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Determination of OM/OC ratios and specific attenuation coefficients (SAC) in ambient fine PM at a rural site in southern Ontario: implications for emission sources, particle aging, and radiative forcing

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Abstract

Ambient particulate matter (PM) samples were collected on quartz filters at a rural site in southern Ontario during intensive studies in 2005 and 2007. The concentrations of organic carbon (OC), pyrolysis organic carbon (POC), and elemental carbon (EC) were determined by thermal analysis. These results were compared to the organic aerosol mass concentration (OM) measured by an Aerodyne Aerosol Mass Spectrometer (AMS) and to the particle absorption coefficient (b_{asp}) obtained from a Radiance Research Particle Soot Absorption Photometer (PSAP). The total organic mass to organic carbon ratios (OM/OC) and specific attenuation coefficients (SAC) were also derived. According to the results, the POC mass is proportional to the approximated oxygen mass in the aerosols and OM/OC ratios can be estimated directly from thermal measurements. The study also suggests that the air masses from the south, with relatively low OC/EC ratios, high EC, sulphate contents and OM/OC ratios, were originated from urban and industrial emissions and subsequently experienced photo-oxidations in the atmosphere, implying that the oxygenated organics could come from both primary and secondary sources. Whereas the air masses from the north, with relatively high OC/EC ratios, low EC, sulphate contents and OM/OC ratios, were dominant by the background clean air with relatively larger contributions from biogenic emissions.

The mean SAC derived from the 2005 and 2007 studies are $4.9\,m^2\,g^{-1}$ and $3.8\,m^2\,g^{-1}$, respectively. When POC mass approaching zero (i.e. the impact of atmospheric aging is minimized), the SAC for primary emitted soot is estimated to be $5.8\,m^2\,g^{-1}$ and $6.3\,m^2\,g^{-1}$ for the northern and southern air masses, respectively, supported by the corresponding values when particulate sulphate concentration approaches zero. A decreasing trend in the SAC value with atmospheric aging of the aerosol was observed at the site, suggesting that during the study, the light absorption enhancement due to the presence of coating on particles was likely to be offset by the decrease in light absorption caused by increasing soot particle diameter and collapsing of soot particle structure. This result may imply that model simulations of atmospheric

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warming by BC could be 50% too high.

1 Introduction

Carbonaceous species, consisting of organic carbon (OC) and elemental carbon (EC), make up a large fraction of the fine atmospheric particulate mass in urban, rural, marine, and forest environments (Hildemann et al., 1996; Novakov et al., 1997; Middlebrook et al., 1998; Shantz et al., 2004; Alves et al., 2006). These species influence air quality, human health, and climate change (Japar et al., 1986; Dockery et al., 1992; Novakov and Penner, 1993; Cheng and Tsai, 2000; Satheesh and Moorthy, 2005; Viana et al., 2008). OC is formed via various mechanisms, including direct organic particulate emissions (e.g. fossil fuel combustions, biomass burning, biogenic emissions), condensation of the low-volatility primary emitted organic gases, and secondary organic aerosol (SOA) formation via photo-chemical oxidation of precursor volatile organic compounds (VOCs) (Kroll and Seinfeld, 2008; Robinson et al., 2007; Cabada et al., 2002). SOA could be formed from both anthropogenic and biogenic origins because VOCs come from various biogenic and anthropogenic sources (Seinfeld and Pandis, 1998). Important biogenic VOCs include isoprene, monoterpenes, and sesquiterpenes from vegetation (Pio et al., 2001; Kavouras et al., 1998; Fehsenfeld et al., 1992), while the major anthropogenic VOCs include various aromatics, alkanes, alkenes, and carbonyls from vehicle emissions (Volkamer et al., 2006; Fraser et al., 1998; Kawamura and Kaplan, 1987). VOCs are oxidized in the atmosphere primarily by hydroxyl radical (OH), ozone (O_3), and the nitrate radical (NO_3), leading to low-volatility products that may nucleate new particles (Laaksonen et al., 2008; Hoffmann et al., 1998) or deposit onto pre-existing particles through gas-to-particle partitioning (Alfarra et al., 2006; Odum et al., 1996). On the other hand, EC comes dominantly from direct emissions (i.e. primary sources) due to incomplete combustions at sources (Horvath, 1993).

Various thermal and thermal/optical techniques have been used to analyse OC and EC from quartz filter measurements (e.g. Cachier et al., 1989a, b; Huntzicker et al.,

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1982; Chow et al., 1993, 2001; Turpin et al., 1990; Huang et al., 2006). Classifications of the OC and EC in the different techniques are subject to the corresponding operating conditions, and therefore, the OC/EC classification is operationally defined (Chow et al., 1993, 2001). A complicating factor in distinguishing OC and EC is the formation of charred organic carbon during the thermal separation procedure. Pyrolysis organic carbon (POC), also referred to as charred OC, is the thermo-decomposed organic matter formed at relatively low temperature (e.g. <550°C) under pure helium environment. Charred OC has similar morphological features as the source OC and decomposes easier than EC (Han et al., 2007). The amount of charring depends on many factors, such as the nature of OC, the amount of oxygenated compounds, heating temperature, heating periods, and the supply of oxygen (Gelencsér, 2004; Cachier et al., 1989a, b).

OM/OC is defined as the total organic matter mass concentration ($\mu g\,m^{-3}$) per unit organic carbon mass ($\mu gC\,m^{-3}$). As atmospheric oxidation processes increase OM/OC ratios, the value of OM/OC has been generally used as an estimate of particle chemical aging (de Gouw et al., 2005; Aiken et al., 2008). The determination of the OM/OC ratio for ambient aerosol particles is subject to many factors, especially the analytical method (Turpin and Lim, 2001). The factor of 1.4 was first determined by White and Roberts (1977) using the data from Grosjean and Friendlander (1975). Turpin and Lim (2001) re-calculated the OM/OC ratio for several published studies and suggested the use of values of 1.6 and 2.1 for OM/OC for urban and rural sites, respectively. Russell (2003) used FTIR spectroscopy to estimate OC for computing OM/OC and found that 90% of the results were within the range from 1.2 to 1.6, with an average of 1.4. El-Zanan et al. (2005) estimated OM and OC in solvent extracts from archived IMPROVE filter samples for US national parks and found that OM/OC ranged from 1.6 to 2.1 with an average of 1.9. Applying the mass balance method to the same samples, El-Zanan et al. (2005) estimated the value of OM/OC to vary between 1.5 and 2.2. Bae et al. (2006) applied a reconstructed mass balance technique to 3-year measurements at two measurement sites and found that the value of OM/OC ranged from 1.5 to 1.9 at the rural site and from 1.3 to 1.6 at the urban site, with the rural results exhibiting a

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discernable seasonal pattern. Zhang et al. (2005a) applied a de-convolution technique to AMS mass spectra measured in Pittsburgh (Zhang et al., 2005b) to extract the mass spectra for oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA). Based on the *m/z* ratios in the individual spectra, the relative contributions from different elemental compositions were determined and the relative C:H:O ratio in OOA and C:H ratio in HOA were estimated. Using those results, the mean value of OM/OC was estimated to be about 1.8. Aiken et al. (2008) used the high resolution Time-of-Flight (HR-ToF) AMS to measure the ambient aerosols in Mexico City over a period of 6 days; the averaged value of OM/OC was 1.71, ranging from 1.41 to 2.15. The study showed observation of higher OM/OC during afternoon as well as downwind from the city due to increased photo-chemistry in the atmosphere.

The specific attenuation coefficient (SAC) is used to convert light absorption measurements (m^{-1}) to equivalent black carbon mass ($g\,m^{-3}$) based on a linear relationship between the two quantities (Jennings and Pinnick, 1980; Japar et al., 1986). The SAC is derived via dividing the light absorption coefficient by the elemental carbon mass concentration, where the latter is measured by a thermal or thermal/optical method. Values of SAC determined from measurements with Aethalometers and with Particle Soot Absorption Photometers (PSAP) measurements have varied from 2 to 55 $m^2\,g^{-1}$ (Liousse et al., 1993; Snyder and Schauer, 2007). Most of the variations in SAC are caused by variations in the properties of the particles, such as chemical composition and/or source, size distribution, shape, refractive index of the aerosol particles, the degree of aerosol aging, and the presence of a less absorbing component in the particles (Bond and Bergstrom, 2006; Bond et al., 2006; Liousse et al., 1993). As a result, sites associated with different chemistry and/or atmospheric processes are likely to have different values of SAC (Liousse et al., 1993; Sharma et al., 2002). Other factors that affect the SAC measurements are the thickness of the filter used in an optical instrument to measure the light absorption (a thicker filter allows particles to become more deeply embedded in the filter matrix) (Snyder and Schauer, 2007) and how EC is defined in the thermal or thermal/optical method.

