Aerosol light absorption and the role of extremely low volatility organic compounds

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Abstract

A month-long set of summertime measurements in a remote area in the Mediterranean is used to quantify aerosol absorption and the role of black and brown carbon. The suite of instruments included a high-resolution Aerosol Mass Spectrometer (HR-ToF-AMS), and a Scanning Mobility Particle Sizer (SMPS) both coupled to a thermodenuder and an aethalometer, a photoacoustic extinctiometer (PAX₄₀₅), a Multi-Angle Absorption Photometer (MAAP), and a Single Particle Soot Photometer (SP2).

The average refractory black carbon (rBC) concentration during the campaign was 0.14 μg m⁻³, representing 3% of the fine aerosol mass. The measured light absorption was two or more times higher than that of fresh black carbon (BC). Mie theory indicated that the absorption enhancement due to the coating of BC cores by non-refractory material could explain only part of this absorption enhancement. The role of brown carbon (BrC) and other non-BC light-absorbing material was then investigated. A good correlation (R²=0.65) between the unexplained absorption and the concentration of extremely low volatility organic compounds (ELVOCs) mass was found.

1. Introduction

Atmospheric aerosol may influence climate in two ways: directly through scattering and absorbing radiation, and indirectly through acting as cloud condensation nuclei (IPCC, 2011) Black carbon is the dominant light absorbing aerosol component. BC is a distinct type of carbonaceous material that is formed mainly during combustion processes. In addition, some
organic aerosol (OA) has the ability to absorb sunlight. The OA with strong light absorption is called brown carbon (BrC) (Andreae et al., 2006).

The absorption of BC depends on its mixing state (Liu et al., 2015, 2017). Usually, BC is coated with scattering material causing its light absorption to increase due to the lensing effect (Fuller et al., 1999; Jacobson, 2001; Bond et al., 2006; Lack and Cappa, 2010). The absorption enhancement \( E_{\text{abs}} \) is defined as the ratio of the aerosol absorption coefficient \( b_{\text{abs}} \) over the \( b_{\text{abs}} \) of the pure BC particles. This enhancement can also be calculated by the ratio of the equivalent mass absorption cross-sections (MAC). The MAC is defined as the ratio of \( b_{\text{abs}} \) over the BC mass.

The \( E_{\text{abs}} \) can be measured by using a thermodenuder (TD) for the removal of the non-refractory coating material from the BC containing particle, or it can be estimated using a theoretical model (for example Mie or Rayleigh-Debye-Gans theory) if the particle morphology is known. Incomplete removal of the non-refractory material in the TD can lead to underestimation of the \( E_{\text{abs}} \) (Healy et al., 2015; McMeeking et al., 2014).

Previous studies have demonstrated that lensing has a strong effect on the light absorption of BC. Liu et al. (2015) found a campaign average \( E_{\text{abs}} \) of 1.3 at wavelength \( \lambda \) equal to 405 nm and 1.4 at 781 nm in a rural area near London during the winter. They also suggested that the lower volatility BrC has stronger absorption than the semi-volatile BrC. Knox et al. (2009) performed measurements in downtown Toronto, during the wintertime using a TD at 340 °C. They reported an \( E_{\text{abs}} \) of 1.43 for fresh particles, based on thermal OC/EC and photoacoustic measurements. Liu et al. (2017) combined laboratory experiments with diesel exhaust emissions and ambient measurements to show that particles with a ratio of non-refractory PM to BC mass \( (R_{BC}) \) less than 1.5 (typical for traffic emissions) had a negligible lensing effect. When the \( R_{BC} \) was above 3, lensing caused significant enhancement of the absorption of BC. Zhang et al. (2018a) presented three years of measurements in a suburban cite outside Paris, France, influenced by both fresh and aged air masses. On average they found an \( E_{\text{abs}}=2.07 \) at 370 nm, and an \( E_{\text{abs}}=1.53 \) at 880 nm. They calculated the \( E_{\text{abs}} \) by measuring the absorption coefficient \( (b_{\text{abs}}) \) with an aethalometer, while the elemental carbon (EC) was measured with thermal methods using daily filters. Zhang et al. (2018b) presented measurements in Beijing, China during wintertime. Using aethalometer measurements, refractory and non-refractory particle size distributions and Mie theory, they calculated that the lensing effect led to an \( E_{\text{abs}} \) ranging from 1.5 to 2 on average at 880 nm. Zanatta et al. (2018) found an \( E_{\text{abs}}=1.54 \) at 550 nm for measurements at the Zeppelin Arctic Station. Lack et al. (2012)
analyzed measurements of biomass burning plumes near Boulder, CO during summertime. Using a TD at 200 °C, they found $E_{abs}$ values as large as 2.5 at 404 nm and 1.7 at 532 nm. Using the absorption Angström exponent (AAE) and Mie theory calculations they showed the presence of BrC.

