Atmos. Chem. Phys. Discuss., 11, 23573–23618, 2011
www.atmos-chem-phys-discuss.net/11/23573/2011/
doi:10.5194/acpd-11-23573-2011

Atmospheric Chemistry and Physics Discussions

Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain

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Received: 26 July 2011 – Accepted: 5 August 2011 – Published: 19 August 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

We present results from the international field campaign DAURE (Determination of the sources of atmospheric Aerosols in Urban and Rural Environments in the western Mediterranean), with the objective of apportioning the sources of fine carbonaceous aerosols. Submicron fine particulate matter (PM_1) samples were collected during February-March 2009 and July 2009 at an urban background site in Barcelona (BCN) and at a forested regional background site in Montseny (MSY). We present radiocarbon (^{14}C) analysis for elemental and organic carbon (EC and OC) and source apportionment for these data. We combine the results with those from component analysis of aerosol mass spectrometer (AMS) measurements, and compare to levoglucosan-based estimates of biomass burning OC, source apportionment of filter data with inorganic+EC+OC speciation, submicron bulk potassium (K) concentrations, and gaseous acetonitrile concentrations.

At BCN, 87 % and 91 % of the EC on average, in winter and summer, respectively, had a fossil origin, whereas at MSY these fractions were 66 % and 79 %. The contribution of fossil sources to organic carbon (OC) at BCN was 40 % and 48 %, in winter and summer, respectively, and 31 % and 25 % at MSY. The combination of results obtained using the ^{14}C technique, AMS data, and the correlations between fossil OC and fossil EC imply that the fossil OC at Barcelona is ~65 % primary whereas at MSY the fossil OC is mainly secondary (~85 %). Day-to-day variation in total carbonaceous aerosol loading and the relative contributions of different sources predominantly depended on the meteorological transport conditions. The estimated biogenic secondary OC at MSY only increased by ~40 % compared to the order-of-magnitude increase observed for biogenic volatile organic compounds (VOCs) between winter and summer, which highlights the uncertainties in the estimation of that component. Biomass burning contributions estimated using the ^{14}C technique ranged from similar to higher than when estimated using other techniques, and the different estimations were highly or moderately correlated. Differences can be explained by the contribution of secondary

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organic matter (not included in the primary biomass burning source estimates), and/or by an overestimation of the biomass burning OC contribution by the ^{14}C technique if the estimated biomass burning EC/OC ratio used for the calculations is too high for this region. Acetonitrile concentrations correlate well with the biomass burning EC determined by ^{14}C. K is a noisy tracer for biomass burning.

1 Introduction

Ambient aerosols have adverse effects on human health (e.g. Nel, 2005; Pope and Dockery, 2006; Krzyzanowski and Cohen, 2008). They also affect climate through their direct (absorption and scattering) and indirect (cloud interactions) effects on the Earth's radiative balance (Forster et al., 2007), ecosystems and crops through their deposition of acids, toxics, and nutrients (e.g. Matson et al. 2002; Grantz et al., 2003), and regional visibility (e.g. Watson, 2002).

Submicron particulate matter (PM_1, particles with an aerodynamic diameter <1 µm) contains substantial fractions of carbonaceous aerosols (Murphy et al., 2006; Jimenez et al., 2009). Carbonaceous aerosols comprise a wide variety of organic compounds, collectively referred to as organic matter (OM), elemental carbon (EC), also called black carbon (BC) as a consequence of its strong optical absorption, and carbonate mineral dust, the latter typically being negligible in submicron aerosol since it is mainly present in the coarse fraction (Sillanpää et al., 2005).

Carbonaceous aerosols are responsible for some of the adverse effects on human health produced by particles (Li et al., 2003; Mauderly and Chow, 2008). Some organic compounds are respiratory irritants (such as carbonyls and acids), carcinogens (such as polycyclic aromatic hydrocarbons (PAHs)), and toxins (Mauderly and Chow, 2008). EC induces respiratory and cardiovascular problems (Highwood and Kinnersley, 2006; and references therein) and may adsorb toxic or carcinogenic organic species which may then be absorbed into lung tissue (Gerde et al., 2001).

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An accurate knowledge of the sources of EC and OM is necessary to design strategies aimed at mitigating the effects of aerosols. The most important sources of carbonaceous aerosols are biomass, biofuel, and waste burning, residential heating, cooking, fossil-fuel combustion (including road traffic emissions), and biogenic emissions. Biogenic emissions contribute to primary organic aerosol (POA) and secondary organic aerosol (SOA), which is formed from biogenic gases such as isoprene and monoterpenes. Biogenic POA is dominantly in the supermicron mode while biogenic SOA is concentrated in the submicron mode (Pöschl et al., 2010).

Radiocarbon (^{14}C) analysis is a powerful tool used to help apportion the sources of carbonaceous aerosols (Currie, 2000; Szidat, 2009), due to its ability to differentiate between aerosol carbon arising from contemporary and fossil sources. In contemporary carbonaceous sources ^{14}C is found at levels similar to those in CO_2 in the present-day atmosphere, or higher for sources of "stored carbon" such as wood burning. In contrast, in fossil sources, whose age greatly exceeds the half-life of ^{14}C (5730 yr), ^{14}C has completely decayed. The radiocarbon content of a carbonaceous sample is expressed as the "fraction of modern carbon" (fM), and is referenced to the ratio $^{14}C/^{12}C$ in atmospheric CO_2 in the year 1950 (Stuiver and Polach, 1977):

$$\mathrm{fM} = \frac{(^{14}C/^{12}C)_{\mathrm{sample}}}{(^{14}C/^{12}C)_{\mathrm{AD1950}}} \quad (1)$$

Values of fM range from zero for fossil sources to more than one for contemporary sources. The fM for contemporary sources exceeds unity due to the atmospheric nuclear weapon tests in the 1950s and 1960s that significantly increased the radiocarbon content of the atmosphere (Levin et al., 2010). Here we will use the term "modern carbon" only to refer to measurements relative to the 1950 standard, and the terms "contemporary" or "non-fossil," and "fossil" carbon to refer to quantities after correction of the excess bomb radiocarbon. Since EC and OC may have different sources, source apportionment of EC and OC separately (as opposed to only total carbon, TC) provides additional valuable information.

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Several previous studies have reported contemporary and fossil fractions of carbonaceous aerosols in urban and rural European areas in PM_1, $PM_{2.5}$, PM_{10} and Total Suspended Particles (TSP, Table 1). In urban areas, EC was found to be 84–97 % fossil in summer or spring and 30–91 % fossil in winter or autumn, whereas the OC fraction was 28–47 % fossil in summer or spring and 32–45 % fossil in winter or autumn. In rural areas, the ranges are very wide, EC was 27–97 % fossil and OC was 9–58 % fossil in any season. In general, the fossil contribution in rural areas was usually lower than the equivalent urban area for both EC and OC. For nearly all sites, the fossil contribution was larger in EC than in OC, and it was more important in summer than in winter for EC, whereas for OC the difference summer-winter was variable, probably due to the different influences of biogenic emissions depending on the site. Other studies in Asian areas such as the Maldives, West India and Japan reported lower fossil contributions to BC (31–58 %, Table 1) and lower or similar fossil contributions to OC (6–38 %, Table 1). This is probably a consequence of the more common use of biomass burning for cooking in Asia with respect to Europe. Finally, in Mexico City the fossil contribution to OC was higher than that found in European or Asian areas (49–62 %), even during high-fire periods (Table 1).

