219.
- Eatough, D. J., Eatough, D. A., Lewis, L. and Lewis, E. L. 1996. Fine particulate chemical composition and light extinction at Canyonlands National Park using organic particulate material concentrations obtained with a multisystem, multichannel diffusion denuder sampler. *J. Geophys. Res.* **101**, 19,515–19,531.
- Fitz, D. R. 1990. Reduction of the positive organic artifact on quartz filters. *Aerosol Sci. Technol.* **12**, 142–148.
- Gundel, L. A., Dod, R. L., Rosen, H. and Novakov, T. 1984. The relationship between optical attenuation and black carbon concentration for ambient and source particles. *Sci. Total Environ.* **36**, 197–202.
- Hegg, D. A., Livingston, J., Hobbs, P. V., Novakov, T. and Russell, P. 1997. Chemical apportionment of aerosol column optical depth off the Mid-Atlantic Coast of the United States. *J. Geophys. Res.* **102**, 25,293–25,303.
- Hering, S. V. et al. 1990. Comparison of sampling methods for carbonaceous aerosols in ambient air. *Aerosol Sci. Technol.* **12**, 200–213.
- Hobbs, P. V., Russell, P. B. and Stowe, L. L. 1996. Tropospheric Aerosol Radiative Forcing Observational Experiment (TARFOX). In: *Atmospheric aerosols: a new focus of the international global atmospheric chemistry project*. Int. Global Atmos. Chem. Project Office, MIT Press, Cambridge, Mass.
- Kuhlbusch, T. A. J., Hertlein, A.-M. and Schütz, L. W. 1998. Sources, determination, monitoring, and transport of carbonaceous aerosols in Mainz, Germany. *Atmos. Environ.* **32**, 1097–1110.
- Lin, C. and Friedlander, S. K. 1988. A note on the use of glass fiber filters in the thermal analysis of carbon containing aerosols. *Atmos. Environ.* **22**, 605–607.
- Liousse, C., Cachier, H. and Jennings, S. G. 1993. Optical and thermal measurements of black carbon aerosol content in different environments: variation of the specific attenuation cross-section. *Atmos. Environ.* **27A**, 1203–1211.
- Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A. and Cahill, T. A. 1994. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *J. Geophys. Res.* **99**, 1347–1370.
- Niessner, R. and Petzold, A. 1995. Intercomparison study on soot-selective methods — field study results from several polluted areas in Germany. *J. Aerosol Sci.* **26** (suppl. 1), 393–394.
- Novakov, T. 1981. Microchemical characterization of aerosols. In: *Nature, aim and methods of microchemistry* (eds. Grasserbauer, M. M. and Belcher, R.). Springer, New York, pp. 141–165.
- Novakov, T. and Penner, J. E. 1993. Large contribution of organic aerosols to cloud–condensation–nuclei concentrations. *Nature* **365**, 823–826.
- Novakov, T. and Corrigan, C. E. 1995. Thermal characterization of biomass smoke particles. *Mikrochimica Acta* **119**, 157–166.
- Novakov, T. and Corrigan, C. E. 1996. Cloud condensation nucleus activity of the organic component of biomass smoke. *Geophys. Res. Lett.* **23**, 2141–2144.
- Novakov, T., Hegg, D. A. and Hobbs, P. V. 1997. Airborne measurements of carbonaceous aerosols on the East Coast of the United States. *J. Geophys. Res.* **102**, 30,023–30,030.
- Nunes, T. V. and Pio, C. A. 1993. Carbonaceous aerosols in industrial and coastal atmospheres. *Atmos. Environ.* **27A**, 1139–1346.
- Posfai, M., Anderson, J. R., Buseck, P. R. and Sievering, H. 1999. Soot and sulfate aerosol particles in the remote marine troposphere. *J. Geophys. Res.* **104**, 21,685–21,693.
- Rivera-Carpio, C. A., Corrigan, C. E., Novakov, T., Penner, J. E., Rogers, C. F. and Chow, J. C. 1996. Derivation of contributions of sulfate and carbonaceous aerosols to cloud condensation nuclei from mass size distributions. *J. Geophys. Res.* **101**, 19,483–19,493.
- Rosen, H., Hansen, A. D. A., Dod, R. L. and Novakov, T. 1980. Soot in urban atmospheres: determination by an optical absorption technique. *Science* **208**, 741–744.
- Saxena, P. and Hildemann, L. M. 1996. Water-soluble organics in atmospheric particles. A critical review of the literature and application of thermodynamics to identify candidate compounds. *J. Atmos. Chem.* **24**, 57–109.
- Shah, J. J. and Rau, J. A. 1990. *Carbonaceous species methods comparison study. Inter laboratory round robin interpretation of results*. Final report to Research Division, California Air Resources Board, Contract no. A832–154.
- Turpin, B. J. and Huntzicker, J. J. 1995. Identification of secondary organic aerosol episodes and quantification of primary and secondary organic concentrations during SCAQS. *Atmos. Environ.* **29**, 3527–3544.