Some studies have argued that Mie theory may overestimate the $E_{abs}$. Cappa et al. (2012) suggested that the absorption enhancement of BC in California in the summertime was low with values equal to 1.13 at 405 nm and 1.06 at 532 nm for $R_{BC}>10$. For their measurements they used a TD operated at 225 °C and 250 °C. Hearly et al. (2015) also reported practically no enhancement in the BC absorption at 781 nm and $E_{abs}=1.19$ at 405 nm in Toronto, Canada during summertime.

During a period associated with wildfires the same authors measured $R_{BC}=6.9$ and $E_{abs}=1.39$ at 405 nm. They argued that there was little evidence of the lensing effect, and that BrC was driving the $E_{abs}$. Cappa et al. (2019) performed measurements in Fresno, CA during wintertime and Fontana, CA during summertime. They found that in Fresno there was absorbing OA, BrC, which was related to biomass burning OA and nitrate-associated OA. In Fresno, they reported average $E_{abs}$ of 1.37, 1.22 and 1.1 at wavelengths equal to 405, 532, 781 nm, respectively, for $R_{BC}$ ranging from 1 to 4. In Fontana the $E_{abs}$ was lower with values of 1.1 at 405 nm and 1.07 at 532 nm.

Laboratory measurements of McMeeking et al. (2014) for biomass burning aerosol indicated higher absorption in lower wavelengths compared to higher ones and thus the presence of BrC. No enhancement of absorption was observed at $R_{BC}<1$. On average they found an $E_{abs}$ equal to 1.25 at 781 nm with a maximum value of $E_{abs}=4$ for $R_{BC}>10$.

Recent studies have suggested that the absorption efficiency of OA could be related to its volatility. Saleh et al. (2014) in their laboratory biomass burning experiments showed that almost all absorbing OA was associated with extremely low volatility compounds (ELVOCs), with an effective saturation concentration $C^*$ of $10^{-4}$ μg m$^{-3}$. In addition, Saleh et al. (2018) using controlled combustion experiments showed that the absorption activity of BrC is proportional to its molecular size.

Despite the significant progress in understanding the absorption of atmospheric fine aerosol there are still remaining questions regarding both the absorption enhancement of black carbon and the absorption of OA as the aerosol evolves in the atmosphere. In this study we try to address these issues for aerosol that has been aged in the atmosphere for at least a few days before arriving at the island of Crete in the Eastern Mediterranean.
2. Experimental Methods

A remote location in the Eastern Mediterranean was used for the study of the absorption and volatility of aged carbonaceous aerosol. The area is characterized by intense photochemistry, especially during the summer (Pikridas et al., 2010) and is affected by pollutants transferred from continental Europe, Turkey, Greece and Africa (Mihalopoulos et al., 1997; Lelieveld et al., 2002; Kalivitis et al., 2011; Bougiatioti et al., 2014). Previous measurements have shown that the OA reaching the area is highly oxidized regardless of its origin (Hidlebrandt et al., 2010, 2011). Lee et al. (2010) showed that these oxidized organic compounds have much lower volatility than fresh SOA. Long-term measurements in the region have revealed relatively high light absorption and scattering by aerosol during the summer (Kalivitis et al., 2011; Vrekoussis et al., 2005).

The FAME-16 field campaign took place from May 9 to June 2, 2016. Measurements were conducted at the Finokalia Station (35° 20’ N, 25° 40’ E, 250 m asl), a remote site on the island of Crete in Greece (Mihalopoulos et al., 1997). The nearest large city is Heraklion with 150,000 inhabitants located 50 km west of Finokalia (Kouvarakis et al., 2000). There are no local sources near the station, allowing the investigation of aged OA from different source regions. During this study, two Saharan dust events occurred from May 12 till May 15 and May 21 till May 22.