The present study is part of the international field campaign DAURE (Determination of the sources of atmospheric Aerosols in Urban and Rural Environments in the western Mediterranean) (Pandolfi et al., 2011; Jorba et al., 2011; http://tinyurl.com/daure09). The objective of DAURE is to study the causes of regional scale aerosol pollution episodes during winter and summer in the Western Mediterranean Basin (WMB). The WMB presents unique atmospheric dynamics regulated by complex climatic and orographic effects which control the concentration, composition and transport of PM (Millán et al., 1997). In summertime, local circulation dominates the atmospheric dynamics over the WMB, enhancing the regional accumulation of pollutants and the stratification of polluted air masses (Millán et al., 1997). In winter, the inflow of clean Atlantic air masses into the WMB favors the reduction of pollution levels. However, during some periods characterized by winter anticyclonic conditions, pollution from the coast

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and valleys is accumulated due to thermal inversions persisting for a few days. After several days under anticyclonic conditions local upslope breezes can be driven by solar radiation pushing polluted air masses from the valley towards rural areas, thereby markedly increasing the PM levels in the rural areas (Pérez et al., 2008a; Pey et al., 2009, 2010). Together with these transport scenarios, the large emissions from the densely populated and industrialized areas, sporadic forest fires, and large shipping emissions give rise to a complex phenomenology for aerosol formation and transformation.

In this context, the present work focuses on characterizing the sources of fine carbonaceous aerosols, by using the ^{14}C method and comparing it to results from other apportionment methods such as receptor modeling of filter PM measurements (inorganic composition, EC and OC concentrations) and Aerosol Mass Spectrometer (AMS) data, and biomass burning source estimates from levoglucosan measurements. This is the first time that these techniques have been applied simultaneously in the Mediterranean region.

2 Methodology

2.1 Sampling

Two sampling sites were selected: Barcelona (BCN), an urban background site (41°23′24″ N 02°06′58″ E, 80 m a.s.l.), and Montseny (MSY), a forested regional background site (41°46′46″ N 02°21′29″ E, 720 m a.s.l.), which is part of the European Supersite for Atmospheric Aerosol Research (EUSAAR) network (http://www.eusaar.net). Sampling was carried out during two different seasons: February–March 2009, called the DAURE winter campaign (DAURE-W), and July 2009, called the DAURE summer campaign (DAURE-S).

Submicron fine particulate matter (PM_1) samples were collected on quartz fiber filters (Munktell in DAURE-W and Pallflex 2500QAT-UP in DAURE-S) using DIGITEL (DH-77

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in DAURE-W and DHA-80 in DAURE-S) high volume (30 $m^3 h^{-1}$) samplers with a PM_1 impactor inlet. Sampling periods were 48 h in winter and 24 h in summer. Samples were kept at −20 °C after sampling and prior to analysis. From all samples collected, 7 samples from each site were selected from DAURE-W and 6 from DAURE-S. These 28 samples were used for ^{14}C analysis. Selection of the samples was based upon simultaneous availability of samples at both sites, preliminary results (at the time of sample selection) from AMS measurements (only winter), and the EC and OC concentrations, to investigate different atmospheric scenarios. All the concentrations are reported under ambient temperature and pressure conditions.

NO_x concentrations were measured at both sites by conventional gas phase air pollution monitors (Thermo Scientific, Model 42i) by the Department of the Environment of the Generalitat de Catalunya.

2.2 Analyses of EC and OC and intercomparison

EC and OC concentrations were determined using the 28 samples collected for ^{14}C analysis by a thermo-optical method with a Sunset OC/EC Field Analyzer (RT 3080, Sunset Laboratory Inc., USA), which was used off-line (Bae et al., 2004). The EUSAAR2 protocol (Cavalli et al., 2010) was used. These results will be referred to as Sunset1. These concentrations of EC and OC were compared to other measurements:

- EC and OC concentrations measured by a different Sunset OC/EC analyzer (laboratory model) using the EUSAAR2 protocol. In DAURE-S, the analysis was carried out on the same filters used for Sunset1. In DAURE-W, it was carried out on PM_1 12 h samples collected on quartz fiber filters (Munktell) using high volume (30 $m^3 h^{-1}$) samplers (DIGITEL DHA-80). These results will be referred to as Sunset2.

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- EC and OC concentrations measured by gauge pressure in a calibrated volume during the EC and OC separation and collection for subsequent ^{14}C analysis (Szidat et al., 2004b, see description in Sect. 2.3).

- OC concentrations calculated from OM concentrations measured by AMS (method details in Aiken et al., 2008) in DAURE-W. For BCN, the calculations were done using OM/OC ratios depending on the type of OM analyzed as determined by PMF (1.3 for hydrocarbon-like organic aerosol (HOA) and cooking organic aerosol (COA), 2 for oxygenated organic aerosol (OOA), and 1.6 for biomass burning organic aerosol (BBOA); Aiken et al., 2008; Sun et al., 2011). For MSY, the calculations were done using OM/OC ratios determined by high-resolution analysis of the AMS mass spectra.

- EC concentrations measured by the Sunset instrument during the CO_2 collection for ^{14}C measurements corresponding to the third stage of the thermal program, as explained in Sect. 2.3

- Black carbon concentrations measured by a Multi Angle Absorption Photometer (MAAP) with a PM_{10} inlet.

The results are generally consistent within the uncertainties in the different measurements, especially in terms of trends, while some differences in the absolute magnitudes are apparent (Fig. S1). At BCN the bulk OC from the AMS was substantially higher than that measured by the rest of the instruments (Fig. S1), which we attribute to higher than usual uncertainties in the calibration of that instrument due to custom modifications of the ionization region. Therefore absolute concentrations of OC from different sources calculated based on these different measurements should be compared with caution, while fractional contributions should be more directly comparable. In the following, the EC and OC concentrations used are those measured by the Sunset1 instrument (using the samples collected for ^{14}C analysis), unless otherwise specified. Associated error bars of EC and OC measured by Sunset1 lower than 20 % of the concentration were

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increased to 20 % to better reflect the uncertainty in the measurements, shown by the differences among different methods (Fig. S1) and based on round-robin tests within EUSAAR project (EUSAAR Deliverable NA2/D10new report).

2.3 Separation of carbonaceous fractions and ^{14}C measurements

The method for the separation of carbonaceous particle fractions is based on the different chemical and thermal behavior of OC and EC in the presence of oxygen gas as shown by Lavanchy et al. (1999). This separation is complicated by the fact that there is not a clear boundary between OC and EC, since OC compounds are less volatile and more optically absorptive with increasing molecular weight and functionality; and the least refractory part of EC may show similar chemical and physical behaviours than high molecular weigh OC. The separation method has been described in detail elsewhere (Szidat et al., 2004a). Briefly, OC is oxidized on a filter at 340 °C in a stream of pure oxygen for 10 min. Evolved CO_2 is trapped cryogenically, quantified manometrically in a calibrated volume, and sealed in ampoules for ^{14}C measurement. Using this method, part of the OC pyrolyses on the filter to form refractory material (an artifact known as "charring") and is therefore not collected. This approach assumes identical fM of the measured and the neglected fraction, which was shown to be correct for "Urban Dust" in NIST reference material SRM 1649a (Szidat et al., 2004b). The uncertainty due to this loss of OC can be estimated as 0.03 of fM_{OC}. This is based on an estimation of ~20 % of OC losses and fM_{EC} measurements with and without water extraction prior to collection and analysis (Szidat et al., 2004a). Therefore, the uncertainties reported here take into account the ^{14}C measurement uncertainty and this 0.03.

