

Characterization of
carbonaceous
aerosols during
MINOS

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Characterization of carbonaceous aerosols during the MINOS campaign in Crete, July–August 2001: a multi-analytical approach

J. Sciare^{1,*}, H. Cachier², K. Oikonomou^{3,*}, P. Ausset⁴, R. Sarda-Estève², and N. Mihalopoulos³

¹Department of Biogeochemistry, Max-Planck-Institute for Chemistry, Mainz, Germany

²Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-sur-Yvette, France

³Department of Chemistry, University of Crete, Heraklion, Crete, Greece

⁴Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France

*Now at LSCE

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Correspondence to: J. Sciare (sciare@lsce.saclay.cea.fr)

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Abstract

During the major part of the Mediterranean Intensive Oxidant Study (MINOS) campaign (summer 2001, Crete Isl.), the Marine Boundary Layer (MBL) air was influenced by long range transport of biomass burning from the northern and western part of the Black Sea. During this campaign, carbonaceous aerosols were collected on quartz filters at a Free Tropospheric (FT) site, and at a MBL site together with size-resolved distribution of aerosols. Three Evolution Gas Analysis (EGA) protocols have been tested in order to better characterize the collected aged biomass burning smoke: A 2-step thermal method (Cachier et al., 1989) and a thermo-optical technique using two different temperature programs. The later temperature programs are those used for IMPROVE (Interagency Monitoring of Protected Visual Environments) and NIOSH 5040 (National Institute of Occupational Safety and Health). Artifacts were observed using the NIOSH temperature program and identified as interactions between carbon and dust deposited on the filter matrix at high temperature ($T=550^{\circ}\text{C}$) under the pure helium step of the analysis.

During the MINOS campaign, Black Carbon (BC) and Organic Carbon (OC) concentrations were on average respectively 1.19 ± 0.56 and $3.62\pm 1.08 \mu\text{gC}/\text{m}^3$ for the IMPROVE temperature program, and 1.09 ± 0.36 and $3.75\pm 1.24 \mu\text{gC}/\text{m}^3$ for the thermal method. Though these values compare well on average and the agreement between the Total Carbon (TC) measurements sample to sample was excellent (slope = 1.00, $r^2=0.93$, $n=56$), important discrepancies were observed in determining BC concentrations from these two methods (average error of $33\pm 22\%$). BC from the IMPROVE temperature program compared well with non-sea-salt potassium (nss-K) pointing out an optical sensitivity to biomass burning. On the other hand, BC from the thermal method showed a better agreement with non-sea-salt sulfate (nss- SO_4), considered as a tracer for fossil fuel combustion during the MINOS campaign. The coupling between these two methods for determining BC brings here new insights on the origin of carbonaceous aerosols in a complex mixture of different sources. It brings also to our

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attention that important deviations in BC levels are observed using three widely used EGA techniques and most probably none of the EGA tested here are well adapted to fully characterize this aerosol mixture.

Spherical, smooth and silico-aluminated fly-ash observed by Analytical Scanning Electron Microscope (ASEM) confirm the influence of coal combustion on the carbonaceous aerosol load throughout the campaign. A raw calculation based on BC/nss-SO₄ mass ratio suggests that biomass burning could be responsible for half of the BC concentration recorded during the MINOS campaign.

From the plot of BC as a function of TC, two linear correlations were observed corresponding to 2 times series (before and after 12 August). Such good correlations suggest, from a first look, that both BC and OC have similar origin and atmospheric transport. On the other hand, the plot of BC as a function of TC obtained from the 2-step thermal method applied to DEKATI Low Pressure Cascade Impactor samples does not show a similar correlation and points out a non conservative distribution of this ratio with 2 super micron modes enriched in OC, correlated with sea salt aerosols and probably originating from gas-to-particle conversion.

1. Introduction

Since its adoption in the mid eighties, the Helsinki protocol on the reduction of sulfur emissions have brought sulfate and carbonaceous aerosols at the same concentration levels in the troposphere over Europe and the Mediterranean Sea (Kryvacsy et al., 2001; Lelieveld et al., 2002).

Carbonaceous aerosol is mainly a combustion aerosol of primary and secondary origin. This aerosol is usually separated in two main components: one is referred to as the organic carbon (OC) and the other as the black carbon (BC). BC radiative impact is significant because of its highly absorptive nature.

Recent model studies reproducing satellite observations have demonstrated that BC aerosols were one of the three major components of aerosols (with sulfate and dust),

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which have very high direct radiative forcing at the top of the atmosphere in surrounding regions of the Mediterranean Basin (Jacobson, 2001). This model estimates a negative radiative forcing for aerosols in the Mediterranean, roughly comparable to that of greenhouse gases (e.g. -3 to -4 W/m^2). During the MINOS campaign, the reduction of surface solar radiation was even larger (-17.9 W/m^2 ; Markowicz et al., 2002), demonstrating the important effect of absorbing aerosols in Mediterranean. These authors also noticed that the BC concentrations recorded during this campaign (see later on) were too low to entirely explain the forcing efficiency at the surface, and proposed, alternatively, a contribution of dust aerosols as another light absorbing material, which could explain their results. This assumption is supported first by important levels of dust aerosols observed in altitude over the Eastern Mediterranean (Andreae et al., 2002; Formenti et al., 2001, 2002; Kouvarakis et al., 2002; Sciare et al., unpublished data); second from the results of the EL CID campaign performed in Crete Isl. in summer 2000 (exactly a year before the MINOS campaign) which showed significant bias in BC calculation based on light absorbance during dust events (Sciare et al., 2002). As a result, there is a great need to better investigate the role of carbonaceous aerosols, their origin and physical, chemical and optical properties in the eastern Mediterranean.

As emphasized by Huebert and Charlson (2000), there are still very large uncertainties in all the published EGA protocols for determining BC and OC content in aerosols, including very similar ones such as thermo-optical protocols (Chow et al., 2001; Yu et al., 2002; Yang and Yu, 2002). If most of these protocols give a good agreement in TC determination, BC concentrations differ substantially for ambient aerosols (Schmid et al., 2001). They usually compare within 20% for urban aerosols but deviations are more important for remote aerosols (e.g. the aerosols collected during MINOS). Running several of these protocols for the same samples, as it is proposed here, will help us to understand the uncertainties in carbon analysis. The work presented here will aim to better characterize BC and OC concentrations over the eastern Mediterranean during the MINOS campaign from different analytical protocols: A 2- step thermal method (Cachier et al., 1989) and a thermo-optical technique using two different temperature

programs (NIOSH and IMPROVE) and a laser transmittance. Origin of carbonaceous aerosols will be discussed from back trajectory analysis, Scanning Electron Microscope (SEM) pictures, comparison between MBL and FT sites, and BC/TC ratio variability.

2. Instrumentation

5 2.1. Sampling sites and overview of the campaign

Two ground-based stations were operating during the MINOS campaign: Finokalia station located in the MBL (35°19' N, 25°40' E; 150 m at sea level (a.s.l.)) was running for the period 25 July–23 August 2001; Skinakas station, located in the FT (35°15' N, 25°50' E; 1500 m a.s.l.) and at 50 km from the MBL site, was running for the period 10 29 July–19 August 2001. These 2 stations were situated within the 2 different aerosol layers (0–1200 m and 1200–3000 m) as observed from the vertical profiles of aerosols properties carried out through all the campaign from flight measurements (Minikin et al., unpublished results).

15 Air mass origins at these two stations during the MINOS campaign are reported with more details in Sciare et al. (unpublished data). Shortly, they originated exclusively from eastern Europe at the MBL site, from both eastern and western Europe at the FT site.