A Scanning Mobility Particle Sizer (SMPS, TSI classifier model 3080, CPC model 3775) was used to measure the number and the size distribution of the particles. The aerosol flow was set at 1 L min⁻¹ and the sheath flow at 5 L min⁻¹. The sampling time was 3 min.

The mass concentration and the chemical composition of the particles were monitored using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.). SQUIRREL 1.56D and PIKA v1.15D were used for the data analysis, while for the elemental ratio calculations the improved ambient calculation approach of Canagaratna et al. (2015) was used. The HR-ToF-AMS was operated in V-mode with a sample time of 3 min. The collection efficiency of the HR-ToF-AMS was calculated using the algorithm of Kostenidou et al. (2007). The average CE was 0.64±0.2. Positive matrix factorization (PMF) analysis (Lanz et al., 2007; Paatero and Tapper, 1994; Ulbrich et al., 2009) was performed using as input the high resolution OA mass spectra and the mass-to-charge ratios (m/z) from 12 to 200.

A Single Particle Soot Photometer (SP2, Droplet Measurement Technologies) was used to measure the BC. The instrument was calibrated using fullerene soot (Alfa Aesar, stock 40971, lot L20W054) (Gysel et al., 2011). The calibration of the SP2 was verified in separate experiments.

Preprint. Discussion started: 20 January 2020
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using a centrifugal particle mass analyzer (CPMA, Cambustion) (Saliba et al., 2016). The data were analyzed using the Probe Analysis Package for Igor. In our measurements, the number concentration of BC was low (<10,000 particles cm$^{-3}$), and thus it was assumed that there were no coincidence artifacts in our measurements. The scattering measurement was calibrated using monodisperse polystyrene latex (PSL) spheres.

A photoacoustic extinction meter (PAX, Droplet Measurement Techniques) with a blue (405 nm) laser was used to measure the absorption ($b_{abs}$) and the scattering ($b_{scat}$) coefficients. Fullerene soot and PSL spheres were used to calibrate the absorption and scattering signals, respectively. An activated carbon denuder was placed in front of the PAX to remove NO$_2$. Furthermore, a seven wavelength aethalometer (AE31, Magee Scientific) was used to measure the $b_{abs}$ at 370, 470, 520, 590, 660, 880 and 950 nm and to calculate the absorption Angstrom exponent (AAE), which describes the wavelength dependence of the $b_{abs}$. The aethalometer measurements were corrected for scattering and multiple scattering artifacts following Saleh et al. (2014) and Tasoglou et al. (2017) using the corrections suggested by Weingartner et al. (2003) and Kirchstetter and Novakov (2007).

The thermodenuder (TD) used in this study, was placed upstream of the HR-ToF-AMS and the SMPS. The TD design was similar to that developed by An et al. (2007) and is described by Louvaris et al. (2017). The TD was operated at temperatures ranging from 25 °C to 400 °C using several temperature steps. One complete cycle from 25 to 400 °C and back to 25 °C lasted approximately 10 h. Sampling was alternated between the ambient line and the TD line every 3 minutes using computer-controlled valves. Changes in particle mass concentration, composition, and size due to evaporation in the TD were measured by the HR-ToF-AMS and the SMPS resulting in thermograms of OA mass fraction remaining (MFR) as a function of TD temperature. The OA MFR was calculated as the ratio of organic mass concentration of a sample passing through the TD at time $t_i$ over the average mass concentration of the ambient samples that passed through the bypass line at times $t_{i-1}$ and $t_{i+1}$. The sample residence time in the centerline of the TD was 14 s at 25 °C, corresponding to an average residence time in the TD of 28 s. The MFR values were corrected for particle losses in the TD due to diffusion and thermophoresis. To account for these losses, sample flow rate as well as size- and temperature-dependent loss corrections were applied following Louvaris et al. (2017) corresponding to the operating conditions during the campaign. The final step of the data analysis was to average the corrected for CE and TD losses MFR data.
based on temperature bins of 10°C. The MFR calculation assumes implicitly that the OA concentration remains constant during the measurement period. To ensure that this condition is satisfied, if two consecutive OA ambient mass concentrations differed by more than 25%, the corresponding MFR was not included in the analysis. Also, in order to ensure that the temperature was constant during the measurement, the absolute difference between the two samples had to be less than 5°C. If this difference for a TD sample was higher, then the sample was not included in our analysis. The same approach was used also for the factors resulting from the PMF analysis of the AMS spectra. However, in this case a minimum concentration threshold of 0.1 μg m\(^{-3}\) was used for the ambient concentrations together with the criterion of the stability of the ambient concentrations during the sampling period. MFR values corresponding to concentrations of the PMF factors below this threshold were not included in the dataset. Approximately 75% of the OA samples satisfied all these constraints and were used in the analysis. The corresponding percentages were 65% and 70% for the two identified PMF factors. In the present work the complete datasets will be analyzed together, averaging the corresponding measurements. More details regarding the data analysis and the sensitivity tests of the TD measurements are provided in the supplementary information.