Isolation of EC for accurate ^{14}C determination targets a complete removal of OC prior to EC collection with the best possible EC recovery. Since the modern fractions of EC and OC can differ significantly (e.g. Szidat et al., 2004a, 2009), incomplete OC removal could bias the result of the fM in the EC fraction (fM_{EC}). For this study, a new method for EC collection (modified from that described by Szidat et al., 2004a) developed in

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our laboratory (Zhang et al., 2011) was used. A detailed description can be found in the Supplement (Sects. S1 and S2, Figs. S2, S3 and S4). Briefly, water extraction is carried out prior to separation and EC collection process, so that water soluble organic and inorganic compounds are removed (Szidat et al., 2004a, 2009). This minimizes a possible positive artifact due to the aforementioned OC charring during the first thermal steps (to remove OC). This charring would produce additional EC-like material, which would be combusted and collected during the EC step at 650 °C. This new method includes the coupling of a Sunset instrument to the cryo-trap system (as opposed to an oven with a fixed temperature with the Szidat et al. (2004a) method), so that the thermal cycles are defined accurately (see Supplement). The combustion process is carried out under pure oxygen. The thermal program is set to minimize a possible negative artifact resulting from removal of the least refractory part of EC in the first thermal steps prior to EC collection. This method allows us to collect more EC compared to 60–80 % recovery obtained with the Szidat et al. (2004a) method and the fM obtained are thus more representative of the complete EC fraction. The EC recovery was on average 90 % and 86 % for DAURE-W and DAURE-S, respectively. A rough estimate of the uncertainty generated by the 10–14 % EC loss would be an underestimation of fM_{EC} by 0.02–0.04 (Perron, 2010), which results in <5 % (absolute percent) possible underestimation of the biomass burning EC contribution. This possible bias in the fM_{EC} should be taken only as an estimate and therefore it is discussed here but not included in the calculations.

The samples from the MSY summer campaign had very low EC concentrations. Therefore six individual combustions of each of the samples were carried out and the CO_2 collected was combined for a single subsequent ^{14}C analysis.

After the separation and collection of OC and EC as CO_2 samples, ^{14}C analyses were performed at ETH Zurich with the Accelerator Mass Spectrometer MICADAS using a gas ion source (Ruff et al., 2007, 2010).

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2.4 Source apportionment of EC and OC using ^{14}C data

Source apportionment of EC and OC is based on their concentrations, ^{14}C isotopic ratios of these two components, and the expected fM of the corresponding sources. The reference values for the different sources used in the present study are $fM_f = 0$ (for fossil sources); $fM_{bb} = 1.083$ (for biomass burning), corresponding to emissions from burning of 25-yr-old trees harvested in 2007–2008 as determined with a tree-growth model as reported by Mohn et al. (2008); and $fM_{bio} = 1.045$ (for biogenic sources), corresponding to 2008–2009 from the long-term series of atmospheric $^{14}CO_2$ measurements at Jungfraujoch research station (Levin et al., 2010). In the case of EC, the fM of non-fossil sources (fM_{nf}) equals fM_{bb} given that biomass burning is the only source of non-fossil EC. In the case of OC, fM_{nf} is assumed to be the average of fM_{bb} and fM_{bio}, given that the fractions from biomass burning and from biogenic sources are not known a priori, and both sources are thought to play a role in this region. An iterative procedure could be used to refine the initial estimates, however the subsequent differences in the results are small, especially compared to the measurement and method uncertainties, and such a procedure is not used here.

EC is apportioned into EC_f and EC_{nf}, the former attributed to combustion of fossil fuels and the latter attributed to biomass burning (EC_{bb}). EC_f can be mainly attributed to road traffic according to previous studies that found that EC in Barcelona is mainly related to road traffic emissions (Pérez et al., 2010). Residential heating as a source of EC_f is not expected to be very high in the study area due to moderate average temperatures during DAURE-W ($13.3 \pm 2.8\,^{\circ}C$ in Barcelona and $9.5 \pm 4.0\,^{\circ}C$ in Montseny; Pandolfi et al., 2011), and due to the fact that only 9 % of the residential heating in Barcelona uses solid or liquid fossil fuel, the rest natural gas (62 %), electricity (28 %), wood (0.4 %) and other minor systems (0.2 %) (INE, 2001). Other sources such as shipping may also make a contribution to EC_f in Barcelona, although their contribution to PM was found to be relatively low (approximately 20 % of the contribution of vehicular exhaust emissions; Amato et al., 2009).

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OC is separated into OC_f and OC_{nf}. OC_f is attributed to POA and SOA from fossil fuel combustion. As per EC_f, the contribution of residential heating to OC_f is expected to be low. As discussed before, OC_{nf} may have different origins, such as biomass burning POA and SOA, as well as biogenic SOA. However, some other sources such as cooking, biofuel combustion, brake lining dust, natural rubber in tire dust, and others may account for a substantial fraction of the total contemporary carbon, especially in urban areas (Hildemann et al., 1994). In particular several recent studies report a high fraction of cooking aerosol in urban areas (Zheng et al., 2007; Allan et al., 2010; Sun et al., 2011; Huang et al., 2010). We first present results as OC_{nf}, without differentiating between biomass burning OC (OC_{bb}), biogenic OC (OC_{bio}), and other OC_{nf} sources.

In a second step, which allows for comparison with results from other methods, the contribution of biomass burning to OC is estimated based on an assumed ratio for EC/OC in biomass burning emissions $(EC/OC)_{bbe}$, together with the EC_{bb} determined by ^{14}C:

$$OC_{bb} = \frac{EC_{bb}}{(EC/OC)_{bbe}} \quad (2)$$

Nevertheless, the wide range of $(EC/OC)_{bbe}$ ratios found in literature (Table S1) leads to high uncertainties in the estimation of OC_{bb}. The $(EC/OC)_{bbe}$ ratio depends on many factors, such as the biofuel type and the combustion method used. For calculations here, an average $(EC/OC)_{bbe}$ ratio of 0.3 was used, based upon the reported values for common biofuel species in the Mediterranean, with similar combustion methods to those used in Spain (Fine et al., 2004; Gonçalves et al., 2010), and agricultural fires (Chow et al., 2010). SOA formation from biomass burning emissions is quite variable, and a recent summary of seven field studies reports that the net addition of OA mass due to SOA formation averages to 25 % of the POA (Cubison et al., 2011). Therefore SOA formation from biomass burning emissions may lead to a ~20 % underestimation of the OC_{bb} on average.

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2.5 Other source apportionment methods and biomass burning tracers

Results from three other methods are used here for comparison with the ^{14}C-based method for DAURE-W. First, measurements of levoglucosan, an organic tracer of biomass burning (Simoneit et al., 1999) are used. Four different data sets of levoglucosan concentrations are available, measured by four different laboratories. Levoglucosan was determined using the same filters used for ^{14}C analyses (PM_1 48 h samples) by two methods: gas chromatography-mass spectrometry (Agilent 6890N gas chromatograph coupled to a mass spectrometer Agilent 5973N) by the Hungarian Academy of Sciences (lev-HAS), and by proton nuclear magnetic resonance (HNMR, Tagliavini et al., 2006) by the Institute of Atmospheric Sciences and Climate of the Italian National Research Council (lev-ISAC). A third levoglucosan dataset was analyzed by the Finish Meteorological Institute (lev-FMI) in 12 h $PM_{2.5}$ samples collected on quartz fiber filters (Munktell) by high volume (30 $m^3\,h^{-1}$) samplers DIGITEL DHA-80, by high-performance anion-exchange chromatography with electrospray ionization mass spectrometry detection (Saarnio et al., 2010). Finally, a fourth levoglucosan dataset was analyzed in 12 h PM_1 samples collected on quartz fiber filters (Munktell) by high volume (30 $m^3\,h^{-1}$) samplers DIGITEL DHA-80, by gas chromatography coupled to mass spectrometry (van Drooge et al., 2009; van Drooge and Ballesta, 2010) by the Institute of Environmental Assessment and Water Research (lev-IDAEA). When simultaneously available, the different levoglucosan measurements agree reasonably well (Fig. S5), especially those analyzed in the same filters (lev-ISAC and lev-HAS). The highest concentrations are reported by FMI, which can be partially due to the coarser fraction ($PM_{2.5}$) analyzed. In this work, we used the average of the concentrations of lev-HAS and lev-ISAC as they are consistent with most of the measurements, and for maximum overlap with the ^{14}C dataset.