2.2. Aerosol sampling

20 Ambient aerosols were collected every 12 h in parallel on quartz filters (QMA, Whatman) for carbon analysis and on Stack Filter Units (SFUs) for gravimetric measurements and ion analysis. Analytical procedures for ion analysis can be found at Kouvarakis and Mihalopoulos (2002).

SFUs consist in an 8 μm pore size 47-mm diameter Nuclepore filter mounted in front of a 0.4 μm pore size 47-mm diameter Nuclepore Filter. All filters are weighed prior to

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exposure. The 50% cut point diameter (D_{50}) of the 8 μm Nuclepore filter was estimated to be of the order of $1.2 \pm 0.1 \mu\text{m}$ for the adopted flowrate (Sciare et al., unpublished results). A total of 56 quartz filters and SFUs were collected at the MBL site (26 July–23 August 2001); 6 quartz filters and 15 SFUs were collected at the FT site (31 July–18 August 2001). Flow rate was on average 51 ± 4 liter per min (lpm) and pressure drops around 100 mbar for the quartz filters collected at the MBL site. Quartz filters, were baked for 24 h at 600°C . Several blanks were taken on the field and analyzed together with the samples (see later on).

Size-segregated aerosols were collected on a 3-day basis at the MBL site using in parallel two low-pressure cascade impactors; a 11-stage Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corporation) operating with 47-mm diameter Nuclepore polycarbonate and teflon filters, for mass, ion, particle-induced X-ray emission (PIXE), short irradiation Instrumental Neutron Activation Analysis (INAA), and optical absorption measurements; and a 13-stage Low pressure cascade Impactor (DEKATI, Dekati Ltd, Tampere, Finland) operating with 25-mm diameter Glass fibre (GFC) filters for BC and OC measurements using the thermal protocol developed by Cachier et al. (1989).

3. Analysis

3.1. Carbonates in aerosols

Carbonates in aerosols play an important role in the carbon analysis as they can interfere the measurement by releasing CO_2 at high temperatures in the range $550\text{--}1020^\circ\text{C}$ (Webb and Kruger, 1970). In a dusty environment such as Crete Isl., this BC positive artifact should be significant especially for our quartz filters, sampled with no cut-off at the inlet and thus collecting any dust aerosols. Carbonates levels in the aerosol can be roughly estimated following the calculations done by Bardouki et al. (2003) and assuming a single dust origin (CaCO_3) and using PIXE INAA analysis of dust end members obtained during the MINOS campaign (such as Fe, Al, Si, Ca, results

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from MOUDI cascade Impactor; Sciare et al., unpublished results). In our samples, the mass percentage of carbon from carbonates would represent 2–15% (average = 6.1 ± 2.6) for the MBL site and 8–13% (average = 10.3 ± 2) for the FT site.

Thus for all the EGA, all the samples were previously decarbonated by HCl fumes using the protocol designed by Cachier et al. (1989). Following decarbonation, 2 standard sized punch of 1×1.45 cm were taken from the quartz filters for thermo-optical analysis, the rest of the quartz filters being dedicated to the thermal analysis.

3.2. Thermo-optical methods

We used a Sunset thermo-optical transmission carbon analyzer system (Sunset Lab., OR, USA) for determining BC and OC in aerosols. The Sunset instrument measurements are performed from standard sized punch of the quartz filters, through temperature and gas control, and by a laser transmission that corrects for the pyrolytically generated “EC” (or char) formed during the analysis of OC materials. The analysis needs two distinct stages. In the first, OC is volatilized from the sample in a pure helium atmosphere. In the second, BC and pyrolytically generated “BC” are oxidized under a mix of 2% of oxygen in ultra high purity (UHP) helium with a concurrent increase in the filter transmittance. Correction for the charring contribution to BC is performed by identifying the point at which the filter transmittance reaches its initial value. Carbon evolved before this split point is considered as OC; carbon evolved after this split point and prior to the peak used for the instrument calibration (final peak) is BC. A more detailed description of the instrument is given by Birch and Cary (1996), Birch (1998) and Chow et al. (2001).

In this study, two temperature programs were implemented in the Sunset instrument and are summarized in Table 1. They correspond to the temperature programs used in the IMPROVE and NIOSH protocols (Chow et al., 1993; NIOSH, 1996, 1998). Although these two protocols use different instruments and optical measurements, the main difference between these two protocols is originating from different temperature programs. It may be noted that a secondary cause of discrepancy between the NIOSH

and IMPROVE protocols originates from the different optical correction and subsequent split time of the two instruments (Chow et al., 2001). This second cause is however minimized for non-heavy loaded filters such as our samples.

Determination of the split point between BC and OC and subsequent absorption measurement is also a critical point for determining the BC content of the filter (e.g. for both NIOSH and IMPROVE protocols). To minimize this absorption measurement and thus check the laser performance of the Sunset transmission, the following analytical strategy was applied: First, an 18-mm circle was taken from the quartz filter samples prior to decarbonation. Aerosol attenuation of this circle was performed using a modified Aethalometer model AE-8 manufactured by Magee Scientific (Hansen et al., 1982). These absorption measurements have shown to be in very good agreement ($r^2=0.90$; $n=56$) with absorption measurements performed in quasi real-time by the mean of a Particle Soot Absorption Photometer (PSAP, Radiance Research; Seattle, USA) (data not shown here). They were also in very good agreement ($r^2=0.93$) with the absorption measurements performed by the laser beam of the Sunset instrument on the 1×1.45 cm punch of the same quartz filters. This good agreement points out the good performance of the Sunset laser transmission measurements and its capability to better constrain the thermo-optical measurements.

3.3. Thermal method

This method was used to determine the BC and OC concentrations from quartz filters (Cachier et al., 1989) sampled at the 2 sampling sites (bulk aerosol) and the GF/C filters sampled with the DEKATI Impactor.

The remaining part of the 47-mm quartz filters previously decarbonated is divided in two, one half gives TC (BC+OC). For the second half, the organic part is removed during a precombustion (at 340°C and under O_2 for 2 h) then the remaining black carbon is analyzed as CO_2 by coulometric titration in a Ströhlein carbon analyzer. BC content is given with an accuracy of $0.02 \mu\text{g}$. The detection limit corresponds to a load on the order of $3 \mu\text{g}$. The precision of the results is primary linked to the sample heterogene-

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ity and has been estimated to be in the range of 10%. This method gave comparable results as various thermo-optical methods for a diesel soot intercomparison (Guillemin et al., 1997) and was in the range of $\pm 1\sigma$ for BC and TC for the first stage round robin test for carbon aerosol (e.g. urban aerosols, Schmid et al., 2001).

5 The calibration of the Ströhlein instrument was checked using either graphitic carbon standards or glucose solutions. The agreement between the two calibrations performed with liquid standards of glucose on both the Ströhlein and Sunset instruments was better than 1%.

10 This thermal method has been also used for determining BC and OC content from a total of 5 runs of a 13-stage DEKATI cascade Impactor. 25-mm diameter GF/C filters have been used for that purpose and were precleaned by a multisolvent (acetone, chloroform, ethanol) soxhlet extraction. Blanks (in μgC) were reproducible and represented on average 5% and 15% of the BC and TC contents for the stages presenting the highest loading.

15 Hereafter BC(Thermal) will refer to BC concentrations from this thermal method developed at LSCE.

3.4. Sampling artifacts

Artifacts due to the absorption of gas-phase organic compounds on the sample substrate were minimized by heating filters during 20 min at 60°C prior to the 2-step 20 Thermal/Thermo-optical analysis. However, such artifacts do not impact significantly the determination of the light absorbing material of the aerosol (e.g. one of the major concerns of the MINOS campaign).