The concentrations of gas-phase pollutants were measured using a Proton-Transfer Reaction Mass Spectrometer (PTR-QMS 500, Ionicon Analytik) and gas monitors. The PTR-MS was calibrated with a standard gas mixture of VOCs. The concentration of O\(_3\) was measured using a continuous O\(_3\) analyzer (Thermo Scientific, 49i) and the concentrations of nitrogen oxides were measured using a NO/NO\(_2\)/NO\(_x\) analyzer (Thermo Scientific, 42i-TL).

3. Theoretical Analysis Methods

The dynamic TD evaporation model of Riipinen et al. (2010) together with the uncertainty estimation algorithm of Karnezi et al. (2014) were used for the determination of the OA volatility distribution. Inputs for the model included the ambient OA concentration, the OA density calculated by the algorithm proposed by Kosteniou et al. (2007), the initial average particle size, TD temperature, the MFR values, and TD residence time. In the volatility basis set framework of Donahue et al. (2006), the volatility distribution is represented with a range of logarithmically spaced C\(^*\) bins along a volatility axis. In this study 6 bins with variable mass fractions were chosen. For this 6-bin solution, the best 2% of the mass fraction combinations with the lowest error were
used to estimate the average mass fraction along with their corresponding standard deviation for
the uncertainty of each bin. Additionally the parameters that affect indirectly the calculated
volatility such as the effective vaporization enthalpy ($\Delta H_{vap}$), and the effective accommodation
coefficient ($a_m$) were estimated following Karnezi et al. (2014). Additional information regarding
the data analysis of the TD measurements are in the supplemental information (sections S1 and
S2).

A Mie theory model based on the work of Bohren and Huffman (1983) was used to
calculate the theoretical MAC and $E_{abs}$. Mie theory describes the extinction of light by spherical
particles due to an incoming planar electromagnetic wave. The calculations were based on the
SMPS and SP2 size distributions. For the BC core we assumed a refractive index of the core
$n_{BC}=1.85+0.71i$ (Bond and Bergstrom, 2006) and a density of 1.8 g cm$^{-3}$ (Mullins and Williams,
1987; Park et al., 2004; Wu et al., 1997). A non-absorbing coating of the BC core was assumed,
with a refractive index of $n_{OA} = 1.55$ (Bond and Bergstrom, 2006). The total aerosol effective
density used was calculated based on the SMPS and HR-ToF-AMS distributions. The average
effective density for the campaign was 1.66±0.11 g cm$^{-3}$. The other inputs of the model were the
measured BC size distributions from the SP2 and the ratio of the total aerosol mass over the BC
mass as measured by the SMPS and the SP2, respectively.

4. Results and discussion

The average rBC concentration of the campaign was 0.14 µg m$^{-3}$ and the average OA
concentration was 1.5 µg m$^{-3}$ (Figure 1). The two major Saharan dust events affected, as expected,
the aerosol optical properties. In the present study we focus only on the non-dust periods. The
dominant PM$_1$ components were sulfate and OA, accounting for 46% and 34% of the PM$_1$,
respectively. The O:C ranged from 0.65 to 1, with an average value of 0.83. These values are
typical in Finokalia during the spring and summer periods (Hidlebrandt et al., 2010).

4.1 OA Volatility

The estimated volatility distribution for the total OA in Finokalia during FAME-16 is
depicted in Figure 2. Use of OA with $C^* = 10^{-8}$ µg m$^{-3}$ was needed to capture the behavior of the
OA at 400 ºC. Almost 40% of the OA consisted of semi-volatile organic compounds (SVOCs),
35% of low volatility organic compounds (LVOCs), and the rest was extremely low volatility organic compounds (ELVOCs).