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Oxygenated organics produced during particle aging alter OM/OC and the light scattering by the particles, thus affecting light absorption also. Based on laboratory studies, the amount of POC, defined as the carbon obtained via a thermal method from 550°C to 870°C under pure helium, is generally proportional to the amount of oxygenated organic carbon in the aerosol particles (Huang et al., 2006). Therefore, studying the relationships of OC/EC, OM/OC, and SAC with POC in ambient conditions provides valuable insight into emission sources, particle aging and possible impact on radiative forcing.

This paper reports measurements from two intensive campaigns at a rural site near Toronto, Ontario. OC, EC, and POC from quartz filters were determined using the thermal method described in Sect. 2.2.1. These measurements were then combined with measurements of OM derived from a C-ToF Aerodyne Aerosol Mass Spectrometer (C-ToF-AMS) and of the particle light absorption coefficient (b_{asp}) measured with a PSAP to estimate OM/OC and SAC. Because the sampling location is influenced both by urban-dominated southern air masses and clean/biogenic northern air masses, this provides an excellent opportunity to study the variations of the OM/OC and SAC for the diverse air masses influenced by different emission sources. In particular, the main objectives of this paper are: 1) to characterize chemical and optical contents of carbonaceous PM via major emission sources, based on prevailing wind directions; 2) to understand the relationship between POC and the degree of oxygenation/aging of the aerosol particles to estimate OM/OC ratios directly from thermal measurements; 3) to examine the influence of POC and sulphate as the impact of aerosol aging on the SAC to estimate the value of SAC for primary emitted soot particles.

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2 Sampling

2.1 Measurement location

Two 1-month intensive field studies were conducted at Egbert, Ontario, in the Center for Atmospheric Research Experiments (CARE) of Environment Canada (44°12′ N, 79°48′ W, 251 m a.s.l.) during the fall of 2005 and the late spring of 2007. CARE is located in an agricultural area, about 70 km north of the city of Toronto. Air that reaches the site from regions of the south contains anthropogenic pollutants originating from the urban and industrial areas of southern Ontario and the northeastern United States (Rupakheti et al., 2005; Chan and Mozurkewich, 2007). In comparison, air from the north is relatively clean, except when the air passes through Sudbury, Ontario (a significant source of SO_2 from metal refineries). During this study, SOA formation from terpenes emitted from forests north of the site contributed significantly to the aerosol mass (Slowik et al., 2009). Contributions from biogenic aerosols in the southern air masses are difficult to distinguish from the relatively large anthropogenic signature.

2.2 Sample collections and measurement methods

2.2.1 Integrated quartz filter measurements

Weekly and daily suspended particulate matter samples were collected on 47 mm prefired quartz filters during the fall of 2005 and spring of 2007 for OC/EC analysis. Ambient air was sampled through a 1.9 cm stainless steel tubing with an inverted U-shaped inlet located about 10 m above ground. A cyclone was installed in the inlet and surrounded by metal shielding to prevent rain drops or snow from entering the inlet line. The 2005 study last from 17 October to 21 November and the weekly samples were sampled through a 2.5 μm cyclone with a nominal flow of 16.7 L min^{-1}. The 2007 study last from 15 May to 15 June and the daily samples were sampled through a 1.0 μm cyclone with a nominal flow of 31.0 L min^{-1}. For both campaigns, blank filters were

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taken during sample collection. All filters were stored in freezers (<−20°C) and analyzed after the field study. The OC, POC, and EC were measured by a thermal optical transmittance (TOT) OC/EC analyzer, manufactured by Sunset Lab (www.sunlab.com). The thermal separation protocol developed by Huang et al. (2006) was used for the analysis. This thermal separation method (also called as "Total-900-EnCan" method) was originally developed for OC/EC isotope measurements and therefore has longer retention times for different carbon fractions to ensure good baseline separation.

During the analysis using Total-900-EnCan method, a 1.5 cm^2 punch of the quartz filter is placed on a quartz boat that sits inside the TOT analyzer. Then, stepwise heating (from room temperature to 900°C) is applied to the filter to separate different OC and EC fractions. Most of the low molecular weight non-refractory organic carbon (OC) masses are released at temperatures up to 550°C under an oxygen-free and VOC-free He flow. In the second stage, the temperature is increased to 870°C to release carbonate carbon (CC) and the pyrolysis organic carbon (POC). The term POC is used here to refer to the carbon mass released from 550°C to 870°C without oxygen. The POC includes the charred OC formed during the first thermal stage (550°C) and the refractory OC (including both oxygenated and non-oxygenated) that possess relatively high bonding energy and could not be released completely at temperatures up to 550°C. The POC mass is proportional to the amount of oxygenated OC based on laboratory studies (Huang et al., 2006). Isotope measurements are required to distinguish between CC and POC during the second stage. Previous isotopic measurements from filter samples collected at Egbert showed insignificant amount of CC, indicating minimum impacts from soil dust and sea-salt aerosols (main sources of CC), and the carbon fraction released during the second stage (550–870°C) was dominated by POC (Huang et al., unpublished isotope data); negligible amount of CC is to be assumed for the measurements from the two studies. At the final stage (i.e. the third stage), all the elemental carbon is released at 900°C with the supply of oxygen (10% O_2 with 90% He). In this thermal technique, EC is separated from POC due to the greater resistance to thermal pyrolysis, relative to the latter. The released CO_2 from each stage is reduced

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to CH_4 inside the methanator in the presence of Ni and H_2, and finally measured by a flame ionization detector (FID). The retention time used in each step can be found in Huang et al. (2006). For both studies, a constant OC blank correction, obtained as the average value of all blank filters taken during individual field study, was applied to all sample filters in the corresponding study. The OC values for all samples after the blank correction are more than twice of the standard deviation of all the blank filters.

2.2.2 Continuous measurements

During the 2005 study, a quadrupole Aerodyne Aerosol Mass Spectrometer (Q-AMS) was used to make 5-min continuous mass measurements of particulate OM, sulphate (pSO_4^{2-}), and nitrate (pNO_3^-); the 2005 study has also been discussed by Chang et al. (2007). During the 2007 study, a C-ToF-AMS was used to make measurements of the same quantities. A short description of the AMS is given below, but details on the design and operation of the AMS can be found elsewhere (e.g. Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2003; Drewnick et al., 2005). Inside the AMS, aerosol particles are focused into a narrow beam in an aerodynamic lens and accelerated to a velocity dependent on their vacuum aerodynamic diameter. The particles impact on a resistively heated surface (~600°C), where the volatile and semi-volatile components associated with the particle vaporize. The vapour is ionized by electron impact and the positive ions are analyzed using standard mass spectrometry. The AMS was operated under common modes switching between measurements of total mass (which ignores the particle sizing) and the time-of-flight mode (that produces size-dependent mass concentrations). The AMS transmission efficiency (TE) is close to 100% for particles from about 100–700 nm vacuum aerodynamic diameter (Liu et al., 2007). The intake point for the sampling was located about 6 m above ground, and the ambient aerosol particles were continuously pulled down through a 1.9 cm OD stainless steel tube at a flow rate of approximately 25 L min^{-1}.

Some of the particles that impact the heated surface inside the AMS may bounce, resulting in a lower particle collection efficiency (CE). Some measurements have shown

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that the CE with the Q-AMS is reduced only in situations for which ammonium sulphate represents a larger fraction (>50%) of the fine particle aerosol. In the 2005 study, the CE of the Q-AMS was assumed to be unity; this assumption was found to be the case in several studies during which the same AMS was deployed (Leaitch et al., 2008; Phinney et al., 2006; Buset et al., 2006; Rupakheti et al., 2005). The CE of the C-ToF-AMS during the 2007 sampling period was obtained from a comparison between the AMS and Scanning Mobility Particle Sizer (SMPS) measurements (Slowik et al., 2009); this CE was averaged to the same filter sampling period and applied individually to different filter samples.

A Radiance Research Particle Soot Absorption Photometer (PSAP) was used to measure the light absorption coefficient of the ambient particles. The PSAP provides a measurement of particle absorption by monitoring the change in the amount of light transmitted through a quartz filter as the particles are being deposited onto the filter. Using Beer Lamberts law, the light absorption coefficient of the sampled aerosol is estimated from the rate of decrease in light transmission through the filter, the sample flow rate, and the filter deposition area (e.g. Bond et al., 1999). The original PSAP data for both studies are in 1-min resolution. After removing occasional outliers and data periods during which the transmittance falls below 50%, the in-situ data were converted to hourly averages, and then integrated to the same sampling interval as the filter measurements. All the absorption coefficient measurements are corrected for filter sampling size and flows. Details of the operation and calibration of a PSAP can be found elsewhere (e.g. Bond et al., 1999; Sharma et al., 2002).