The contribution of primary OC from biomass burning can be estimated from levoglucosan concentrations together with the levoglucosan/OC ratio in biomass burning emissions $(lev/OC)_{bbe}$:

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$$OC_{bb} = \frac{lev}{(lev/OC)_{bbe}} \quad (3)$$

However, the variability of $(lev/OC)_{bbe}$ ratio in the literature is large (Table S1), and the data available for Europe, compared to the US, is scarce (Szidat et al., 2009 and references therein), which results in substantial uncertainty for the results from this method. It is also known that levoglucosan can be oxidized photochemically in the atmosphere (Hennigan et al., 2010; Cubison et al., 2011) and that it can evaporate due to its semi-volatile character (Oja and Suuberg, 1999). Thus estimates from this method using ratios measured for concentrated primary emissions should be considered lower limits. An average $(lev/OC)_{bbe}$ ratio of 0.12 was used (Fine et al., 2004; Schmidl et al., 2008; Sullivan et al., 2008; Szidat et al., 2009; Gonçalves et al., 2010; Saarnio et al., 2010). Nevertheless, given the wide range of ratios reported in the literature, uncertainties were calculated to cover the ratios ranging from 0.07 to 0.17.

A second method used here for the estimation of OM sources, including OM_{bb}, is based on factor analysis of AMS measurements. Two high-resolution AMSs were deployed at the BCN and MSY sites (Mohr et al., 2011; Pandolfi et al., 2011). The AMS instruments, data processing, and analysis techniques have been described in detail elsewhere (DeCarlo et al., 2006; Canagaratna et al., 2007). Positive Matrix Factorization (PMF) of the organic mass spectral data matrix provides information on different sources/components of the OA (Lanz et al., 2007; Ulbrich et al., 2009), such as hydrocarbon-like organic aerosol (HOA), used as a surrogate for urban combustion POA, BBOA as a surrogate for POA from biomass burning, and oxygenated OA (OOA) as a surrogate for total SOA. As discussed above, biomass burning emissions can give rise to SOA from organic gases and also from semi-volatile species from the evaporation of the POA (DeCarlo et al., 2010; Cubison et al., 2011). The SOA formed from biomass burning emissions produces similar mass spectra to SOA from other sources (Jimenez et al., 2009) and thus it is lumped together in the oxygenated OA (OOA) factor.

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The third method used to estimate the biomass burning contribution is based on receptor modeling of offline filter data. Positive Matrix Factorization (PMF by means of the ME-2 scripting; Paatero, 1999; Amato et al., 2009) was applied to a dataset including elemental composition, secondary inorganic compounds, and EC and OC concentrations in PM_1, referred to in this study as PMF-OF (OF standing for offline filter dataset). The offline dataset is discussed in detail elsewhere (Pandolfi et al., 2011). Briefly, 12 h PM_1 samples were collected on quartz fiber filters (Munktell) using DIGITEL DHA-80 high volume (30 $m^3 h^{-1}$) samplers. Major and trace elements, and nitrate, sulfate, ammonium and chloride concentrations were determined following the procedure described in Querol et al. (2001). OC and EC concentrations were measured by a Sunset laboratory instrument (results inter-compared in Sect. 2.2, reported as Sunset2). Details on the receptor model and individual uncertainties are available in Amato et al. (2009). This method provides, among other data products, an estimate of the biomass burning contribution to bulk submicron OC.

Finally, the correlations of the different biomass burning OA estimates and tracers with EC_{bb} (which is the most direct biomass burning tracer) were evaluated. PMF-AMS BBOA was used for DAURE-W. Levoglucosan concentrations (average of lev-HAS and lev-ISAC data sets) were used for DAURE-W. Acetonitrile concentrations measured by a High Sensitivity Proton Transfer Reaction Quadrupole Mass Spectrometer (PTR-MS; Lindinger et al., 1998) at BCN in DAURE-W and DAURE-S, and by a Proton Transfer Reaction Time of Flight (PTR-TOF, Graus et al., 2010; Müller et al., 2010) at MSY in DAURE-W were used. Submicron potassium (K) concentrations were used for DAURE-W and DAURE-S. K concentrations were part of the PMF-OF dataset discused above (Pandolfi et al., 2011). Soluble K concentrations were determined in water extractions of the same samples and they were very similar to total K concentrations. Hence, total K concentrations were used. Although some biomass burning estimates reported in literature are based on K, several recent studies have concluded that fine K can in some instances be dominated by other sources and can be a poor tracer for biomass burning (Zhang et al., 2010; Aiken et al., 2010).

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3 Results and discussion

3.1 EC and OC concentrations

The carbonaceous aerosol at BCN and MSY during the DAURE campaigns showed differences in concentration, fractional composition, and source influences (Figs. 1 and 2). At BCN, the contribution of EC to total carbon was substantially higher than at MSY both in DAURE-W and DAURE-S, representing, on average, 32–37 % at BCN and 15–16 % at MSY. Conversely, the OC fractional contribution was higher at MSY than at BCN (Fig. 1), although the absolute concentrations of OC were higher at BCN (Fig. 2) during DAURE-W, and similar to those at MSY in DAURE-S. OC/EC average ratios (1.7–2.1 at BCN and 5.3–5.8 at MSY) were similar and lower, respectively, than those reported by previous studies at the same sampling sites (2.5 for PM_1 at BCN and 11 for $PM_{2.5}$ at MSY; Pérez et al., 2008b; Pey et al., 2009).

3.2 EC sources

During the winter period, EC_f accounted for 87 ± 1 % (average ± propagated measurement uncertainty of only ^{14}C measurements) of EC at BCN, whereas at MSY this percentage was 66 ± 3 %. In summertime, these values were 91 ± 1 % and 79 ± 4 % at BCN and MSY, respectively. As explained above, EC_f is attributed to fossil fuel combustion, mostly road traffic, and EC_{nf} to biomass burning.

The high contribution of fossil fuel combustion to EC concentrations in BCN is in agreement with Pérez et al. (2010) and Reche et al. (2011), who found that black carbon concentrations varied mainly according to road traffic conditions. In both seasons, the EC_f contribution to EC at the urban site is higher than at the rural site, as expected. In absolute values, the difference is larger. EC_f at BCN was 6.3 times higher than at MSY in winter and 4.5 times higher in summer (Fig. 2). This is consistent with the BCN/MSY ratios found for NO_x concentrations, 9 and 6 for winter and summer, respectively, although the instruments do not measure purely NO_x and also include

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some of the more oxidized nitrogen species (NO_z, Steinbacher et al., 2007; Dunlea et al., 2007). Assuming that a substantial fraction of the NO_x at MSY comes from the coastal polluted regions similar to the BCN urban area, these ratios can be considered estimates of the dilution of urban and regional pollution during transport to MSY. CO concentrations were not available for comparison. The fact that the ratios are higher for NO_x than EC is consistent with the fact that NO_x is a reactive tracer with a lifetime on the order of 1 day and some of the reaction products (HNO_3) deposit very quickly to the surface and are not sampled by NO_x analyzers, while EC is unreactive. The higher contributions of EC_{nf} in winter with respect to summer are likely due to higher emissions from residential heating and open burning of agricultural biomass (banned by law from 15 March to 15 October, Decreto 64/1995), as wild fires are expected to have low impact, from negligible to 1 $\mu g\,m^{-3}$ of OC (Fig. S6).

3.3 Fossil vs. contemporary OC

During the winter period, OC_f (thought to be mainly due to road traffic, as explained above) was 40 ± 4 % of OC at BCN and 31 ± 4 % at MSY. These values are similar to those obtained during winter at Zurich, Switzerland (32 % OC_f/OC, Szidat et al., 2006), and at Göteborg, Sweden (35–45 % at an urban site and 35–40 % at a rural site, Szidat et al., 2009). A priori, it could be expected that fossil sources may have a higher influence in Spain due to the lesser use of wood burning for residential heating (less than 1 % of the heating energy, INE, 2001). On the other hand, biogenic SOA may be higher under milder Spanish winter conditions compared to Switzerland or Sweden since the temperatures are higher, and biogenic volatile organic compounds (VOCs) emissions still occur in winter albeit at lower intensity than in summer (Seco et al., 2011). Therefore the differences in both sources may compensate each other, leading to similar OC_f fractions.