A very good agreement for BC and TC concentrations was obtained between our quartz bulk filters and the DEKATI cascade impactor samples which have been collocated throughout the campaign (Sciare et al., this issue). The slope close to 1 found 25 between the two sampling techniques – with all data points lying within 10% errors in mass concentrations- suggests that sampling artifacts, which are not corrected by our pre-treatment at 60°C, did not affect significantly the whole OC mass concentration of

our samples.

Such conclusion reinforces the ability of our measurements to be used for the mass closure experiments of sub micron aerosols as performed by Sciare et al. (unpublished results) during the MINOS campaign.

5 4. Comparison between the different EGA protocols

4.1. Comparison between NIOSH and IMPROVE Temperature programs

Figure 1 shows a thermogram obtained applying the NIOSH analysis protocol for one of the samples obtained at the MBL site. This figure shows that the laser transmission increases during the pure He 870°C step (OC4), clearly indicating important loss of a black component. Such a whitening of the sample has been reported in previous works which can be either due to an increased rate of reaction between oxygen-containing minerals and EC particles in the filter deposit (Chow et al., 2001), or due to the evolution of light absorbing organic material (present in wood smoke samples for instance). Yu and Yang (2002) have also shown that this transmission increases with inorganic salts (such as ammonium sulfate). These three possibilities could occur during the analysis since our quartz filters collected a mixture a dust containing mineral oxides, biomass burning smoke and important levels of ammonium sulfate.

It must however be noted that the whitening of the filter could not originate from the decomposition of carbonate since 1) our samples were pre-treated with HCl, 2) carbonate does not absorb at the wavelength of the laser.

On the origin of the BC loss under pure helium:

Several tests were performed to better understand the origin of this analytical artifact. First, the IMPROVE Temperature program was applied to all our samples, without showing any loss of absorbing material under the pure He step. Such a result

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is expected since no BC loss was observed at the third plateau (615°C) using the NIOSH temperature program (Fig. 1). Interestingly, although IMPROVE and NIOSH temperature program are reaching the same high temperatures under He/O₂ (i.e. 850–890°C), only the quartz filters analyzed by the IMPROVE temperature program

5 showed an orange color, probably due to the color of iron-rich dust aerosols. This assumption was confirmed as the quartz filters presenting the most pronounced orange color corresponded to dusty events with dust loadings higher than 20 μg/m³.

Submitting these colored filters to the whole NIOSH temperature program did not show any change in the laser transmission, nor carbon evolved during this program.

10 But more surprisingly the orange color of the filters disappeared whereas it previously remained during the IMPROVE temperature program. In other words, a fraction of dust aerosols probably decomposed (and produce O₂) under the pure helium step between 615 and 870°C, and thus produced a partial thermal evolution of BC (aerosol or pyrogenic).

To verify this assumption, 20 μl of glucose standards were used as a surrogate of pyrogenic BC and added to one of these orange filters. As expected, the thermogram clearly shows a decrease and then an increase in the laser transmission increase at 870°C during the last helium step (as observed in Fig. 1 with an actual environmental

15 sample). Such trend clearly indicates that BC produced from the pyrolysis of glucose is then released at this step in the presence of dust. Neither light absorbing organic nor inorganic sea salt (such as ammonium sulfate) could explain this increase in transmission. Since important charring corrections may bring major uncertainties in BC assessment (Yang and Yu, 2002) and as dust aerosols were ubiquitous during the MINOS campaign, the IMPROVE temperature program was then the EGA protocol

20 used for BC and OC determinations.

25

On the choice of the last temperature step under pure helium:

It is worthwhile noting here that the choice of this last temperature step under

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helium remains on open question. Conny and Slater (2002) used a NIOSH protocol (900°C for the last Helium plateau) for the determination of BC/TC ratios from fresh particles of crown fires in the Canadian forest. Their BC/TC ratio values range between 8 and 0.8% for flaming and smoldering stages respectively, and represent the lowest ratios proposed for biomass burning in the literature. The question is thus raised if the last temperature stage under helium fixed by the NIOSH protocol could not be too high as suggested by Chow et al. (2001). Alternatively the last stage fixed under helium by the IMPROVE protocol (550°C) could be too low, involving a possible OC underestimation and BC overestimation and consequently a BC/TC ratio too high. Figure 1 shows that at 615°C the laser transmission is still decreasing, suggesting strictly speaking, that OC is evolving at this temperature. However, a strict comparison between the two programs is not possible due to differences in plateau time duration.

An alternative solution to analyze complex samples would be to design a temperature program with a prolonged last helium step until laser transmission is not changing and the evolution of carbon component has stopped. Such a procedure is however not totally satisfactory since the absorption coefficient of BC particles is likely to change while the OC component is escaping the filter matrix. This remark applies particularly to aged particles totally found as internal mixtures (Cachier, 1998). Anyhow to avoid important loss of BC during the last helium step, we decided to adopt a last step of 550°C as described by the IMPROVE protocol.

Assuming 1) the last step under He being the most important parameter for BC calculation, 2) 550°C and 870°C being the minimal and maximal temperature which have to be set for this step, one can estimate the uncertainties in BC concentrations from the difference between NIOSH and IMPROVE temperature programs. In the case of our Crete samples, a difference as high as 50% was calculated for the averaged BC concentrations between these two methods (the IMPROVE temperature program giving higher BC concentrations). This difference can be considered as representative of the possible maximum error for the determination of BC concentrations given by a thermo-optical method.

4.2. Comparison between Thermo-optical (IMPROVE) and 2-step Thermal protocols

Such a comparison has been performed for the samples collected at the MBL and FT sites. The TC measurements compared very well for both sites with a slope of 1.0 and $r^2=0.93$ for all data points. Conversely important deviations were found for BC, although on average, BC concentrations were comparable with 1.09 ± 0.36 and 1.19 ± 0.56 for 2-step Thermal and IMPROVE methods, respectively. Deviations as high as 88% were observed on individual samples between the two BC dataset (average error = $33\pm 22\%$). These results are somehow surprising since these two methods showed a good agreement for urban aerosols (Cachier, 2003). On the other hand, one must keep in mind that part of carbonaceous aerosols sampled during MINOS originates from aged biomass burning smoke and are likely to be functionalized (Andreae, 1991; Cachier 1998), with thus different chemical properties compared to urban carbonaceous aerosols (fossil fuel origin).

To better assess the origin of BC during the MINOS campaign, both BC(IMPROVE) and BC(Thermal) were compared with 1) sub micron nss-K used here as a tracer for biomass burning (see for instance Andreae 1983, Echalar et al., 1995, 1998); and 2) with sub micron nss-SO₄ used here as a tracer for fossil fuel combustion. BC concentrations have been set to the same scale in Fig. 2 to better emphasize the difference in concentration between the two EGA. Most of the time a good agreement was found between BC (Thermal) and nss-SO₄ (when the two biomass burning events are removed, $nss-SO_4 = 0.09 BC + 0.44$; $r^2=0.47$; $n=39$). On the other hand, BC(IMPROVE) better correlated with nss-K ($nss-K = 0.51BC - 0.16$; $r^2=0.89$; $n=56$). In more details, the three anthropogenic events reported in Fig. 2 are observed in BC(Thermal), whereas BC(IMPROVE) remains “insensitive” to these events. Conversely the two biomass burning events reported in this figure are observed in BC(IMPROVE), whereas BC(Thermal) remains “insensitive” to these events. Such results are quite striking and, to our best knowledge, have never been reported in literature. In the following, we tentatively explain the reasons why BC(Thermal) and BC(IMPROVE) could be exclusively

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sensitive to anthropogenic and biomass burning emissions respectively.