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3 Results and discussion

3.1 Characterization of carbonaceous species

Figure 1 shows the variations of OC, OC_{tot} (i.e. OC+POC), EC, and the ratios of OC_{tot}/EC and OC_{tot}/TC for the entire 2007 spring study. Measurements of OM, sulphate, and b_{asp}, obtained by averaging the in-situ measurements to the same sampling interval as the filter samples, are also included. Generally, the OM, the b_{asp}, and sulphate vary similarly as a group during most of the sampling period (except for 9–14 June); this is mainly due to the fact that the source areas are mostly in the same direction and regional meteorology has a major influence on the appearance of these tracers. For the ratios of OC_{tot}/EC, opposite trends as that of the OM are observed.

The filter measurements are separated into groups according to the predominant wind direction that occurred during the course of each filter sampling period. In order to examine the anthropogenic and biogenic emission influences on the ambient air conditions, this analysis focuses on measurements taken within two main wind directions: either from the north (300°–60°; relatively clean air and containing relatively more biogenic emissions) or from the south (120°–240°; largely impacted by anthropogenic pollutants). In most cases, back trajectories (not shown here) are consistent with the local wind directions; hourly local wind directions are used for the separation by wind direction. Periods with mean wind speeds $<2\,m\,s^{-1}$ were excluded from the analysis to avoid isotropic wind behavior (Kim and Hopke, 2004). The predominant wind direction within the sampling period of each filter measurement is determined based on two criteria: 1) The predominant wind direction has to occupy at least 40% of the time within the given sampling interval. 2) The second predominant wind direction can not occupy more than 10% of the time within the same period. Based on these two criteria, the predominant wind direction is categorized as "north" (N), "south" (S), "mixed" (M: only criterion 1 is fulfilled), and "others" (O: the predominant wind direction is from east or west and/or when criterion 1 is not fulfilled). With the consideration of the predominant wind direction, the results (Fig. 1) indicate that for the southern air masses, the values

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of EC and b_{asp} are generally higher than those in northern air masses. At the same time, air masses from the south also show lower values of OC_{tot}/EC, reflecting relatively larger contributions to EC from anthropogenic sources. The southern air masses also show relatively higher concentrations for OC, OM, and sulphate than those in the northern air masses except from 9–14 June. During the period of 9–14 June, winds were predominantly from the north, and there was a continuous increase in OC and OM. The 9–14 June period is one with a strong and continuous contribution from biogenics to the OM (Slowik et al., 2009) and is hereafter referred to as the biogenic period. There are also other days with large increase in OM relative to EC for northerly air masses, including 17, 22, and 30 May. During the biogenic period, the average value of the OC_{tot}/TC is 76% (SD=5.0%), similar to the average value of 74% (SD=6.1%) for the northern air masses during other periods. In contrast, the OC_{tot}/TC is about 67% (SD=6.4%) from the southern air masses due to the larger contributions from EC. A similar time series for the 2005 fall study is shown in Fig. 2 for comparison. Although there are only a few measurements in Fig. 2, the tendencies of all traces are consistent with those from the 2007 spring study.

Table 1 shows the average concentrations for selected species and the ambient temperatures during the two field studies based on the predominant wind direction. For the 2007 spring study, results for the northern air masses are separated into three categories: 1) using all northern measurements (all), 2) including only the biogenic period from 9–14 June (bio), and 3) excluding the biogenic period (bg). For both studies, average value of OC, POC, EC, OM, and b_{asp} for the southern air masses are much higher than that for the northern air masses. The difference in concentration between the southern and the northern air masses is reduced during the biogenic period from the 2007 spring study.

Also included in Table 1 are the average values of OC_{tot}/EC and OC_{tot}/TC (means of the ratios). Generally, a low value of OC/EC is interpreted as having larger contributions from primary anthropogenic emissions due to the higher EC content emitted from urban sources. Observations from other studies show that the value of OC/EC

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derived either from the use of emissions inventory data or ambient measurements with limited SOA formation varies from 0.9 to 3.1 (e.g. Gray, 1986; Turpin and Huntzicker, 1991, 1995; Strader et al., 1999; Cabada et al., 2004). With large contributions of SOA, the value of OC/EC can be much higher (e.g. 4.1–7.3 in Turpin and Huntzicker, 1991). However, these absolute values are source dependent. At Egbert, the average value of OC_{tot}/EC for the southern air masses during the 2007 and 2005 studies are found to be 2.2 (SD=0.9) and 2.0 (SD=0.5, N=2), respectively. For the northern air masses, values are 3.3 (SD=1.1) and 4.6 (N=1) for the spring and fall studies, respectively. The larger OC_{tot}/EC values for the northern air masses suggest that SOA makes a relatively larger contribution to the total organic carbon than the amount of EC compared with the southern air masses. This does not imply that all organics in the southern air masses reaching Egbert are from primary emissions. During the 2007 spring study, direct evidence of SOA formation in the southern air masses was observed (Sect. 3.2.1).

The coefficients of determination (R^2) between various quantities when the air masses were from the north and from the south are given in Table 2a and b, respectively. Values in Table 2a represent R^2 (N=7) for the northern air masses excluding the biogenic period (9–14 June), and values in the parenthesis represent R^2 (N=4) observed during the biogenic period only. In the case of N=7, probabilities for getting R^2 of 0.64 and 0.81 due to pure random correlation are 3.1% and 0.6% respectively. With N=4, these probabilities increase to 20% and 10% respectively (Taylor, 1982). For the southern air masses (N=8), the R^2 among POC, OC, EC, and OM are all 0.80–0.90. The strong correspondence of EC with POC and with OM suggests that the oxygenated organics from the south are primarily from anthropogenic sources. When the air mass comes from the north (Table 2a), the R^2 among POC, OC, EC, and OM are 0.34–0.83 without the biogenic period and 0.01–0.93 during the biogenic period. The lower R^2 for EC with POC, OC, and OM exclusive of the biogenic period (0.41–0.83) and the higher values of OC_{tot}/EC in the northern aerosol (Table 1) suggest a contribution from SOA. The corresponding R^2 are even lower for the biogenic period (0.01–0.50) consistent with biogenic SOA formation (Slowik et al., 2009). During 2007 spring, there was

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a short period of biomass burning that influenced the site (9 June, 20:45 to 10 June, 8:55) and could have contributed to the higher EC and OC concentration. However, no increase in EC and OC concentration were observed from the filter sample that covers the biomass burning period compared to other measurements during the biogenic period.

3.2 Relationship between OM/OC and POC

3.2.1 Relationship between OM/OC and SOA formation

It is known that the value of OM/OC_{tot} (which is equivalent to the conventional "OM/OC ratio" in literatures) has been widely used to infer information about the atmospheric aging of the particles and the contribution of SOA to the particles. Both toluene and benzene are aromatic hydrocarbons that are emitted dominantly from anthropogenic emission sources. Reactions of both with O_3 and NO_3 in the atmosphere are too slow to be considered as removal processes. The only significant atmospheric removal process is by the reaction with OH radicals. Under the same atmospheric condition, toluene reacts about five times faster than benzene (Atkinson, 1990). Based on typical daily average OH radical concentration (10^6 radicals cm^{-3}), the atmospheric lifetimes for toluene and benzene are about 1.9 and 9.4 days, respectively. Toluence to benzene ratio (Tol/Bene) is found useful in estimating the age of an air mass from vehicular emission sources (e.g. Gelencsér et al., 1997). Examining the variation in the OM/OC_{tot} relative to the Tol/Bene provides a mutual constraint to the mechanism of particle aging.

The top panel in Fig. 3 shows the values of OM/OC_{tot} (dotted line) and the values of Tol/Bene (solid line) obtained from the regular VOC measurements conducted at CARE (Brickell et al., 2003). In the bottom panel of the figure is the difference in mass between OM and OC_{tot} (i.e. OM-OC-POC); this gives the approximate oxygenated compound mass excluding carbon in the aerosol particles observed for the 2007 spring study. Also included in the bottom panel is the oxygen mass determined with a HR-ToF-AMS (W-ToF) during the 2007 spring study. In this method, fragments

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of nominally equal *m/z* ratio are quantified as C_xH_y, $C_xH_yO_z$, $C_xH_yN_j$, and $C_xH_yN_jO_z$, using a custom formulated algorithm (Liggio et al., 2009) that is based on the work of Aiken et al. (2007, 2008) and then, the oxygen mass is estimated. In the bottom panel of Fig. 3, the variation patterns in the oxygen mass (i.e. oxygenated compound mass excluding carbon) derived from the two methods show high consistency (R^2=0.89), indicating that the oxygen mass time series in ambient aerosols is well captured by the two methods. Although it will not be discussed in detail here, the difference in the absolute concentration for the oxygen mass determined from the two methods is likely due to a combination of the different configurations and CE in the two AMSs (C-ToF vs. W-ToF), as well as the decrease in W-ToF-AMS TE for relatively large particles which contribute considerable mass at times.