In summer OC_f was 48 ± 4 % of OC at BCN and 25 ± 5 % at MSY; this again being comparable to contributions at Göteborg, Sweden, in summer (31–47 %, Szidat et al., 2009). Summer results for BCN (with the highest OC_f fraction from the present study)

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are comparable to results from Mexico City (49–62 %, Aiken et al., 2010). Absolute OC_f concentrations in winter were higher than in summer (by 0.4 $\mu g\,m^{-3}$) at BCN. This was likely due to stronger accumulation of pollutants during the cold season with lower atmospheric dispersion, and perhaps to higher fossil combustion such as for residential heating.

At MSY, OC concentrations were similar for both seasons (Fig. 2). The ratio BCN/MSY for OC_f concentrations was 2.1–2.4, which is lower than the corresponding ratio for EC_f mentioned above (4.5–6.3). This is consistent with formation of fossil SOA during transport from urban and regional sources to the MSY site, and also consistent with the higher NO_x ratios discussed above. Further evidence is provided by the comparison of the ratios of OC_f/EC_f for both sites. The average ratio ± standard deviation (variability) was 1.0 ± 0.1 in winter and 0.9 ± 0.2 in summer at BCN, and 2.6 ± 0.7 in winter and 1.8 ± 0.5 in summer at MSY. The error for MSY in summer (0.5) is the propagated measurement uncertainty, since no variability is available because there was only one pooled sample for EC. The low variability of the ratios in BCN suggests that the OC_f is mainly primary, or that the secondary fraction changes little, e.g. if it is formed fast enough (Robinson et al., 2007; Chirico et al., 2010) so that it still correlates with the EC_f. This is also supported by the good correlation between OC_f and EC_f ($R^2 = 0.81$, Fig. S7). At MSY the larger ratios indicate that a substantial fraction of the OC_f may be due to fossil SOA formation driven by photochemical reactions during the transport to the rural site. The larger variability of the OC_f/EC_f at MSY, although partially due to the relatively high measurement uncertainty, indicates that the formation of fossil SOA may be more variable. The difference in the ratio in winter and summer at MSY is not significant due to the high uncertainties.

OC_{nf} at BCN was twice as high in winter than in summer. This can be attributed to a higher contribution of biomass burning and reduced mixing in winter with respect to summer in the Barcelona region, as indicated by the fact that EC_{nf} was also twice as high in winter. At MSY, OC_{nf} was similar in summer and winter, despite the lower biomass burning contribution in summer as evidenced by the lower EC_{nf}. This can

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likely be explained by a higher contribution of biogenic SOA in summer, due to higher biogenic emissions and enhanced photochemistry. Seco et al. (2011) report summer/winter ratios of ~10 for biogenic VOCs ambient concentrations at the rural site.

3.4 Further source apportionment of the non-fossil OC

OC_{nf} can be apportioned to the different sources with some additional assumptions. The estimations carried out in the present study include biomass burning (OC_{bb}), biogenic SOA (OC_{bio}) and other non-fossil contributions called in this study as urban non-fossil OC (OC_{urb-nf}), such as cooking and tire wear. Results are shown in Fig. 3. OC_{bb} was estimated with the method described in Sect. 2.4 (Eq. 2). OC_{bb} is estimated to account for 30–35 % of the OC_{nf} at both sites and seasons (17–21 % of total OC), with the exception of MSY in summer, where it only accounted for 16 % of the OC_{nf} (12 % of total OC). The contribution from OC_{urb-nf} was calculated from the OC_f contribution, based on the assumption that OC_{urb-nf} is ~20 % of the total urban OC contribution (OC_f + OC_{urb-nf}) (Hildemann et al., 1994; Hodzic et al., 2010). OC_{urb-nf} was estimated as 0.2–0.3 $\mu g\,m^{-3}$ at BCN, which is 16–23 % of the OC_{nf} (10–12 % of total OC). At MSY, the OC_{urb-nf} was lower (0.14 and 0.11 $\mu g\,m^{-3}$ in winter and summer, respectively, 8–11 % of the OC_{nf}, 6–8 % of total OC). As discussed above, OC_{urb-nf} may be underestimated if recent studies of a cooking contribution similar to the traffic OC contribution are applicable to this region. The OC_{bio} contribution was slightly higher in summer (1.0 $\mu g\,m^{-3}$) than in winter (0.7 $\mu g\,m^{-3}$) at MSY, while OC_{bio} was lower in summer at BCN. The absence of a strong increase in OC_{bio} concentration between winter and summer, compared to a factor of 10 increase in biogenic VOCs is very surprising. Although a larger fraction of the biogenic SOA species may remain in the gas-phase in the summer compared to the winter, this effect is thought to be small (e.g. Martin et al., 2010). This disagreement remains unexplained with the tools available at the moment, and further research will be needed to find out the possible causes, but it highlights the uncertainties in the estimation methods.

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3.5 Day-to-day variation

There was only moderate day-to-day variation in the fractional contributions to TC throughout the winter period. The fossil fraction of TC (TC_f) (48 h averages) varied between 42–68 % at BCN and between 27–50 % at MSY (Fig. 4). The different meteorological scenarios during the campaign are described in detail by Pandolfi et al. (2011). Briefly, there were three types of scenarios during winter: A, characterized by recirculation of air masses and accumulation of pollutants with both MSY and BCN within the mixing layer; B, when the mixing layer height was very low and hence MSY was above it; and C, with Atlantic advection which resulted in flushing pollutants from the region. There were some transition periods between different scenarios indicated as T in Fig. 4. Note that due to the sampling periods (48 h in winter and 24 h in summer) more than one type of scenario may correspond to a single sample. In these cases the prevailing scenario is in bold in Fig. 4.

Samples from 17 March to 25 March were collected during periods with prevailing scenario A conditions. For those samples TC concentrations at BCN were about twice those at MSY. The TC_f, EC_f and OC_f contributions at BCN and MSY for these samples were highly correlated (R^2 = 0.83–0.98; Fig. 5). When TC_f was more dominant at BCN (19 March–21 March, 68 % of TC), the contribution of TC_f at MSY increased with respect to the rest of the days (reaching 50 %). Conversely, when TC_f showed a lower contribution at BCN (21 March–23 March and 23 March–25 March; 42 % and 45 %, respectively), TC_f was also lower at MSY (32 %) (Fig. 4a and b), which reflects the stronger coupling of both sites due to the shared mixed layer.

Under scenario B conditions, concentrations of TC at BCN were about 3 times those at MSY and the fractional contributions were different, consistent with the meteorological characterization of a decoupling between the two sites. There was no correlation for the samples collected under scenario B (Fig. 5). At BCN, EC_f contributed substantially to TC (29–30 %), whereas at MSY its contribution was lower as typical for this site (9–13 %) and OC_{nf} accounted for more than 50 % of TC (Fig. 4a and b).

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During the summer campaign, a time-resolved comparison of TC_f between both sites is not possible due to the lack of time-resolved data for the EC fractions at MSY, as explained above. TC_f varied between 47–75 % at BCN (Fig. 4c and d). The different meteorological scenarios during the summer campaign are described in detail by Pandolfi et al. (2011). Briefly, scenario D was characterized by regional pollution; E was characterized by Atlantic advection (similar to winter scenario C); and F was influenced by air masses coming from North Africa. Even though 9 July–10 July and 11 July–12 July samples were collected under the same type of scenario (D scenario), the first sample showed TC concentrations at BCN 3 times those at MSY, whereas for the second sample the concentrations were similar between sites, suggesting some variability in dispersion between those periods. For the rest of the samples, collected under scenario F, the fractional contribution variations were similar at MSY and BCN, although there was not a clear correlation in concentrations as that found for winter (Fig. S8).