4.3. Comparison with Absorption measurements

Alternatively, the levels of BC in aerosols can be also approached from their light absorbing properties. Absorption measurements were performed for that purpose during the campaign using a PSAP, and were compared with BC(IMPROVE) in Fig. 3. Absorption measurements performed from the PSAP were corrected from the multiple scattering induced by the aerosol deposit and misinterpreted as absorption (Bond et al., 1999). As shown in Fig. 3, a significant correlation is found between the two datasets ($r^2=0.90$; $n=54$), which is not really a surprising result since the split point between BC and OC in the Thermo-optical method is precisely based on the optical properties of aerosols measured also by the PSAP. In opposite, when PSAP absorption measurements (Abs(PSAP)) are compared with BC(Thermal) or nss-SO₄, no correlation is obtained. In other words, optical and thermo-optical measurements behave the same and seem to be entirely related to biomass burning whereas anthropogenic emissions are only reflected in the thermal measurements. Note that these results should not lead to misinterpretation such as BC(Thermal) concentrations being entirely representative of the anthropogenic fraction of BC. The same caution has to be taken to interpret the BC(IMPROVE) concentrations as entirely representative for the biomass burning fraction of BC.

On the reason why BC(Thermal) better correlates with fossil fuel combustion:

The presence of potassium and sodium in aerosols may oxidize BC particles, and thus decrease their temperature of combustion (Novakov and Corrigan, 1995). Martins et al. (1998) reached the same conclusion from the analysis of biomass burning smoke samples by the 2-step thermal method used here (Cachier et al., 1989). Martins et al. (1998) found that samples with K/BC(Thermal) mass ratios higher than 0.78 were significantly influenced by catalytic reactions between BC

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and K, inducing an underestimation of BC(Thermal). Our K/BC(Thermal) mass ratio typically averaged 0.4 ± 0.2 with values exceeding 0.8 during the two biomass burning events depicted in Fig. 2. Then, during these events a significant fraction of BC originating from biomass burning was removed during the first oxidative step of our thermal method. The remaining fraction of BC, determined as BC(Thermal), correlates with nss-SO_4 and thus has an anthropogenic origin. Note that the conclusion of the existence of a significant BC fraction of anthropogenic origin cannot be reached from optical or thermo-optical measurements, which look very sensitive to biomass burning. A major question is thus raised here on the reliability of optical and thermo-optical methods (PSAP, IMPROVE) in determining BC content for a mixture of carbonaceous aerosol from different sources.

On the reason why absorption measurements better correlate with biomass burning:

A possible explanation could originate from different Mass Absorption Efficiencies (MAE) for biomass burning and fossil fuel combustions respectively. This coefficient can be estimated from the relationship:

$$\text{Abs} = \text{MAE} \times \text{BC}. \quad (1)$$

A higher MAE for biomass burning would induce a higher sensitivity of optical measurements as it appeared here. Lioussé et al. (1993) reported important variability in MAE (from 5 to $20 \text{ m}^2/\text{g}$) that may be related to the variability of aerosol mix and the aging of the atmospheric particulate phase. For smoke aerosols, many authors use a model based on a highly absorbing BC core surrounded by a nonabsorbing shell (Martins et al., 1998, and references therein). This internal mixture leads to higher MAE than pure BC particles and can reasonably well explain the observed absorption sensitivity to biomass burning.

Further considerations on the influence of biomass burning on absorption measurements:

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From a source-receptor model, Sciare et al. (2003) reported that the main sources of BC, SO₂ and nss-SO₄ observed at the same MBL sampling station during the summer 2000 were located in central Europe and would probably correspond to coal power plant emissions. This result is supported by the SO₂ emission maps provided by UNECE/EMEP and available from the EMEP website (<http://www.emep.int>) and by observations of SO₂ over northern Greece (Zerefos et al., 2000; Formenti et al., 2001).

During this summer 2000, the eastern Mediterranean Sea was not influenced by biomass burning and Sciare et al. (2003) reported a significant correlation between BC (from PSAP measurements) and nss-SO₄ in aerosols during the summer 2000. This result goes well with an exclusive fossil fuel origin for BC but it is completely different from the one obtained during the MINOS campaign. These contrasted results support the previous findings on higher MAE for biomass burning compared to fossil fuel combustion during the MINOS campaign.

All these results bring to our attention an important limitation of the thermo-optical and optical methods in determining BC concentration in a mixture of carbonaceous aerosols from different sources. The thermo-optical methods are based on an optical correction and, for that reason, will critically be influenced by the source of BC having the highest MAE (biomass burning in our study).

5. Mass absorption efficiency calculation

We demonstrated before that significant artifacts could have altered both BC(IMPROVE) and BC(Thermal) concentration results. One must keep in mind these limitations in the following calculations of the MAE. We can estimate here a MAE from our two BC dataset using Eq. (1).

We reported in Fig. 4 the ratio between Abs(PSAP)/BC(Thermal) versus the nss-K concentration. This ratio can be seen as the MAE of BC (expressed in m²/g) and calculated for each sample. It can be seen also as the relative contribution of biomass

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burning to fossil fuel combustion. As shown on this figure the decrease of BC(Thermal) relatively to Abs(PSAP) is proportional to the increase of nss-K. It can be interpreted as the influence of the catalytic reaction between BC and potassium (see the previous discussion in Sect. 4.2). But it can also be interpreted as an increase of MAE when moving to higher BC contribution from biomass burning (e.g. higher nss-K). Conversely, it can be interpreted as a decrease of MAE when moving to higher BC contribution from fossil fuel combustion (e.g. lower nss-K). This result fits the assumption that MAE is more important for biomass burning BC particles.

Based on thermo-optical measurements, this coefficient remains fairly constant at $7.5 \pm 1.5 \text{ m}^2/\text{g}$ (Fig. 3), and thus is not sensitive to different mixture of biomass burning and fossil fuel combustion as observed previously.

An independent calculation can be done to estimate this MAE from the model described by Martins et al. (1998) for smoke particles, and assuming a BC core with a surrounding nonabsorbing shell (ammonium sulfate and organic carbon). Taking a size distribution for BC centered at $0.4 \mu\text{m}$ Aerodynamic Equivalent Diameter (A.E.D) (see later on), and a mass ratio BC/(Ammonium Sulfate + Particulate Organic Matter, POM) of 7.5% as calculated during the campaign, we obtain a MAE of the order of $7\text{--}8 \text{ m}^2/\text{g}$, in good agreement with the previous calculations.

6. Origin and size distribution of carbonaceous aerosols

The only source reported in literature for acetonitrile is biomass burning (Holzinger et al., 1999; 2001). Measurements of this compound were performed during the MINOS campaign and reported by Salisbury et al. (2003) who reached the conclusion that most of the time MBL air masses were influenced by biomass burning. Such result is in agreement with our correlation observed between BC (IMPROVE) and nss-K for the whole campaign duration. The most important biomass burning event is observed on BC (IMPROVE) for the period 8–12 August (Fig. 2), and reported in Fig. 5 using 5-day back trajectories for this period, drawn every 4 h. On this figure a MODIS map

provided by <http://firemaps.geog.umd.edu/> displays numerous fire spots in Ukraine, in the northern Black Sea region as well as in the western Black Sea (Bulgaria and Romania). In these regions, fires were still observed during the second decade of August and thus for the second biomass burning event (Fig. 2) which also originated from the northern part of the Black Sea.