Due to the lack of sources for toluene and benzene to the north, only the two highlighted persistent southern wind periods in Fig. 3 are considered here. At the beginning of period B (29 May–2 June), a sudden switch of air masses (from north to south) causes a rapid change in both the OM/OC_{tot} and Tol/Bene. During this period, a continuous decrease in Tol/Bene indicates progressive gas phase oxidation in the atmosphere (i.e. photochemical aging). At the same time, such changes are accompanied by a stepwise increase in OM/OC_{tot} and the oxygen mass, both of which suggest increasing degree of oxygenation of the aerosols due to SOA formation. A similar pattern is also seen during period A (22–25 May). In this case, the high value of Tol/Bene on 24 May is a result of covering mostly nighttime measurements, during which the concentration of both toluene and benzene are high due to the formation of a stable inversion layer and lack of OH formation. Despite this, the qualitative trends during the two periods are consistent with SOA formation. With the limited time resolution from the filter measurements, the given results provide evidence that the value of OM/OC_{tot} is a qualitative indicator of the degree of oxygenation in the aerosol within air masses from similar sources. Because atmospheric oxidation of VOCs also includes reactions with O_3 (daytime and nighttime) and NO_3 (nighttime), which are not reflected in Tol/Bene, the extent of atmospheric oxidation inferred from Tol/Bene represents a minimum gas

phase oxidation.

3.2.2 OM/OC ratio in the northern and southern air masses

Figures 4 and 5 show the variations of the OM, OC_{tot}, as well as the values of OM/OC_{tot} during the two field studies. All the values of OM/OC_{tot} are above 1 except on 17 May, during which the concentration of OM and OC_{tot} are close to within measurement uncertainty. The values of OM/OC_{tot} determined here are subject to some uncertainties. In the OM measurements, occasional data gaps occur due to instrument zero checks, switching to different measurement modes, and instrumental problems (Slowik et al., 2009). Averaging those OM measurements causes problems when there are significant changes in the atmosphere during those missing periods. This was less of an issue for the 2005 fall data because the AMS was not used for other experiments as during 2007 spring (Slowik et al., 2009) and the averaging interval is much longer. Another factor contributing to the uncertainty is the difference in particle cut off size between the AMS (due to transmission efficiency) and the cyclone used in the filter measurements (1.0 μm for 2007 spring and 2.5 μm for 2005 fall). This is an issue during periods where significant OM mass is present in particles larger than ~500 nm, about the point at which AMS TE decreases; this lowers the OM mass and reduces the value of OM/OC_{tot}. The determination of the AMS CE using the comparison between SMPS and AMS measurements may not represent the AMS CE for the entire size distribution due to the different compositions of the aerosol particles at different particle sizes. Other possible sources of discrepancies are OC contamination of the sample filters due to transportation and/or handling during sampling or analysis. Contamination from transportation is removed via blank correction. OC artefacts from condensation during sampling as well as reduction in OC due to evaporation during the sampling (Turpin et al., 2000; Viana et al., 2006) can not be corrected based on the current setup.

The mean values of OM/OC_{tot} are shown in Figs. 4 and 5, which are also summarized in Table 3, according to predominant wind directions from the north and south,

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respectively. The average values of OM/OC_{tot} for 2007 spring are 1.9 (SD=0.5) and 2.5 (SD=0.5) for the northern (all data) and southern air masses, respectively. A relatively larger value of OM/OC_{tot} during the biogenic period (discussed in Sect. 3.1) was observed, which could be the result of the initial oxidation of the pinene and terpene molecules emitted during the period. During the 2005 fall study, the OM/OC_{tot} varied between 1.2 and 1.8 (Fig. 5) with the smallest value for northern air and the largest value for southern air. Direct comparison of the OM/OC_{tot} values for the two field studies is not meaningful due to the use of different AMSs to determine the OM.

The OM/OC_{tot} values for the northern air masses during the 2005 fall study are similar to the two OM/OC values reported by Turpin and Lim (2001) (1.2 and 1.3, see Table 3) on primary biogenic emissions and background aerosols from west coast of US, respectively. Pio et al. (2001) measured the organic compounds present in the total suspended PM collected in a forest in Central Greece during July and August of 1997. Based on the 50 reported compounds that are formed by direct oxidation from VOC emitted by vegetation (e.g. α-pinene and β-pinene), the concentration weighted OM/OC is estimated to be 1.5.

The average value of OM/OC_{tot} obtained from the 2007 spring and 2005 fall studies for the southern air masses are 2.5 (SD=0.5) and 1.6 (SD=0.4), respectively. The 2005 value is similar to the OM/OC value calculated for downtown Los Angeles (1.7) and the west Los Angeles (1.6), reported by Turpin and Lim (2001) using data from Rogge et al. (1993b).

3.2.3 Estimation of the OM/OC ratios from POC

The concentration of POC determined from the current thermal method is expected to be proportional to the amount of oxygen mass in the aerosol (Huang et al., 2006). Figure 6 shows the relationship between the POC and the oxygen mass estimated from $OM\text{-}OC_{tot}$ (i.e. OM-OC-POC). Measurements from both studies and from all directions show good agreement (R^2=0.84) with a slope of 8.07±0.64 and an intercept of −2.17±0.44. The relationship in Fig. 6 is wind direction and season independent

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(spring and fall); this allows estimation of the oxygen mass in ambient aerosol from thermal POC and OC measurements, which can then be used to indirectly estimate the value of the conventional OM/OC. That is,

$$\text{“OM/OC ratio”} \approx 1 + \frac{8.07 \times \text{POC} - 2.17}{\text{OC} + \text{POC}} \quad (1)$$

Note that the quantities “OC” and “POC” on the right side of the equation are defined in Sect. 2.2.1 and obtained by the thermal.

3.3 Relationship between SAC and POC

3.3.1 Observed SAC at Egbert

The particle light absorption coefficient (b_{asp}) is plotted against the EC mass concentration for the 2005 fall and 2007 spring studies in Fig. 7. Also, the ranges of the sulphate mass concentrations are represented by the area of the markers. The data from the north and from the south for each study appear to be well represented by a linear regression. From the slope of the regression of all the 2005 fall and 2007 spring data, the specific attenuation coefficient (SAC) is estimated at $3.8 \pm 0.2\,m^2\,g^{-1}$. This result is within the SAC range ($3.5–5.0\,m^2\,g^{-1}$) reported by Sharma et al. (2002) for Egbert.

3.3.2 Relationship between SAC and POC

The SAC is defined as the ratio of the aerosol light absorption to the EC concentration. The magnitude of SAC reflects the ability of absorbing light by EC. The light absorption of a soot particle measured in this study with a PSAP is affected by two groups of factors, a) factors that change the absorption of the suspended particles include the amount of coating present as well as the structure and size of the soot particle; and b) factors that potentially modify the ratio of PSAP measured absorption and the real absorption of suspended particles include loading effects, single scattering albedo

effects, humidity sensitivity, and sensitivity to high OC and POC concentrations. First the SAC measurements are discussed assuming that the PSAP measures the correct absorption of the suspended particle. This is followed by a discussion of possible measurement artifacts.

Assuming the thermal EC mass is independent of the factors influencing the light absorption of the suspended particles, the first group of factors mentioned above are related to the atmospheric aging of the particles. Based on Figs. 3 and 6, the POC is related to the oxygenated OC. Although the oxygenated OC could be either primary or secondary in nature (Liggio et al., 2009), a positive correlation between POC and sulphate (Fig. 8) suggests that the increase in POC was likely due to atmospheric aging of the aerosol particles. Thus, POC is used as a tracer for atmospheric aging processes in this study. As a result, the relationship between the SAC and the POC provides information for understanding the impacts of aerosol aging process on SAC and also suggests a hypothetical value of SAC for primary emitted soot when POC mass approaching zero (i.e. the atmospheric aging is minimized).

Plotting the SAC against POC mass without separating data according to predominant wind direction gives small negative correlation between the two quantities (R=−0.30). When separating the data according to the predominant wind direction, the negative relationship between the SAC and POC mass increases significant (R=−0.61 for north and R=−0.75 for south; Table 4); this is also illustrated in Fig. 8. The significant increase in correlation coefficient indicates that the relationship between the SAC and POC appears to be wind direction dependent. To further understand the negative correlation between SAC and POC, it is important to understand the factors which impact the aerosol light absorption when the aerosols are aged.