The estimated value of the effective vaporization enthalpy was $80 \pm 20 \text{ kJ mol}^{-1}$. This value was in agreement with the reported value by Lee et al. (2010) of $80 \text{ kJ mol}^{-1}$ for the FAME-08 campaign. The estimated accommodation coefficient was 0.27, ranging from 0.1 to 0.8. This value was a little higher than the 0.05 value reported in the earlier study. However, both suggest only moderate resistances to mass transfer during the evaporation in the TD.

The corresponding measured and predicted thermograms are depicted in Figure 3. Almost 30% of the OA had not evaporated even after heating at 400 °C. The temperature at which half of the OA evaporated was $T_{50}=120 \, ^\circ\text{C}$, a value similar to that observed by Lee et al. (2010). The composition of the OA leaving the TD changed significantly as temperature increased according to the model. At 125 °C the LVOCs and ELVOCs contributed equally to the remaining OA mass. For further temperature increases the LVOC fraction was reduced until 375 °C, at which point only the ELVOCs remained.

PMF analysis resulted in a two-factor solution (Florou et al., in prep.). Factor 1 corresponded to more oxidized oxygenated OA (MO-OOA) and Factor 2 to a less oxidized component (LO-OOA). The average contribution of the two factors was 47% for the MO-OOA and 53% for the LO-OOA. The O:C for the MO-OOA was 0.95 (OS$_C$ = 0.59) and for the LO-OOA it was 0.56 (OS$_C$ = -0.27). The Finokalia area is characterized by the absence of local sources and as result the absence of fresh OA. The OA during FAME-08, was also found to consist entirely of OOA with no primary OA present (Hildebrandt et al., 2010). POA evaporates and gets oxidized rapidly in the photochemically active environment of the Eastern Mediterranean during its transport from its sources to this remote site.

The volatility distributions of the two PMF factors were estimated following the same approach as that for the total OA. The measured thermograms for the two PMF factors are shown in Figure 4. Almost 50% of both the MO-OOA and the LO-OOA evaporated at 150 °C. Almost 30% of the MO-OOA mass, and about 20% of the LO-OOA did not evaporate even at temperatures as high as 400°C. The model reproduced the observed MFR values for both factors. Both factors contained components with a wide volatility range. The MO-OOA exhibited a bimodal volatility distribution with peaks at effective saturation concentrations of $10^{-8}$ and 10 μg m$^{-3}$. Its effective enthalpy of vaporization was approximately $90 \pm 35 \text{ kJ mol}^{-1}$ and its accommodation coefficient...
was 0.27. The estimated volatility distribution of the LO-OOA was a little more uniform peaking
at an effective saturation concentration of 1 μg m\(^{-3}\). The calculated average volatility of LO-OOA
was 0.016 μg m\(^{-3}\), an order of magnitude higher than that of the MO-OOA. The LO-OOA enthalpy
of vaporization was 70 ± 20 kJ mol\(^{-1}\), 20 kJ mol\(^{-1}\) lower than that of the MO-OOA. Its
accommodation coefficient was approximately 0.1 indicating small mass transfer resistances. MO-
OOA consisted of approximately 40% SVOCs, 30% LVOCs, and 30% ELVOCs. On the contrary,
LO-OOA consisted of almost 45% SVOCs, 40% LVOCs and only 15% ELVOCs.

The fitting of the individual factor thermograms implicitly assumes that each factor had the
same size distribution as the total OA and also that the two factors were externally mixed. The
uncertainty introduced by these two assumptions was implicitly evaluated comparing the estimated
total OA of volatility distribution with the composition-weighted average of the volatility
distributions of the two OA factors. The two distributions agreed within a few percent for \(10^{-3} < C^* < 10^0\) and within 10% for the lowest and highest volatility bins.

4.2 Aerosol optical properties

The measured \(b_{\text{scat}}\) at 405 nm ranged from 11.5 to 47 Mm\(^{-1}\) with an average campaign value
of 26.5 Mm\(^{-1}\) (Figure 5). Similarly, \(b_{\text{abs}}\) at 405 nm ranged from 0.64 to 5.6 Mm\(^{-1}\) with an average
value of 2.1 Mm\(^{-1}\).

Acetonitrile is a known biomass burning marker and can help identify the potential
influence of the site by biomass burning events or wildfires during the campaign. The acetonitrile
concentration measured by the PTR-MS remained close to 0.4 ppb during the campaign, which is
the local background level. This together with the low BC levels indicate that the site was not
impacted by nearby biomass burning during the study.