6.1. Scanning electron microscopy

Selected Nuclepore filters collected at the MBL site have been analyzed by Analytical Scanning Electron Microscope (ASEM) Jeol 6301F fitted with an X-Rays Energy Dispersive Spectrometer (EDS), Oxford Link Isis. SEM and X-ray analysis revealed the presence of residues of incomplete wood combustion of several micrometers, composed by important content of C associated with K, in agreement with the correlation between BC (IMPROVE) and nss-K observed before. This emphasizes also that super micron biomass burning aerosols can be transported in the MBL at more than 3000 km from their source.

Figure 6a become from the observation of particles deposited on the filters sampled on 1 August. Their sphericity, their smooth surface, their granulometry (few μm) and their silico-aluminated chemical composition are characteristic of fly-ash emitted during coal combustion (Ramsden and Shibaoka, 1982). Same typical fly-ash have been also observed on many other samples through the MINOS campaign including the 2 major biomass burning events, and bring further evidence of a mixture of different aerosol sources. The presence of coal fly-ash is consistent with the conclusions reached by Sciare et al. (2003) on the origin of anthropogenic aerosols in the eastern Mediterranean. Moreover these conclusions are confirmed by the presence of aggregates of soot particles isolated (Fig. 6b) or stacked on the fly-ash.

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6.2. Attempt to estimate the fraction of BC originating from fossil fuel

A correlation was observed between BC(PSAP) and nss-SO₄ during the summer 2000 at the MBL site (report to Sect. 4.3). A similar correlation was observed during the MINOS campaign between BC(Thermal) and nss-SO₄. We propose here to use the BC/nss-SO₄ ratio obtained during the summer 2000 as well as the nss-SO₄ (and SO₂) concentrations of the MINOS campaign to estimate the contribution of fossil fuel of this last campaign.

A strong care must be taken when the BC/nss-SO₄ ratio is using since this ratio is not conservative and will decrease with increasing oxidation of SO₂ into nss-SO₄. The mass ratio nss-SO₄/(SO₂+nss-SO₄) was calculated to be 47% and 53% for the campaigns in summer 2000 and 2001 respectively (Mihalopoulos et al., unpublished data). In other words, the fraction of SO₂ oxidized in nss-SO₄ is about the same for the two years and thus BC/nss-SO₄ ratios obtained in summer 2000 could be used also for summer 2002. Taking an averaged ratio of 12% for BC/nss-SO₄ typical for central/eastern Europe (Sciare et al., 2003), would lead to BC concentrations of the order of 0.7 μg/m³ for fossil fuel for summer 2001. Such concentration would represent more than half of the total BC concentration recorded during the MINOS campaign, the remaining being biomass burning. This calculation should be seen as an estimate of the order of magnitude of the fraction of BC originating from fossil fuel combustion, which is here comparable to the one of biomass burning contribution.

6.3. Carbonaceous aerosols in the FT

Table 2 reports BC and TC concentrations from the two previous protocols (Thermal and IMPROVE) as well as nss-SO₄ and nss-K observed at the 2 sites. The previous conclusions obtained for the MBL site on the thermal and thermo-optical BC values and their correlation with nss-SO₄ and nss-K respectively, are applicable to the data obtained at the FT site too, suggesting also here a mix of carbonaceous aerosols of different origins. The correlation between BC (IMPROVE) and nss-K at the FT site is

within the one obtained at the MBL site. Assuming a conservative ratio between BC and nss-K, such a result would suggest that the fraction of BC from biomass burning in altitude is similar as that observed in the MBL. Although there is a factor of two differences in the concentrations between the 2 sites, the two important biomass burning events observed at the MBL site are also seen in altitude (data not shown here).

6.4. Variability of the BC/TC ratio

We reported the BC/TC ratio in Fig. 7 using BC (IMPROVE) for the carbon dataset from the MBL and FT sites. The good agreements between BC and TC suggest similar sources. BC/TC ratios for the altitude site are within those found for MBL, which could indicate that the two atmospheric layers are influenced by the same sources. Two slopes are seen in this Fig. 7; before and after 12 August. This change in the slopes between BC and TC is not seen when BC(Thermal) is taken instead of BC(IMPROVE). In other words, we can reasonably assume that the changes in the BC/TC ratios depicted in Fig. 7 are more related to biomass burning. The two biomass burning events depicted in Fig. 2 originate from the same area (Northern Black Sea, Fig. 5) but have different slopes, suggesting different biomass burning combustion processes or/with different absorbance properties.

Correlations between carbon monoxide (CO) and BC measurements are widely used to characterize different combustion processes (Chen et al., 2001; Dickerson et al., 2002; Baumgardner et al., 2003) and were performed in the field using a fully automated gas chromatograph instrument for CO (Gros et al., 1998a, b), and a PSAP for absorbance measurements. As mentioned earlier correlation between BC(IMPROVE) and Abs(PSAP) was excellent all along the duration of the campaign; Abs(PSAP) was used together with CO instead of BC(IMPROVE) in order to provide a better temporal resolution of their ratio. A change in the Abs(PSAP)/CO ratio was observed also on 12 August, which was not related in its slope but in its intercept (decrease of absorbance by a factor of 2 relatively to CO). This shift fits that observed for the BC/TC ratio the same day and thus brings further evidence of different combustion processes (with

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different optical properties) observed before and after 12 August.

6.5. Size distribution of BC, OC and BC/TC ratio

A total of 5 size distributions of BC and TC (Thermal method) were obtained at the MBL site from a 13-stage Impactor (DEKATI) and a time resolution of around 3 days. Contrarily to thermo-optical methods, the 2-step thermal method used here does not require homogeneous deposit of aerosol on the filter and thus is well adapted to the non-uniform and concentrated deposit of the filters collected with the DEKATI Impactor.

Averaged size distribution for BC, OC and BC/TC are reported in Fig. 8. Two modes around $0.4\ \mu\text{m}$ and $3\ \mu\text{m}$ A.E.D for both BC and OC are found all along the campaign, the sub micron mode representing around $80\pm 3\%$ and $75\pm 12\%$ of their total mass, respectively. The nss-K distribution obtained in parallel from the MOUDI impactor presents also a clear mode around $0.4\ \mu\text{m}$, which represents almost 90% of its total mass.

An interesting result comes from an extra mode present for OC around 1m A.E.D and observed all along the campaign. This mode does not correlate with BC, nss-K or nss-SO₄ distributions; it corresponds to the lowest BC/TC ratio (Fig. 8), and thus has little chance to originate from primary combustion processes. Interestingly is the correspondence between the two supermicron modes of OC with two modes observed on the sea salt distribution as well as on nitrate and light organics such as oxalate (results from the MOUDI impactor; Sciare et al., unpublished results). This fraction of super micron OC is not negligible ($\approx 20\%$ of the total mass) and would suggest adsorption processes of acidic gases (VOCs) onto basic sea salt particles similar to that observed for oxalate and nitrate (Bardouki et al., 2003).