It is widely expected that aerosol light absorption is enhanced with increasing aerosol chemical age, assisted by an increase in the light scattering due to the presence of coating on soot particles (Bond and Bergstrom, 2006; Bond et al., 2006). The degree of enhancement depends on factors such as the position of the soot particle within the coating (Fuller et al., 1999), as well as the amount and refractive index of the coating

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materials (Fuller et al., 1999; Slowik et al., 2007). The light absorption enhancement in direct radiative forcing by BC particles, due to secondary coating, is often included in global models (e.g. Jacobson, 2001; Chung and Seinfeld, 2002; Kim et al., 2008).

A negative relationship between the SAC and the POC suggests that aerosol light absorption decreases with increasing atmospheric lifetime of the aerosol particles. Possible explanations for this are the collapse of the soot particle aggregates (when particles are wet or aged) (Liousse et al., 1993; Bond and Bergstrom, 2006; Fuller et al., 1999; Iskander et al., 1991), and an increase in the soot particle diameter (Bond et al., 2006; Bond and Bergstrom, 2006; Dillner et al., 2001). However, comprehensive numerical calculations (Liu et al., 2008) have shown that the collapse can yield both decrease and increase of light absorption, generally of less than 10%. The magnitude of these changes, i.e. the decrease in absorption of up to a factor of 2 observed here (in Fig. 8) cannot be explained. However, it is possible that the particles observed here are not included in the parameter space explored by Liu et al. (2008) and a larger reduction of absorption is encountered.

Potential artifacts in the PSAP measurements include I) loading corrections have been applied following Bond et al. (1999), which should be corrected to within a few % (Virkkula et al., 2005), II) single scattering albedo corrections (Virkkula et al., 2005) have not been applied as Schmid et al. (2006) did which were not found necessary since they should further decrease the true absorption relative to that given here for increasing single scattering albedo due to increasing POC, III) humidity sensitivity has been reported to increase reported PSAP absorption for high humidity (Arnott et al., 2003; Sedlacek and Lee, 2007) but the correction algorithm suggested by Schmid et al. (2006) has not been used here, IV) artifacts due to high OC and POC concentrations have been reported to increase PSAP readings proportional to OC and/or POC concentrations (Cappa et al., 2008; Lack et al., 2008), which has not been observed here. In short, none of these potential artifacts in the PSAP measurement could result in the negative relationship between the SAC and POC observed here, as a result, they could strengthen it.

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Due to the influences from both long and mid range transport, the negative relationship between SAC and POC found in Egbert studies (Fig. 8) is likely a net result of competing between different factors. Possible explanations include an increase in soot particle diameter at higher overall mass concentrations, collapse of the primary soot particle structure with increased mass concentrations and relatively more absorbing materials in the OC or POC (brown carbon, Kirchstetter, 2004) at lower concentrations.

For the northern and southern air masses, the extrapolated intercepts when POC mass approaching zero are 5.8±1.0 $m^2\,g^{-1}$ and 6.3±0.6 $m^2\,g^{-1}$, respectively; these values are supported by the corresponding intercepts of 4.8±0.6 $m^2\,g^{-1}$ and 5.4±0.4 $m^2\,g^{-1}$ obtained from the relationship between SAC and sulphate. The intercepts obtained when POC and sulphate masses approaches zero represent a hypothetic SAC for primary emitted soot particles with a minimum impact from atmospheric aging. Intercepts obtained in Table 4 are close to a model calculation value of 5 $m^2\,g^{-1}$ reported by Fuller et al. (1999) for amorphous carbon spheres from primary sizes diesel soot particles.

The mean SAC value observed during the periods of the studies at Egbert is 3.8 $m^2\,g^{-1}$, which is 20–40% lower than the range of hypothetic primary SAC values mentioned above. If the results from this study are correct, the modelled results by global models that increase the particle light absorption due to the presence of coatings in simulating radiative forcing by BC particles could be much less than the current values. Also, the observation of this study shows the needs for further investigation to better understand the effect of particle aging on aerosol light absorption.

4 Conclusions

The values of OM/OC_{tot} for ambient fine particles collected at a rural site from two intensive studies were determined based on the OM measured with C-ToF-AMS (or Q-AMS) and OC determined from a thermal analysis of filters. During the 2007 spring study, the value of OM/OC_{tot} was 1.9 when the air was from the north (i.e. more influenced by

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biogenic emissions) and 2.5 when the air was from the south (i.e. strongly influenced by anthropogenic emissions). For the 2005 fall study, the values of OM/OC_{tot} for the north and south are 1.2 and 1.6, respectively. Those results suggest that the air masses from the south, with relatively low OC/EC ratios, high EC, sulphate contents and OM/OC ratios, were originated from anthropogenic emission at urban and industrial area and subsequently experienced photo-oxidations during atmosphere transport, implying that the oxygenated organics could come from both primary and secondary sources. Whereas the air masses from the north, with relatively high OC/EC ratios, low EC, sulphate contents and OM/OC ratios, were dominant by the background clean air with relatively larger contributions from biogenic emissions. It is shown that the POC determined from the thermal filter method is proportional to the oxygen mass [OM-OC] in the aerosols. Since this relationship is independent of wind direction and season in this case, it can be used to derive the value of OM/OC in PM via using only OC and POC from thermal measurements.

The SAC of the ambient aerosol particles at the rural site were estimated based on the b_{asp} measured by a PSAP and the EC determined by the thermal method. The overall SAC derived from the combined 2005 fall and 2007 spring data set is $3.8\,m^2\,g^{-1}$. A decrease in the SAC value with atmospheric aging of the aerosol was observed at the rural site, suggesting that during the field study period, the light absorption enhancement due to the presence of coating on soot particles was likely to be offset by the decrease in light absorption caused by increasing soot particle diameter and collapsing of soot particle structure. Extrapolation of the y-intercept in the relationships of SAC with POC, sulphate, and the sum of both masses yield a general average SAC value for primary emitted soot of about $5.2\,m^2\,g^{-1}$ and $5.7\,m^2\,g^{-1}$ for the northern and southern air masses, respectively.

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Table 1. Average values for different species, the average total organic carbon to elemental carbon ratio (OC_{tot}/EC; OC_{tot}=OC+POC), and the average total organic carbon to total carbon ratio (OC_{tot}/TC) measured during the 2007 and 2005 studies for different predominant wind directions. For the 2007 study, results for the northern air masses are calculated using all northern data (all), excluding the biogenic period from 9–14 June (bg), and only the biogenic period (bio). The value given in the parenthesis is SD. SD is not given for 2005 field data due to the lack of measurements. Also included are the average temperatures during different periods. Organic carbon (OC), pyrolysis organic carbon (POC), and elemental carbon (EC) data are obtained from filter measurements, b_{asp} data are obtained from PSAP, OM data during 2007 and 2005 are from C-ToF-AMS and Q-AMS, respectively.

	2007 N (all)	2007 N (bg)	2007 N (bio)	2007 S	2005 N	2005 S
OC, $\mu g\,m^{-3}$	1.51 (±0.99)	0.97 (±0.32)	2.47 (±1.08)	2.51 (±0.91)	0.70	0.99
POC, $\mu g\,m^{-3}$	0.51 (±0.19)	0.40 (±0.11)	0.71 (±0.11)	0.94 (±0.30)	0.23	0.39
EC, $\mu g\,m^{-3}$	0.65 (±0.31)	0.48 (±0.21)	0.96 (±0.18)	1.82 (±0.95)	0.20	0.72
OM, μg^{-3}	3.91 (±2.33)	2.52 (±1.15)	6.34 (±1.75)	9.14 (±3.82)	1.13	2.33
b_{asp}, $(Mm)^{-1}$	2.05 (±0.84)	1.86 (±0.94)	2.39 (±0.62)	6.98 (±2.25)	1.18	3.56
OC_{tot}/EC	3.27 (±1.14)	3.23 (±1.30)	3.33 (±0.96)	2.17 (±0.85)	4.61	2.04
OC_{tot}/TC	0.75 (±0.06)	0.74 (±0.06)	0.76 (±0.05)	0.67 (±0.06)	0.81	0.67
Temp(°C)	13.76 (±4.65)	11.52 (±4.06)	17.67 (±2.64)	20.82 (±2.45)	4.24	5.93

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Table 2a. The coefficients of determination (R^2) between different species measured during the 2007 spring study under heavy influence by northern air masses. Values given in the table represent R^2 (N=7) excluding the biogenic period (9–14 June). Values in the parenthesis represent R^2 (N=4) during the biogenic period.