3.6 Combination of ^{14}C and PMF-AMS results

A comparison of the relative contributions to OC determined by the ^{14}C and PMF-AMS techniques is shown in Fig. 6 (DAURE-W only). We compare fractional contributions as they should not be affected by concentration inaccuracies in either method. To compare the results from the ^{14}C method to PMF-AMS measurements, OC was calculated from PMF-AMS OM as explained in Sect. 2.2. These calculations result in hydrocarbon-like organic carbon (HOC), cooking organic carbon (COC), biomass burning organic carbon (BBOC), and oxygenated organic carbon (OOC) contributions. To facilitate comparison to ^{14}C results, the sources identified by PMF-AMS were divided into fossil and non-fossil. HOC from BCN was included in the fossil sources. For MSY, HOC was assumed to be 80 % of fossil origin (HOC_f) and 20 % from urban non-fossil sources (HOC_{nf}) (based on Hildemann et al., 1994). COC and BBOC were included in the non-fossil sources. As OOC is thought to be a surrogate for total secondary OC and originates from both fossil and contemporary sources, OOC was divided in fossil and non-fossil (OOC_f and OOC_{nf}) according to the OC_f/OC_{nf} ratio identified by the ^{14}C

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method, so that the resulting total OC_f/OC_{nf} ratio from PMF-AMS sources equals the OC_f/OC_{nf} ratio from ^{14}C method.

At BCN, OC_f is estimated to be ~35 % secondary, so a major fraction of the OC_f in BCN is estimated to be primary (~65 %). This fossil secondary percentage is relatively low when compared to findings from Robinson et al. (2007), who predict a high proportion of SOA formation from vehicle emissions. OC_{nf} is a combination of COC, OOC_{nf} and primary BBOC. OOC, a surrogate for total secondary OC, is mostly non-fossil (~70 %), with this fraction being due to biogenic sources, biomass burning, and urban non-fossil sources.

At MSY, OC_f is estimated to be ~85 % secondary. This is consistent with previous conclusions based on the higher OC_f/EC_f ratio at MSY than at BCN (see Sect. 3.3), which also indicated a higher contribution of fossil SOA at MSY. Like at BCN, the OOC determined with the AMS is mostly non-fossil (~70 %), and may have different origins such as biogenic sources or biomass burning. Hence, the combination of both techniques allows a better characterization of the carbonaceous aerosol sources, distinguishing the primary and secondary contributions.

3.7 Comparison of biomass burning OC determined by different approaches

In Fig. 7 we compare the biomass burning OC (OC_{bb}) concentrations during winter estimated using ^{14}C data with those from several other techniques, including PMF-AMS, PMF-OF, and the tracer-based method using levoglucosan. Note that for the results from the PMF-AMS and levoglucosan methods the concentrations refer to only primary BBOC (Grieshop et al., 2009; DeCarlo et al., 2010). No biomass burning source was identified at BCN by PMF-OF although this technique enabled identification of such a source at MSY. Lack of identification at BCN may be due to the presence of multiple additional sources, which complicate the identification of relatively small sources (the relative contribution of BBOC to OC was lower than that at MSY according to AMS-PMF results).

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Biomass burning contributions estimated by the ^{14}C technique are similar or in most cases slightly higher than those from other techniques. The difference compared to the AMS and levoglucosan results may be partially explained by the presence of biomass burning SOC, which is not included in the OC_{bb} calculated using these methods, and would be expected to be ~25 % of POA (Cubison et al., 2011). It is also possible that the biomass burning OC contribution estimated by the ^{14}C method is overestimated, if the $(EC/OC)_{bbe}$ assumed for our calculations is too low for the biomass burning taking place in the study area. Nevertheless, the different estimates follow the same time trend, with the exception of PMF-OF. Thus it appears that PMF-OF is less accurate in the retrieval of this source.

It is of interest to further evaluate the similarities of the different biomass burning estimation methods and tracers, without the possible systematic uncertainties associated with the conversion factors used to estimate the OC_{bb} from different tracers (such as $(EC/OC)_{bbe}$, $(lev/OC)_{bbe}$, and OM/OC for biomass burning). Scatter plots of the different tracers and estimates are shown in Fig. 8. BBOA estimated by PMF-AMS correlates well with EC_{bb} ($R^2 = 0.84$, using all samples), as seen in Fig. 8a. The correlation of levoglucosan concentrations with EC_{bb} shows an $R^2 = 0.57$ with a slope of 0.20 using all samples (Fig. 8b). The slope is the lev/EC_{bb} ratio, which is in the lower range of the lev/EC_{bb} values found in the literature, which vary from 0.15 to 2 in most cases (Schmidl et al., 2008; Sullivan et al., 2008; Gonçalves et al., 2010; Saarnio et al., 2010), although much higher values (up to 10 or 15) have also been reported (Fine et al., 2004; Sullivan et al., 2008). This may indicate lower initial emission ratios, or some oxidation or evaporation of levoglucosan during atmospheric transport.

Acetonitrile concentrations show correlation with EC_{bb} ($R^2 = 0.67$, Fig. 8c). Although concentrations at MSY were close to typical acetonitrile continental background concentrations (e.g. Aiken et al., 2010), they are consistent with low EC_{bb} concentrations.

K concentrations show lower correlation with EC_{bb} for low concentrations (Fig. 8d), with $R^2 = 0.51$ in DAURE-W and $R^2 = 0.48$ in DAURE-S. The winter data suggest the presence of a background level of bulk K (intercept when $EC_{bb} = 0$) of ~40 ng m^{-3}, that

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may be due to other sources than by biomass burning, such as food cooking (Hildemann et al., 1991; Schauer et al., 1999), vegetative detritus (Hildemann et al., 1991), fly ash (Lee and Pacyna, 1999), and dust such as feldspars and clay minerals. This is consistent with findings by Zhang et al. (2010) and Aiken et al. (2010), and the latter authors reported a background non-biomass burning K concentration of ~120 ng m^{-3} in Mexico City. Moreover, K emissions depend on the burning conditions. The influence of cooking on the K concentrations is supported by the higher R^2 (0.74) found for multilinear regression of K concentrations vs. BBOA and COA concentrations found by PMF-AMS at BCN, compared to the R^2 (0.54) for K concentrations vs. BBOA. Nevertheless, the noise in the K data is quite high (see measurement uncertainty as error bars for two data points in Fig. 8c), which should be considered when evaluating the robustness of the conclusions from these data. Therefore, given the moderate correlation of K with EC_{bb} and the high uncertainty in K concentrations, K is not the best tracer for biomass burning emissions for the present study.

4 Conclusions

The contribution of EC to TC at BCN was substantially higher than at MSY both in the winter and the summer campaign. The OC contribution, although higher at MSY as a fraction of TC, was higher at BCN in absolute concentration.

At BCN, 87 and 91 % of the EC, in winter and summer, respectively, had a fossil origin (mainly road traffic), whereas at MSY these percentages were 66 and 79 %, respectively. In absolute values, EC_f at BCN was 4.5–6.3 times that at MSY, which is in agreement with dilution ratios estimated from NO_x concentrations. Higher concentrations of EC_{nf} were found in winter than summer and attributed to a higher biomass burning contribution during winter.

The contribution of fossil sources to OC (mainly POA and SOA from road traffic) was 40 % at BCN and 31 % at MSY in winter, and 48 % at BCN and 25 % at MSY in summer. These values are similar to those observed in Zurich, Switzerland, and in

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Göteborg, Sweden. The highest contribution of fossil sources to total carbon found in the present study is similar to the average values from Mexico City. The absolute OC_f concentrations in winter were slightly higher than in summer at BCN due to stronger accumulation of pollutants due to reduced dispersion, whereas at MSY the concentrations were similar for both seasons. By combining results from the ^{14}C and PMF-AMS techniques, we can estimate that the OC_f at BCN is ~65 % primary. The formation of secondary OC_f appears to be rapid enough that the OC_f/EC_f stays about constant for the timescales of our samples. At MSY the OC_f is mainly secondary (~85 %), as determined both by the high OC_f/EC_f ratio at MSY, and the combination of ^{14}C and PMF-AMS results.