On the choice of the 2-step thermal method for determining BC and OC mass size distribution:

As mentioned before, the non-uniform deposit of aerosols obtained on the DEKATI

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cascade impactor filters does not allow any optical corrections as done with a thermo-optical method. The split between BC and OC requires other methodologies, that are often based on parallel sampling of cascade impactor with quartz filters (see for instance Viidanoja et al., 2002 and Matta et al., 2002). A correction of BC from pyrolytic OC is then calculated from these quartz filters and is applied for all the stages the cascade impactor to derive BC and OC concentrations. To do so, one must make the assumption that thermal properties (and corresponding pyrolytic OC) of carbonaceous aerosols do not depend on the size distribution. Our supermicron fraction of OC, which probably originates from condensation of VOCs onto sea salt particles, has little chance to have thermal properties similar to submicron OC. Hence, and due to its relatively small contribution to the total mass of OC, this supermicron fraction will not significantly influence the pyrolytic OC correction of BC which could be performed from our quartz filters sampled in parallel of our cascade impactor. The above assumption that thermal properties of carbonaceous aerosols do not depend on the size is not applicable in our samples and would probably lead to a misinterpretation of the supermicron fraction of OC. The 2-step thermal method used here in our DEKATI impactor samples is probably partially affected by artifacts (potassium catalytic reaction, report to Sect. 4.2). On the other hand, it offers an interesting alternative to the methodologies currently used to estimate the BC and OC mass size distribution and highlight here a non-negligible source of secondary OC.

7. Conclusions

Along the MINOS campaign, air masses were influenced by long-range transport of biomass burning located in the northern and western Black Sea, at more than 2000 km from the receptor site in Crete Isl. Evidence was brought that an important fraction of carbonaceous aerosols collected in Crete was originating from these biomass burnings (back trajectory analysis, SEM analysis, correlation between BC and nss-K, gas phase measurements).

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The monthly mean Black Carbon concentration calculated for the summer 2001 is a factor of 3 higher compared to the one calculated a year before at the same location. Its composition is a complex mixture from different origins (biomass burning, fossil fuel) having different optical properties and mixing state. These results highlights at least the need for multiple year measurements for carbonaceous aerosols in Crete Isl., as such dataset would be used lately for validating models calculating the direct radiative forcing of aerosols over the eastern Mediterranean Sea.

We have brought here evidence that three of widely used analytical procedures for determining BC and OC failed to fully characterize a complex mixture of aerosols originating from biomass burning and fossil fuel combustions (e.g. NIOSH and IMPROVE thermo-optical protocols as well as a 2-step Thermal protocol).

Dust aerosols have shown to interfere with the determination of BC and OC in the NIOSH method. Attention was brought that filter-based absorption measurements performed during the campaign (PSAP or Aethalometer) as well as the IMPROVE thermo-optical method were significantly influenced by the optical properties of the BC fraction originating from biomass burning and thus could have possibly underestimated the anthropogenic fraction of BC. Valuable information on the origin of BC and OC could be obtained from the 2-step Thermal method and evidenced a non-negligible fraction of BC originating from fossil fuel combustion. Furthermore, this 2-step thermal method was applied satisfactorily to the analysis of heterogeneous impactor samples and could show the existence of a supermicron OC mode that could be of secondary origin. In the absence of an universal analytical protocol for particulate carbon, these findings highlight the need for further crossed comparison exercises between different methods for determining BC and OC at locations influenced by different aerosol sources, as observed in the eastern Mediterranean Sea. It points out also the strong care needed when designing a single and common analytical protocol for carbon analysis within network and intensive field studies.

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Table 1. Experimental parameters of the two thermo-optical methods used in this study

Carrier Gas	NIOSH Temp program	IMPROVE Temp program
He-1 (OC1)	310°C, 60 s	250°C, 150 s
He-2 (OC2)	475°C, 60 s	450°C, 150 s
He-3 (OC3)	615°C, 60 s	550°C, 250 s
He-4 (OC4)	870°C, 90 s	
He/O ₂ * (BC1)	550°C, 45 s	550°C, 200 s
He/O ₂ (BC2)	625°C, 45 s	
He/O ₂ (BC3)	700°C, 45 s	700°C, 160 s
He/O ₂ (BC4)	850°C, 45 s	850°C, 200 s
He/O ₂ (BC5)	890°C, 120 s	

* A mix of 2% of oxygen in UHP helium

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Table 2. Mass concentration ($\mu\text{g}/\text{m}^3$) of BC, OC (IMPROVE temperature program + Thermal method), nss-K and nss-SO₄ for the MBL site (25 July–23 August; n=56) and FT site (31 July–18 August; n=6 for BC and OC; n=15 for nss-K and nss-SO₄)

	MBL Site (150 m a.s.l.)	FT Site (1500 m a.s.l.)
BC (IMPROVE)	1.19±0.56	0.79±0.28
OC (IMPROVE)	3.62±1.08	2.70±0.49
BC (Thermal)	1.09±0.36	0.70±0.19
OC (Thermal)	3.75±1.24	2.38±0.45
nss-SO ₄	6.19±2.21	3.60±1.27
nss-K	0.43±0.31	0.26±0.11

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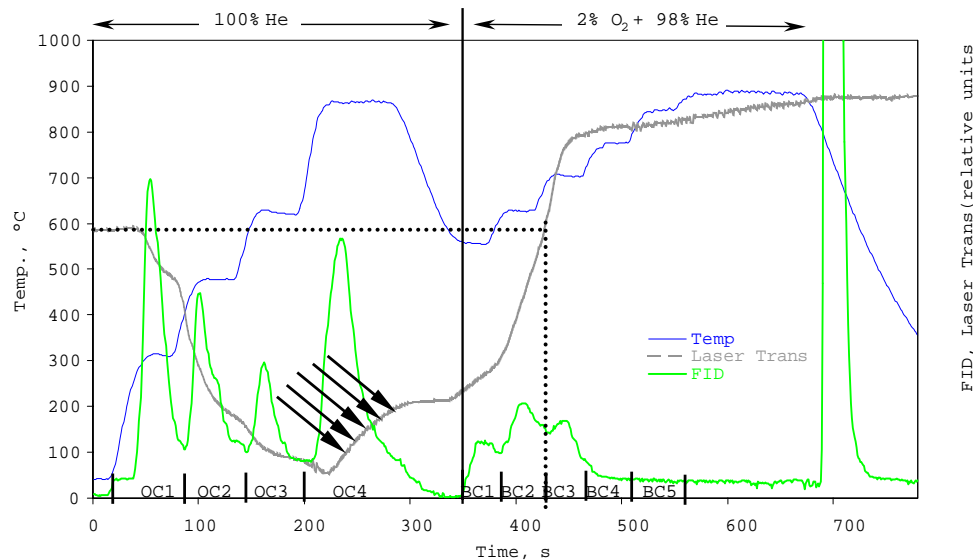
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FID, Laser Trans (relative units)

Fig. 1. NIOSH temperature program on a quartz filter sampled during MINOS. Black arrows indicate increase in laser transmission (BC loss) at the last temperature step (870°C) under pure helium. OC1-4 and BC1-5 described in Table 1 have been reported here for each temperature step. The optical correction performed by the instrument is reported here (black dash).