2007 North	OC	POC	EC	OM	SO_4^{2-}	b_{asp}
OC	1	0.34 (0.64)	0.41 (0.30)	0.46 (0.93)	0.00 (0.01)	0.64 (0.25)
POC	0.34 (0.64)	1	0.56 (0.01)	0.57 (0.58)	0.45 (0.00)	0.18 (0.66)
EC	0.41 (0.30)	0.56 (0.01)	1	0.83 (0.50)	0.28 (0.22)	0.59 (0.05)
OM	0.46 (0.93)	0.57 (0.58)	0.83 (0.50)	1	0.43 (0.03)	0.56 (0.37)
SO_4^{2-}	0.00 (0.01)	0.45 (0.00)	0.28 (0.22)	0.43 (0.03)	1	0.00 (0.35)
b_{asp}	0.64 (0.25)	0.18 (0.66)	0.59 (0.05)	0.56 (0.37)	0.00 (0.35)	1

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Table 2b. The coefficients of determination (R^2) between different species measured during the 2007 spring study under heavy influence by southern air masses.

2007 South	OC	POC	EC	OM	SO_4^{2-}	b_{asp}
OC	1	0.80	0.88	0.88	0.59	0.50
POC	0.80	1	0.82	0.85	0.76	0.84
EC	0.88	0.82	1	0.90	0.71	0.67
OM	0.88	0.85	0.90	1	0.85	0.74
SO_4^{2-}	0.50	0.76	0.71	0.85	1	0.81
b_{asp}	0.51	0.84	0.67	0.74	0.81	1

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Table 3. The values of OM/OC_{tot} observed during the 2007 and 2005 field studies under heavy influence by northern and southern air masses. The value given in parenthesis is SD. Also included are reference values of OM/OC observed from primary biogenic emissions dominated environments, off coast background, as well as urban environments.

Data source	OM/OC_{tot}	Comments	Predominant wind direction
Egbert 2007 North (all data points)	1.88 (±0.46)	N=11, all measurements from north	North
Egbert 2007 North (exclude 9–14 June)	1.80 (±0.55)	N=7, exclude biogenic period	North
Egbert 2007 North (only 9–14 June)	2.04 (±0.23)	N=4, biogenic period	North
Egbert 2005 North (all)	1.21	N=1	North
Pio et al. (2001)	1.45	50 VOC oxidation products average concentration	n/a
Turpin and Lim (2001)	1.20	Data from Rogge et al. (1993a) (primary biogenic)	n/a
Turpin and Lim (2001)	1.29	Data from Rogge et al. (1993b) (off coast background)	n/a
Egbert 2007 South (all data points)	2.50 (±0.51)	N=8, all measurements from south	South
Egbert 2005 South (all data points)	1.64 (±0.35)	N=2, all measurements from south	South
Turpin and Lim (2001)	1.65	Data from Rogge et al. (1993b) (LA downtown)	n/a
Turpin and Lim (2001)	1.63	Data from Rogge et al. (1993b) (west LA)	n/a
Aiken et al. (2008)	1.71	~2.1 as Mexico City regional OM/OC from aircraft	n/a

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Table 4. Correlation coefficient (R) and coefficient of determination (R^2) between specific attenuation coefficient (SAC) and different tracers. Also given are the estimated SAC for primary emitted soot particles with minimum degree of aging for the northern and southern air masses based on the combined 2005 and 2007 data sets.

Compare quantities	R(N)	R^2(N)	SAC_{soot}(N)	R(S)	R^2(S)	SAC_{soot}(S)
SAC vs. POC	−0.61	0.37	5.8±1.0	−0.75	0.56	6.3±0.6
SAC vs. SO_4^{2-}	−0.65	0.42	4.8±0.6	−0.77	0.59	5.4±0.4

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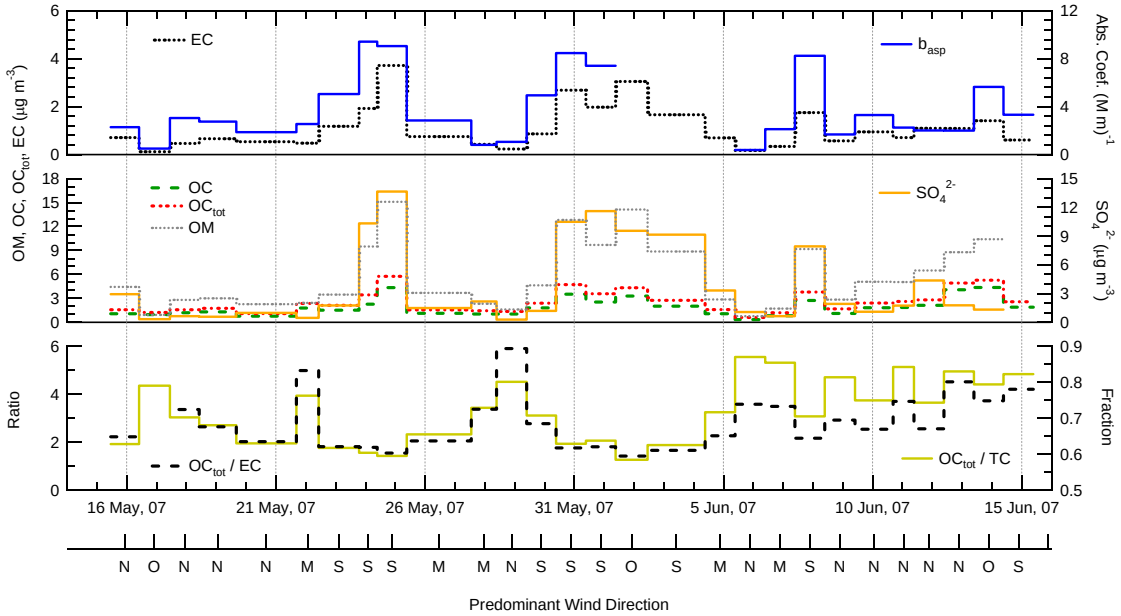

Fig. 1. Variations of organic carbon (OC), total organic carbon (OC_{tot}: OC+POC, i.e. pyrolysis organic carbon), elemental carbon (EC), organic aerosol mass (OM), sulphate, aerosol light absorption coefficient (b_{asp}), and the ratios of OC_{tot}/EC and OC_{tot}/TC during the 2007 spring study. Also given on the graph is the predominant wind direction for each corresponding filter sampling period (N=north, S=south, M=mixed, O=others).

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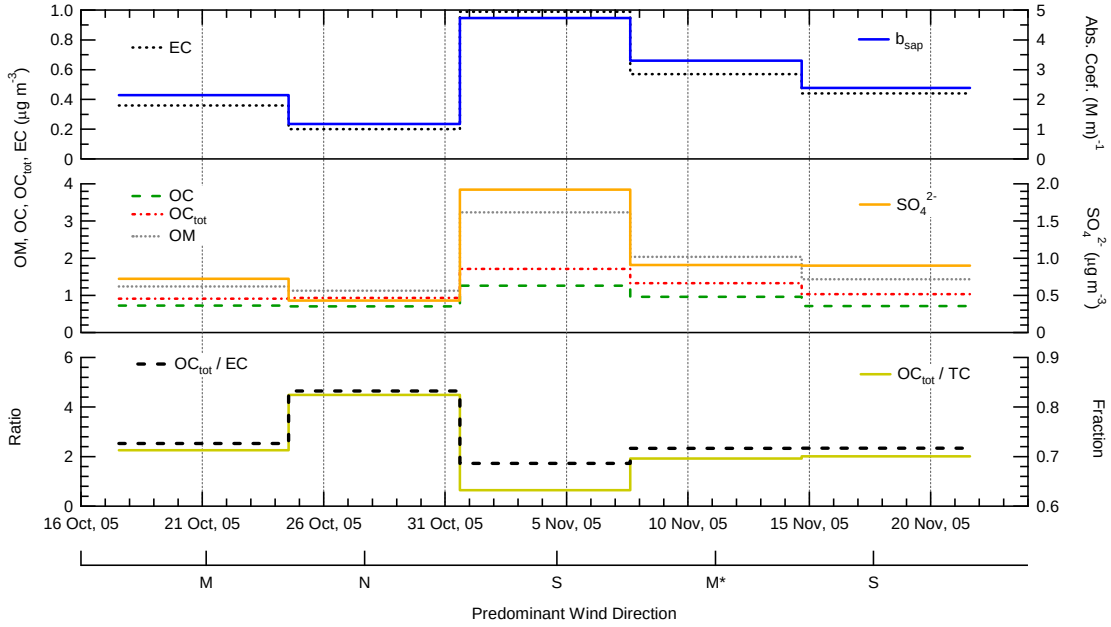

Fig. 2. Similar plot as Fig. 1 for the 2005 fall study. During the sampling period from 7 to 14 November (labelled as M*), 44% of the time was impacted by air masses from the south versus 27% from the north. These conditions do not meet the criteria to be considered as "south" although the site was impacted heavily by the southern air masses during that period.