OC_{nf} at BCN was higher in winter than in summer probably due to a higher contribution of biomass burning. At MSY, OC_{nf} was higher in summer which is explained by a higher contribution of biogenic emissions (partially offset by decreased biomass burning). Nevertheless, the estimated biogenic secondary OC does not increase proportionally to the order-of-magnitude increase observed for biogenic volatile organic compounds (VOCs) between winter and summer, which highlights the uncertainties in the estimation of that component.

There was moderate day-to-day variation throughout the study periods (with the fossil contribution to total carbon being between 42–68 % at BCN and 27–50 % at MSY in winter, and between 47–75 % at BCN in summer), but the differences between BCN and MSY in TC levels and source contributions depended largely on the meteorological conditions. Hence, during regional pollution accumulation episodes, concentrations and source distributions were similar at both sites; whereas during stagnation episodes when the boundary layer was below the MSY sampling site, the sites were decoupled and the total carbon levels and fossil sources contribution were higher at BCN than at MSY.

Biomass burning OC contributions estimated by the ^{14}C technique were similar or slightly higher than those from other techniques, nonetheless they were reasonably correlated. The difference with the PMF-AMS and levoglucosan method results could

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be partially explained by the contribution of SOA formed from biomass burning emissions (not included in the OC_{bb} from these methods), and/or an overestimation of OC_{bb} contribution due to a non-representative biomass burning EC/OC ratio used for the calculations. Bulk submicron K concentrations, although commonly used as tracer for biomass burning, appear influenced by other sources other than by biomass burning during winter, as observed in some previous studies. PMF-AMS BBOA and acetonitrile concentrations are the biomass burning markers that correlate better with EC_{bb}.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/23573/2011/acpd-11-23573-2011-supplement.pdf.

Acknowledgements. This work was supported by the Acción Complementaria DAURE CGL2007-30502-E/CLI, the GRACCIE project CSD2007-00067, and the VAMOS project CGL2010-19464/CLI. This work was also supported by the EU FP6 project EUCAARI and the IMBALANCE project within the Centre of Competence for Environment and Sustainability (CCES). M. C. Minguillón was partially supported by a Postdoctoral Grant in the frame of Programa Nacional de Movilidad de Recursos Humanos del Plan nacional de I-D+I 2008–2011 from the Spanish Ministry of Science and Innovation. D. A. Day, A. M. Ortega, and J. L. Jimenez were partially supported by US NSF grants ATM-0920940 and ATM-0919189 (from Atm. Chem. and OISE – Office of International Science and Engineering), and by NOAA grant NA08OAR4310565. A. M. Ortega was supported by DOE SCGF (ARRA/ORISE/ORAU) Fellowship DE-AC05-06OR23100. J. Peñuelas and R. Seco were supported by the Spanish Government projects CGL2010-17172 and Consolider Ingenio Montes CSD2008-00040.

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Table 1. Compilation of literature values of % fossil carbon in different fractions and sites and results from the present study.

Reference	Fraction	Location	Comments	EC method*	EC/BC	OC	TC
Szidat et al. (2006)	PM_{10}	Zurich urban	summer	Theodore	94	31	
			winter		75	32	
			spring		88	28	
Szidat et al. (2007)	PM_{10}	Alpine Valleys	winter	Theodore	29–96	9–28	
Szidat et al. (2007)	PM_1	Alpine Valleys	spring	Theodore	27–82	9–58	
Perron et al. (2010)	PM_{10}	Industrial Alpine Valley	winter	Theodore	53–82	16–45	
Szidat et al. (2009)	PM_{10}	Sweden urban	summer	Theodore	84–97	31–47	
			winter		87–91	35–45	
Szidat et al. (2009)	$PM_{2.5}$	Sweden rural	winter	Theodore	64–70	35–40	
Zencak et al. (2007)	TSP	Sweden background	winter	BC, CTO375	12		
Zencak et al. (2007)	TSP	Sweden urban	winter	BC, CTO375	30		
Andersson et al. (2011)	TSP	Sweden background	winter	BC, CTO375	62		
			autumn		55		
Andersson et al. (2011)	TSP	Sweden urban	winter	BC, CTO375	57		
			autumn		65		
Gilardoni et al. (2011)	$PM_{2.5}$	Italy rural	year	None, calculated indirectly	52	22	
Gelencser et al. (2007)	$PM_{2.5}$	Aveiro, Portugal, rural	winter	None, calculated indirectly	17	20	
			summer		92	17	
Gelencser et al. (2007)	$PM_{2.5}$	Puy de Dome, France, elevated rural	winter	None, calculated indirectly	94	26	
			summer		97	14	
Gelencser et al. (2007)	$PM_{2.5}$	Schauinsland, Germany, elevated rural	winter	None, calculated indirectly	86	15	
			summer		95	17	
Gelencser et al. (2007)	$PM_{2.5}$	Sonnblick (Austrian Alps), free troposphere	winter	None, calculated indirectly	80	29	
			summer		95	16	
Gelencser et al. (2007)	$PM_{2.5}$	K-Puszta, Hungary, rural	winter	None, calculated indirectly	59	25	
			summer		90	10	
Gustaffson et al. (2009)	TSP	Maldives rural	winter	BC, CTO375	31		
Gustaffson et al. (2009)	TSP	West India mountain	spring	BC, CTO375	36		
Handa et al. (2010)	PM_{10}	Okinawa Island, Japan	Asian dust event (spring)	BC, CTO375	59	38	
			non Asian dust event (spring)	BC, CTO375	33	6	
Aiken et al. (2010)	PM_1	Mexico City	low fire (winter–spring)	–		62	72
			high fire (winter–spring)	–		49	59
This study	**PM_1**	**Barcelona urban**	**summer**	**Modified**	**91**	**48**	
			winter		**87**	**40**	
This study	**PM_1**	**Montseny rural**	**summer**	**Modified**	**79**	**25**	
			winter		**66**	**31**	

* Method for isolating the elemental carbon: Theodore method (Szidat et al., 2004a and b) has yields of 60–80 % of the total EC determined by thermo-optical methods; BC, CTO375 method (Gustafsson et al., 1997 and 2001) recovers a fraction called BC, having yields of around 10 % of the total EC determined by thermo-optical methods.

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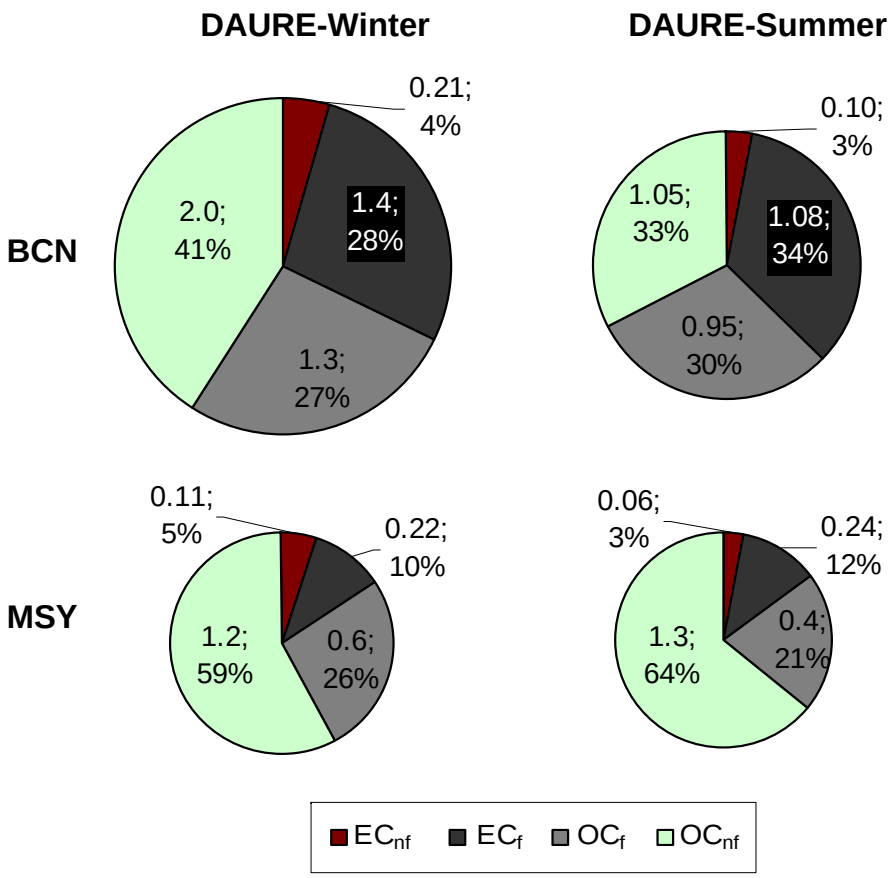