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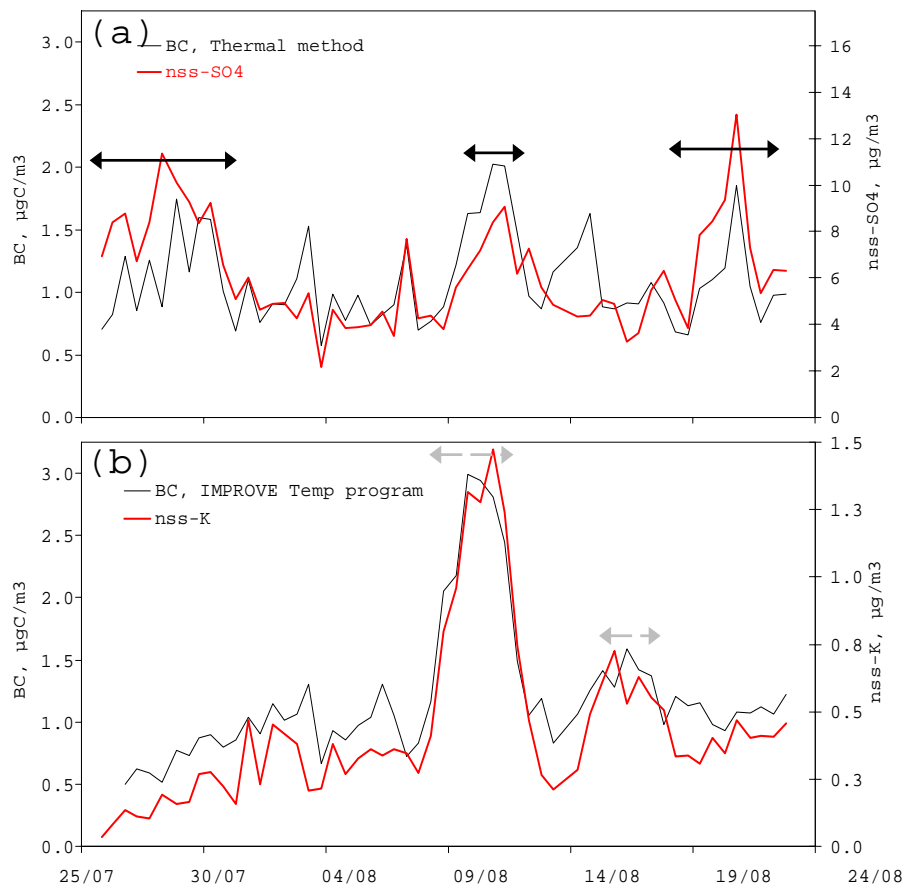


Fig. 2. BC from thermal method and nss-SO₄ concentrations (a); BC from thermo-optical IMPROVE method and nss-K (b) at the MBL site for the duration of the MINOS campaign. Black arrows correspond to the anthropogenic influence. Grey arrows correspond to the 2 biomass burning events of the campaign.

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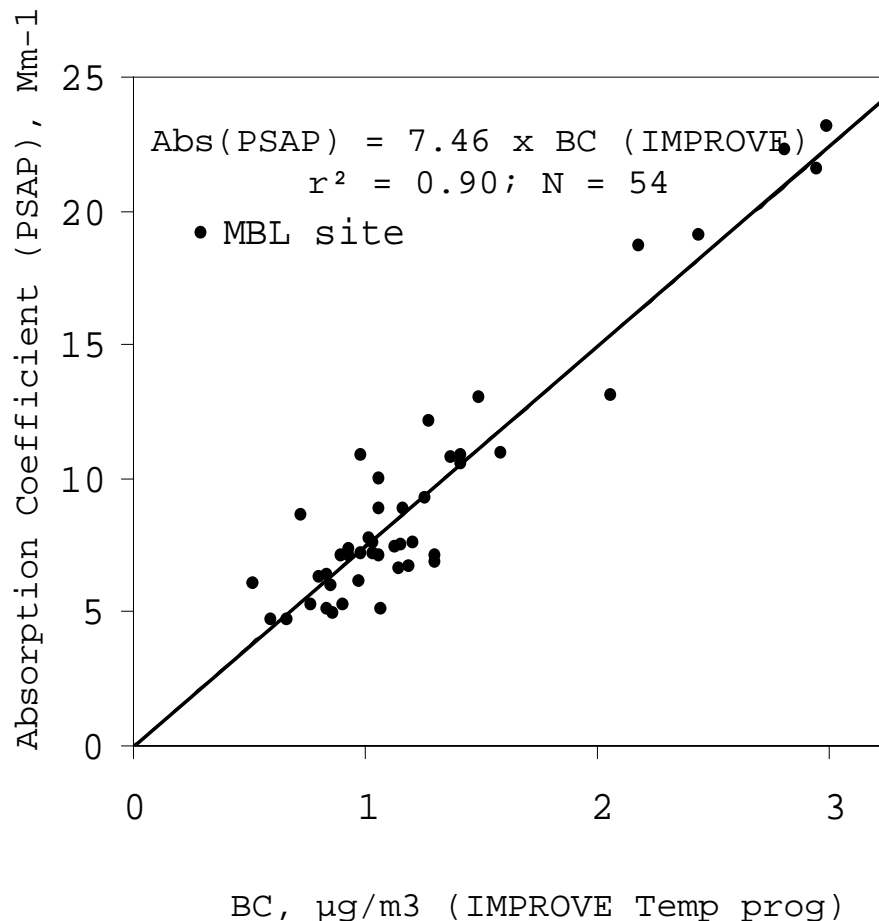


Fig. 3. Correlation between BC concentration (IMPROVE Temp prog.) and absorption measurements performed in the field from PSAP. PSAP data are corrected from multiple scattering following the recommendation of Bond et al. (1999).

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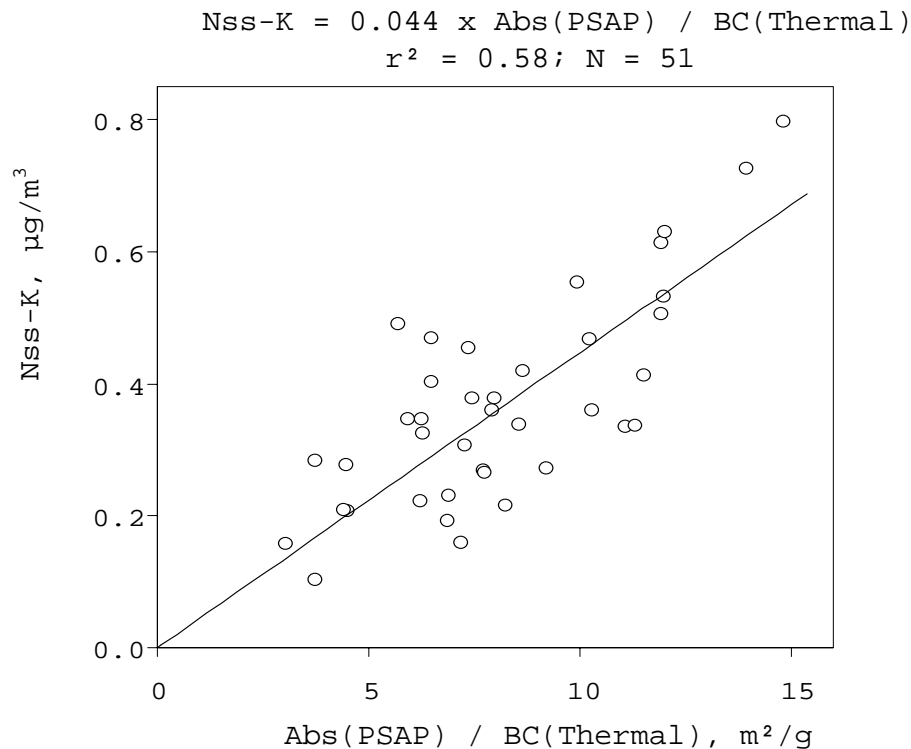


Fig. 4. Correlation between nss-K concentration and the mass absorption efficiencies (MAE) calculated from the ratios Abs(PSAP) and BC(Thermal). The first biomass burning event has been excluded.