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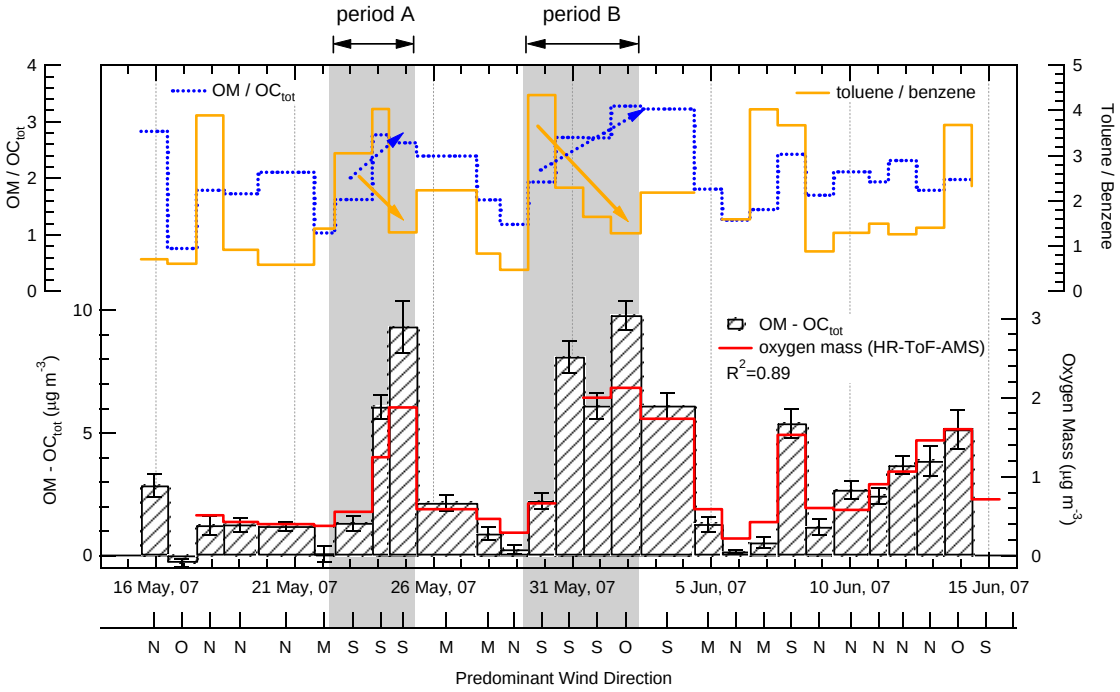

Fig. 3. The top panel shows the variations of the values of OM/OC$_{tot}$ and toluene/benzene for the 2007 study. Bottom panel shows the difference in mass concentration between OM and OC$_{tot}$ (i.e. OM-OC-POC). Uncertainties are twice the standard error. Also included in the bottom panel is the oxygen mass determined from the HR-W-ToF-AMS. The highlighted regions are the two periods with persistent southern winds. The two sets of arrows indicate the general trends of the OM/OC$_{tot}$ (dotted line arrow) and toluene/benzene (solid line arrow) during the corresponding periods.

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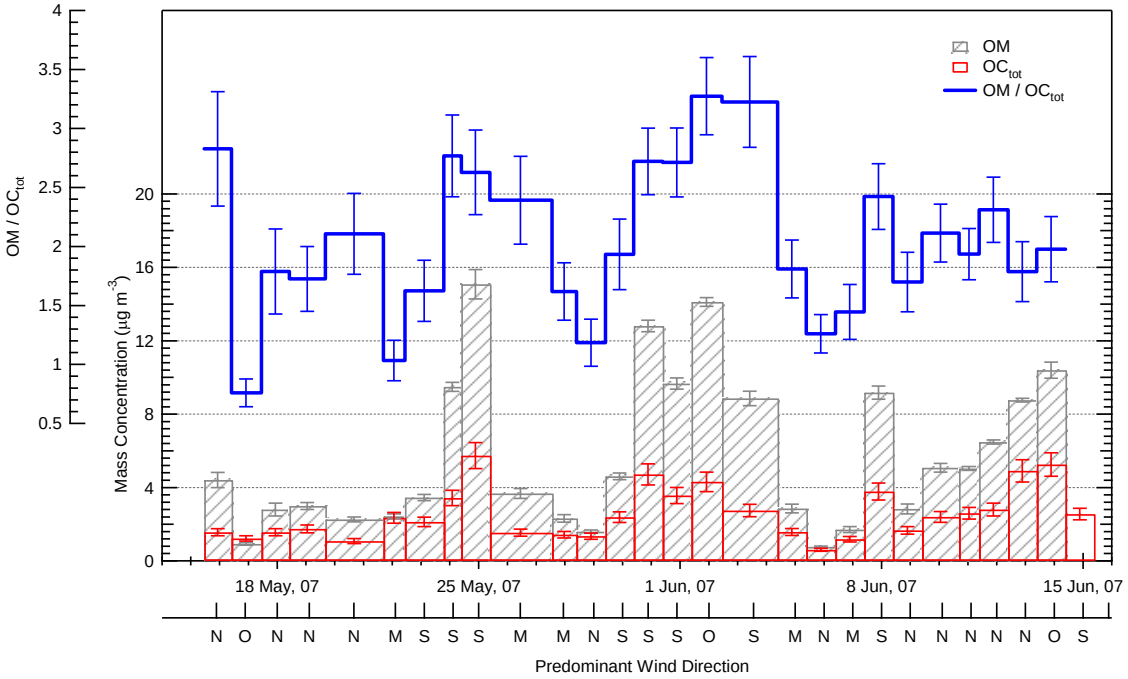

Fig. 4. The daily OC_{tot} concentration, integrated AMS OM measurements, and the value of OM/OC_{tot} for the 2007 spring study. Uncertainties are twice the standard error. Uncertainties in OM reflect only counting statistics and do not include uncertainties such as AMS transmission and collection efficiencies.

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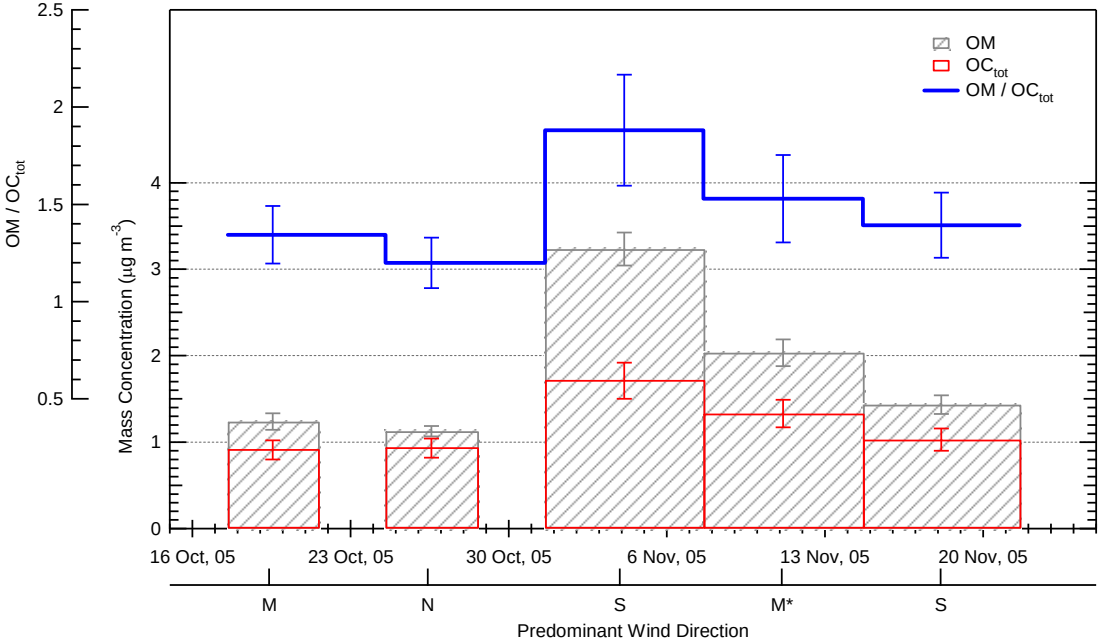

Fig. 5. The weekly OC_{tot} concentration, integrated AMS OM measurements, and the value of OM/OC_{tot} for the 2005 fall study. Uncertainties are twice the standard error.