The \(b_{\text{abs},405}\) variation followed that of the rBC (R\(^2\)=0.74 for the hourly averages). The ratio
of the \(b_{\text{abs},405}\) over the rBC, MAC\(_{405}\), was equal to 16.3±4.2 m\(^2\) g\(^{-1}\). Previous studies have shown
that freshly generated BC has a MAC\(_{532}\) of 7.5 m\(^2\) g\(^{-1}\) (Clarke et al., 2004; Bond and
Bergstrom, 2006). Using the definition of the AAE,

\[
\text{AAE} = -\frac{\ln[\text{MAC}_{405}/\text{MAC}_{532}]}{\ln[405/532]},
\]

we can calculate the MAC of freshly generated BC 405 nm. Assuming that the AAE is equal to
unity for BC particles, we find that the MAC\(_{405}\) of BC was approximately 9.9 m\(^2\) g\(^{-1}\). The difference
between the measured and the theoretical value of MAC$_{405}$ can be due to the coating of BC by other PM components (lensing effect) and/or the existence of other absorbing material. This will be explored below.

The campaign average AAE of PM for wavelengths ranging from 370 to 950 nm was 0.97±0.22. The AAE of coated BC cores can deviate from the typical AAE=1 with values greater or lower than unity (Gyawali et al., 2009). In addition, Lack and Cappa (2010) suggested that an AAE>1.6 should confirm the presence of non-BC absorbing material, however an AAE<1.6 does not exclude its presence.

Mie theory calculations were performed in order to estimate the MAC$_{405}$ and the $E_{\text{abs}}$ due to the lensing effect of the shell covering the BC core. Initially, a non-absorbing shell was assumed. The predicted MAC$_{405}$ had an average value of 14.1 m$^2$ g$^{-1}$. The average $E_{\text{abs}}$ due to lensing effect was 2.07. The average predicted MAC$_{405}$ was 13% lower than the measured suggesting the existence of non-refractory absorbing material (Figure 6).

In the next step, the Mie theory calculations were repeated assuming an absorbing shell with a refractive index of $n_{\text{OA}} = 1.55 + ki$, where the imaginary part, $k$, was allowed to vary from 0 to 0.4. This range of $k$ values was selected based on previous literature (Kirchstetter et al., 2004; Alexander et al., 2008; Chakrabarty et al., 2010; Chen and Bond, 2010; Saleh et al., 2014; Chakrabarty et al., 2016, Li et al., 2016; Saleh et al., 2018). One third of the resulting $k$ values during the campaign were zero, suggesting a non-absorbing shell, while the other two thirds were positive. More specifically, 22% of the estimated $k$ values ranged from 0.01 to 0.1, 22% from 0.11 to 0.2, 19% from 0.21 to 0.3, and 4% of the $k$ values ranged from 0.31 to 0.4.

### 4.3 The role of ELVOCs

The hypothesis that the presence of ELVOCs could explain the higher aerosol light absorption was tested. The unexplained MAC ($\Delta$MAC) difference of measured and predicted values was compared with the total ELVOC mass concentration. The ELVOC concentration was estimated based on the results on the volatility analysis of the two PMF factors:

$$\text{[ELVOC]} = 0.15 \text{[LO-OOA]} + 0.3 \text{[MO-OOA]}$$

The least-squares fit between the 3-hour averaged $\Delta$MAC and ELVOC had $R^2$=0.65 (Figure 7). This result suggests that the ELVOCs were probably contributing to the total absorption and could explain the difference in the MAC.
5. Conclusions

A month-long campaign was conducted at a remote site, in Finokalia, Crete during May of 2016. The dominant PM$_1$ components were sulfate and aged organics with O/C=0.81. The average ambient OA concentration was 1.5 µg m$^{-3}$ and the rBC was 0.14 µg m$^{-3}$. Continuous monitoring of biomass burning markers revealed that there was no detectable impact of wildfires on the site during the campaign. PMF analysis resulted in two secondary OA factors: one more oxidized (MO-OOA) and one less oxidized (LO-OOA). Total OA consisted on average of 40% SVOCs, 35% LVOCs and 25% ELVOCs. Both OA components with a wide range of volatilities.

Approximately 30% of the MO-OOA was ELVOCs, 30% LVOCs and 40% semi-volatile material. The LO-OOA was more volatile on average with 40% consisting of LVOCs and 45% of SVOCs and 15% of ELVOCs.