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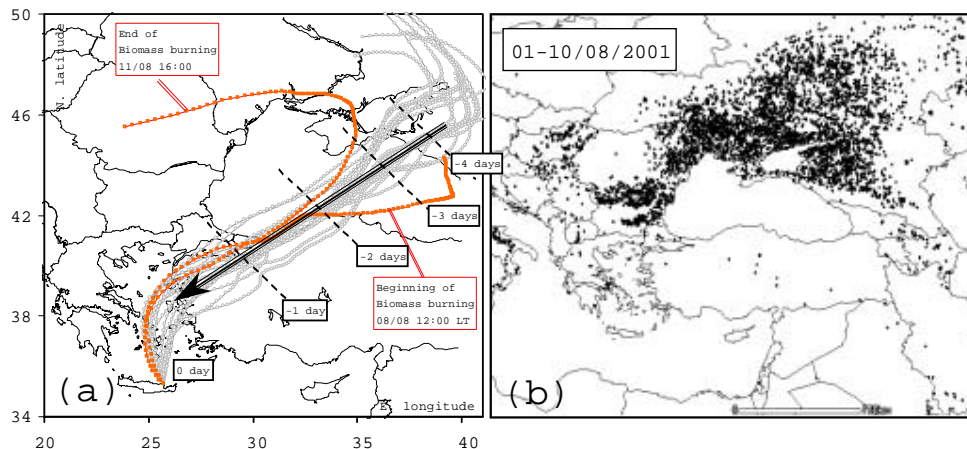


Fig. 5. (a) 5-day back trajectories generated every 4 h from the HYSPLIT model for the period (8 August, 12:00 LT–11 August, 16:00 LT). The back trajectories are arriving at 500 m a.s.l. Those set in red correspond to the beginning and the end of the first biomass burning depicted in Fig. 3. A Temporal scale has been added to better the location of air masses. (b) Fire maps (MODIS satellite) available at <http://firemaps.geog.umd.edu/>. Each black point corresponds to a fire for the first decade of August 2001.

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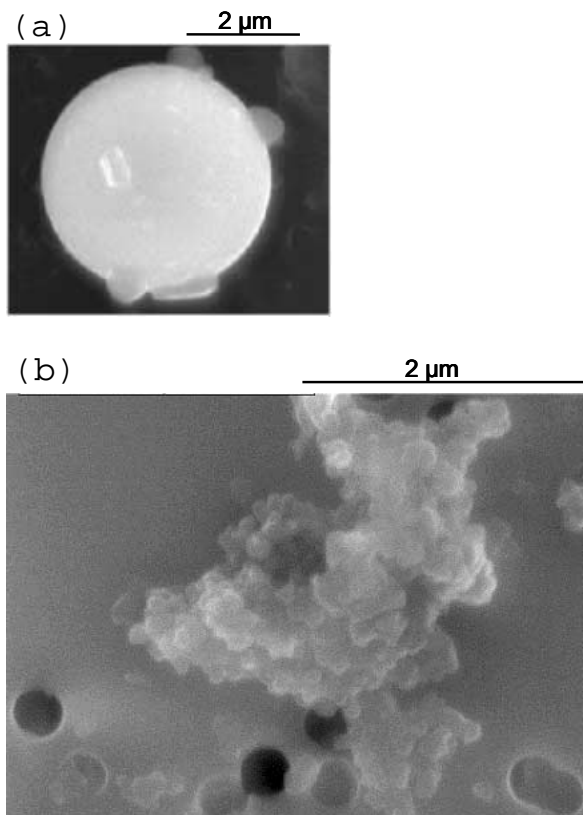


Fig. 6. Fly-ash from coal combustion **(a)** and carbonaceous soot particles **(b)** collected on $8\ \mu\text{m}$ and $0.4\ \mu\text{m}$ Nuclepore membranes respectively on 1 August 2001.

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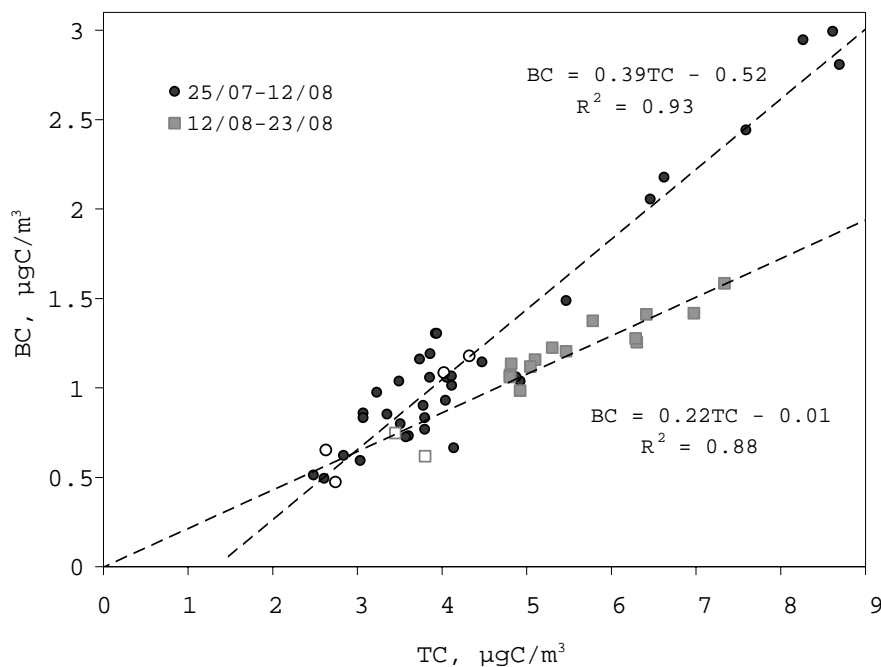


Fig. 7. BC (IMPROVE Temp program) versus TC concentrations for the 2 periods (25 July–12 August) and (12 August–23 August). Circles correspond to the first period, squares to the second. Open circles and open squares correspond to FT samples.

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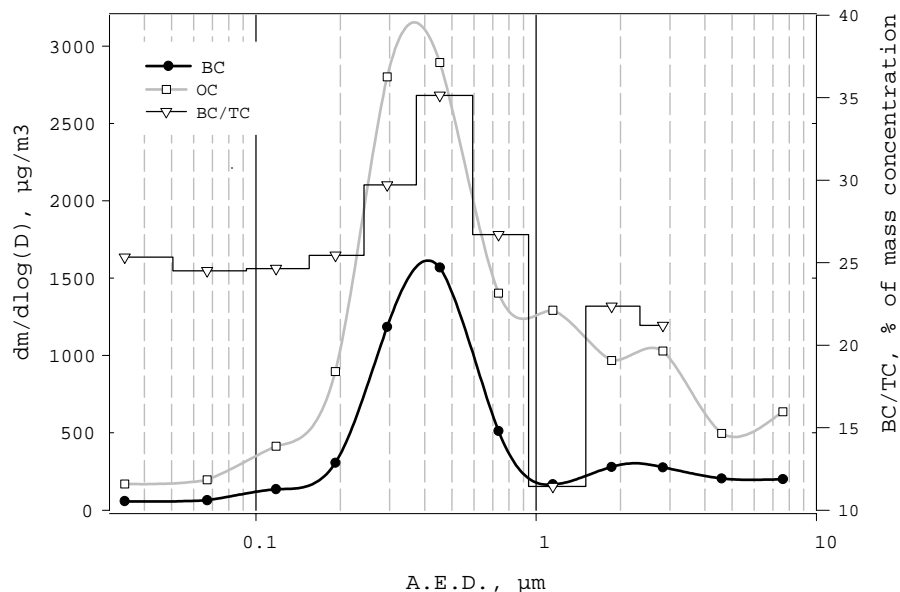


Fig. 8. Averaged mass size distribution of BC, OC and BC/TC ratio from the 2-step thermal method.

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