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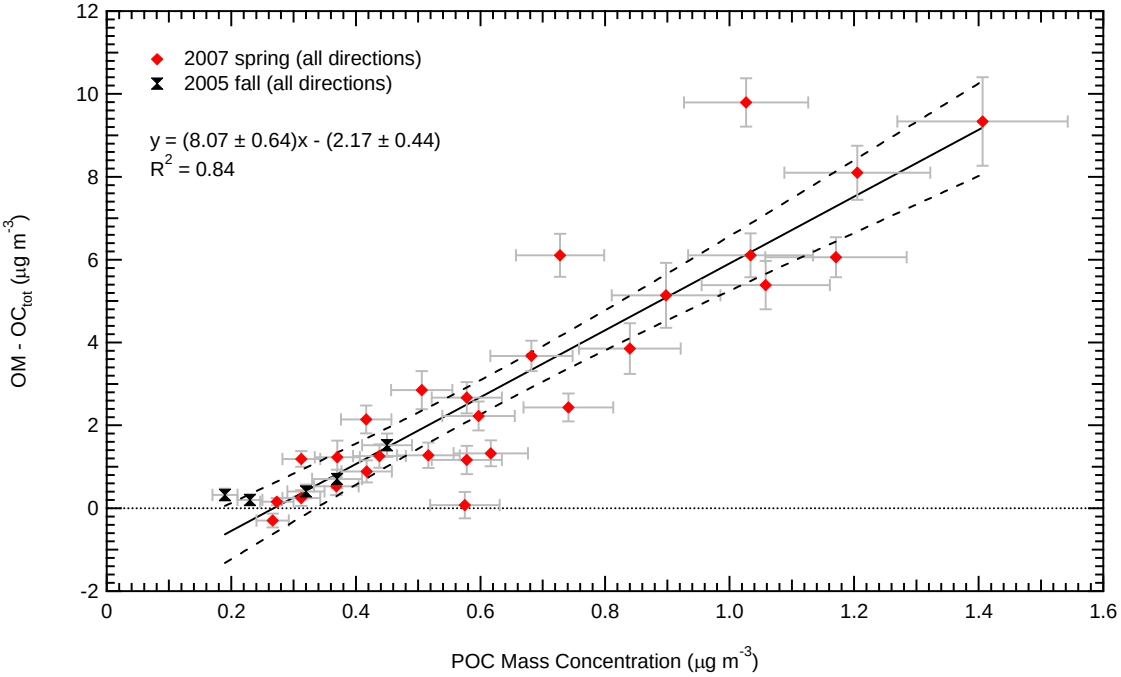

Fig. 6. Relationship between the estimated oxygen mass (i.e. OM-OC-POC) and the POC mass for the 2007 (diamonds) and 2005 (double triangles) studies. Uncertainties are twice the standard error. Solid line is the least squares best fit for all data. Dotted curves represent 95% confidence interval bands.

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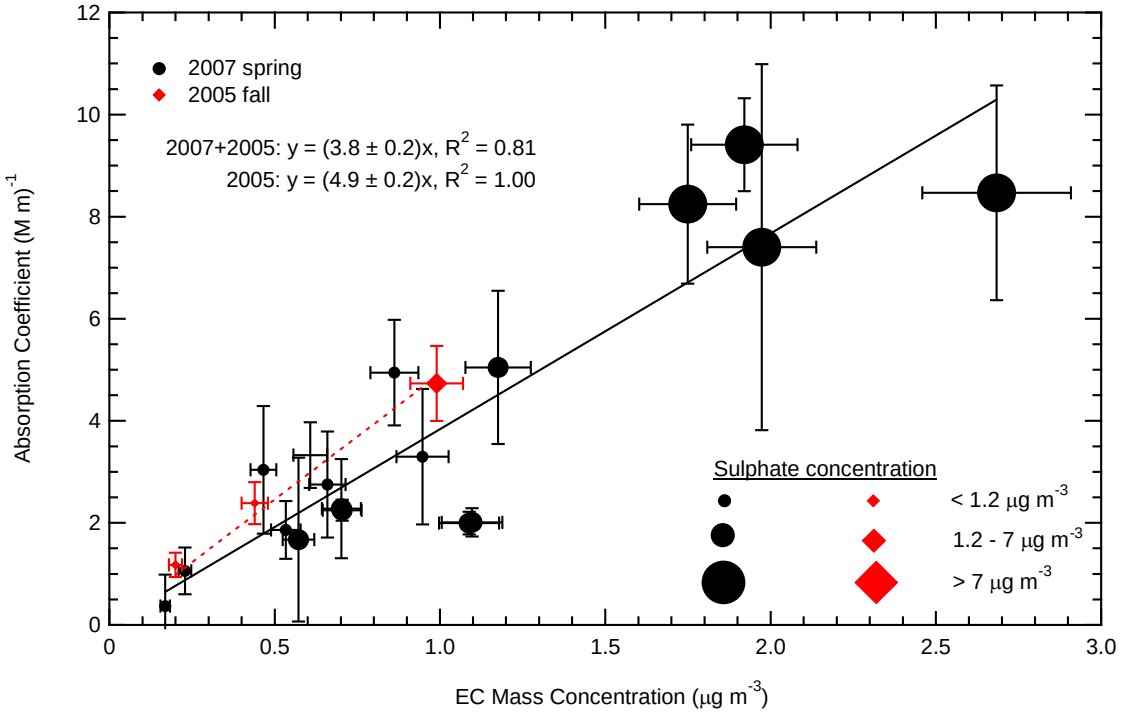

Fig. 7. Relationship between the b_{asp} and the EC for the 2007 (black solid circles) and 2005 (red solid diamonds) studies. The areas of both sets of markers represent the approximate range of sulphate concentration.

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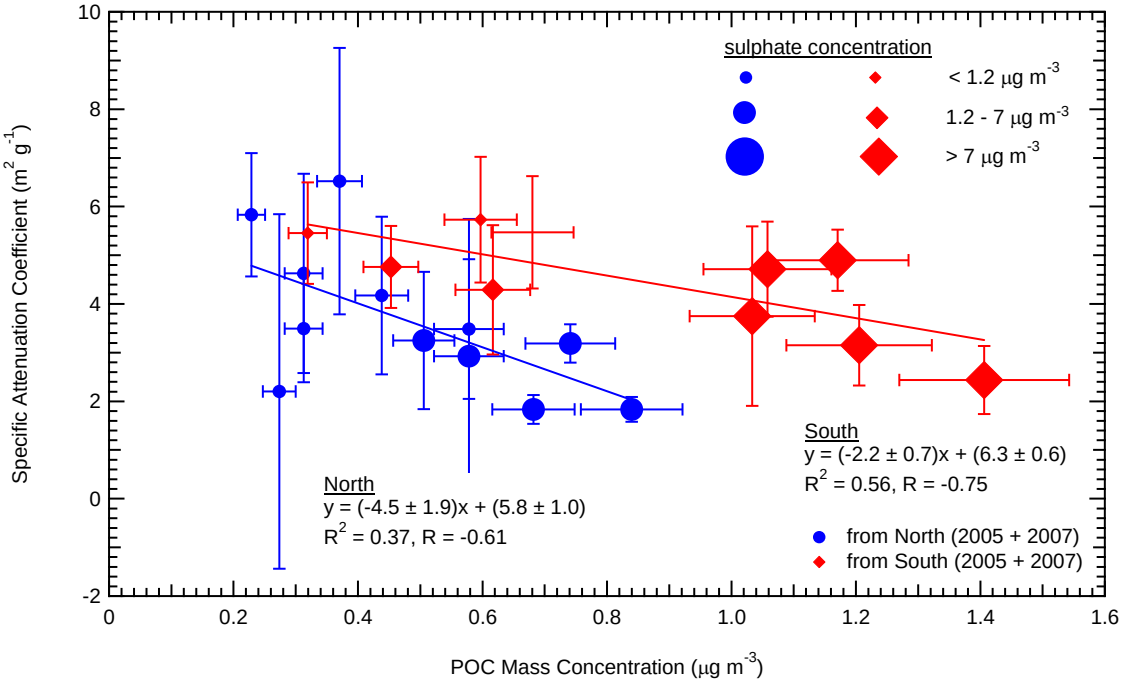

Fig. 8. Relationship between the specific attenuation coefficient (SAC) and the pyrolysis organic carbon (POC) at Egbert for the northern (blue circles) and southern (red diamonds) air masses. The areas of both sets of markers represent the approximate range of sulphate concentration.

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