Aerosol optical properties were measured. The average $b_{\text{scat}}$ at 405 nm was 26.5 Mm$^{-1}$ and the average $b_{\text{abs}}$ at 405 nm was 2.1 Mm$^{-1}$. Furthermore, the average AAE was 0.97 and the MAC$_{405}$ was 16.3. Mie theory calculations were able to reproduce one third of the measured MAC$_{405}$ values assuming core-shell morphology and a non-absorbing shell ($k=0$). We estimated that the non-absorbing shell was causing an enhancement of the absorption by a factor of 2.07. For the other two thirds of the measurements the presence of an absorbing shell with an average $k$ of 0.21 was needed to explain the measurements.

The ELVOCs mass concentration was estimated using the volatility distributions of the two factors. The ELVOC concentration was highly correlated ($R^2=0.65$) with the difference of the unexplained MAC$_{405}$, defined as the difference of the measured MAC$_{405}$ the measured and the one predicted by Mie theory for $k=0$.

Data availability. The data in the study are available from the authors upon request (spyros@chemeng.upatras.gr).

Author contributions. AT conducted the absorption measurements, analysed the results and wrote the paper. EL performed the thermodenuder measurements and analysed the results. KF performed the AMS measurements and analysed the results. AL performed the PTR-MS measurements and analysis. EK was responsible for the OA volatility analysis. CK coordinated the field campaign and assisted with all measurements. NW assisted with all measurements SNP was responsible for
the design and coordination of the study and the synthesis of the results. All co-authors contributed to the writing of the manuscript.

**Competing interests.** The authors declare that they have no conflict of interest.

**Acknowledgements**

This work was supported by U.S. Environmental Protection Agency STAR program [grant number R835035]. Travel support was provided by the European Research Infrastructure ACTRIS. The authors would like to thank the Finokalia station personnel for the accommodation and for providing the aethalometer measurements.

**References**


Figure 1: Evolution of the aerosol chemical composition based on the HR-TOF-AMS and SP2 measurements during FAME-16: a) the non-refractory aerosol components; b) rBC concentration. The shaded areas represent the dust events periods.
Figure 2: (a) Total OA volatility distribution along with its uncertainty estimated by the Karnezi et al. (2014) approach. The error bars represent the corresponding variability (± 1 standard deviation). (b) OA composition. Magenta color represents the ELVOCs, red the LVOCs, and white the SVOCs.
Figure 3: (a) Average loss-corrected total OA thermograms. Red circles represent the measured total OA MFR and the error bars the corresponding variability (±2 standard deviations of the mean). The solid lines are the model predictions (b) Mass fraction of the total OA for different effective saturation surrogate species with concentrations as a function of TD temperature. Yellow color represents the contribution of the effective saturation concentration \(C^* = 10^{-8}\) μg m\(^{-3}\), red the contribution of the \(C^* = 10^{-3}\) μg m\(^{-3}\), green the \(C^* = 10^{-2}\) μg m\(^{-3}\), blue the \(C^* = 10^{-1}\) μg m\(^{-3}\), cyan the \(C^* = 10^{0}\) μg m\(^{-3}\), and magenta the \(C^* = 10\) μg m\(^{-3}\).
Figure 4: (a) Estimated volatility distribution of the MO-OOA factor along with its corresponding uncertainties by using the approach of Karnezi et al. (2014). (b) Estimated volatility distribution of the LO-OOA factor along with its corresponding uncertainties. (c) Measured (in circles) and predicted thermograms for the LO-OOA factor. The error bars represent ± 2 standard deviations of the mean. (d) Measured (in circles) and predicted thermograms for the LO-OOA factor. The error bars represent ± 2 standard deviations of the mean.
Figure 5: The timeseries of the aerosol optical properties at $\lambda=405$ nm. The black squares represent the absorption coefficient, $b_{abs}$, while the red circles represent the scattering coefficient, $b_{scat}$. The shaded areas represent the dust events periods.
**Figure 6:** Results from the Mie theory calculations, assuming a non-absorbing shell ($k=0$): a) predicted (blue circles) and measured $\text{MAC}_{405}$ (red circles). b) Predicted $E_{\text{abs}}$ values. The shaded areas represent the dust events periods.
Figure 7: Difference between the measured and the predicted MAC405 as a function of the estimated concentration of the ELVOCs.