Fig. 1. Fossil (f) and non-fossil (nf) fractions of total carbon; concentrations in $\mu g\,m^{-3}$ and % of total carbon.

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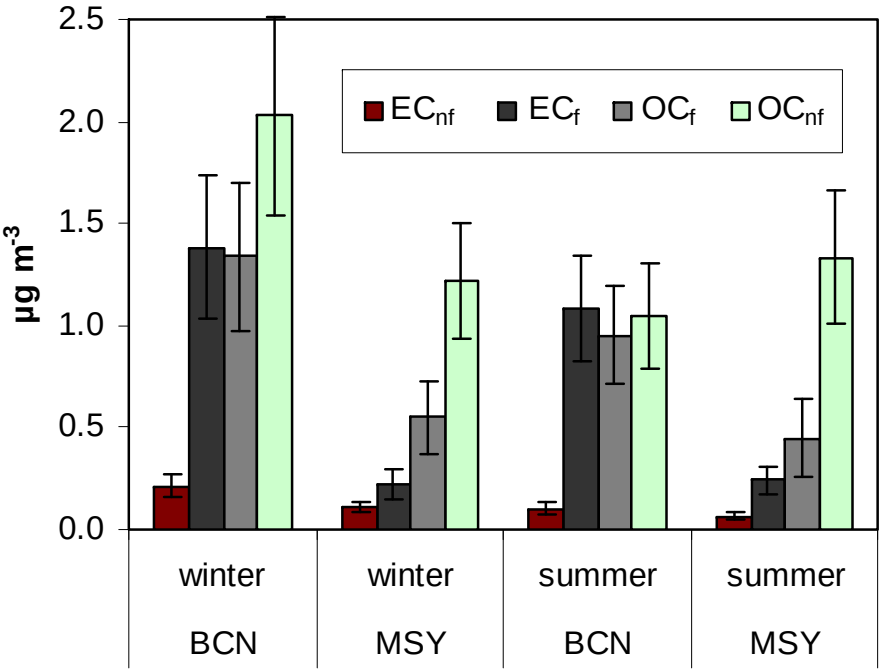

Fig. 2. Average absolute concentrations of the fossil (f) and non-fossil (nf) fractions of EC and OC ($\mu g\,m^{-3}$).

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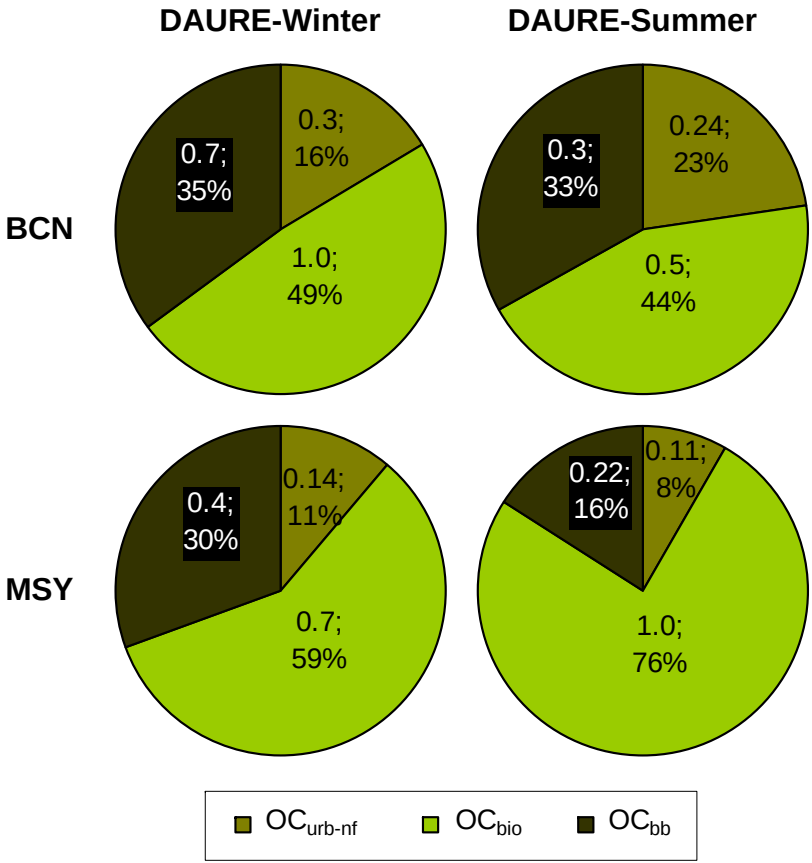

Fig. 3. Source apportionment to non-fossil organic carbon ($\mu g\,m^{-3}$). OC_{urb-nf}: urban non-fossil organic carbon; OC_{bio}: biogenic organic carbon; OC_{bb}: biomass burning organic carbon.

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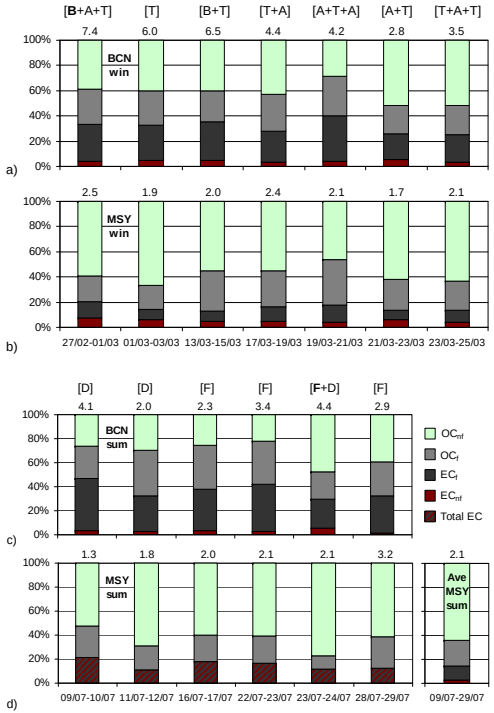

Fig. 4. Variation of the fossil (f) and non-fossil (nf) fractions of EC and OC during the study periods (date format: dd/mm). The atmospheric scenarios and the total carbon concentrations are listed on top of each bar in $\mu g\,m^{-3}$. Scenario A: air masses recirculation and accumulation of pollutants (MSY and BCN within the mixing layer); B: mixing layer height below MSY; D: regional pollution; F: air masses from North Africa; T: transition between different scenarios. In bold the prevailing scenario when more than one occurred during the same sampling period. **(a)** winter BCN; **(b)** winter MSY; **(c)** summer BCN; **(d)** summer MSY. For summer MSY, no distinction of EC_f vs. EC_{nf} is given for the individual days, because samples were pooled for analyses (see text).

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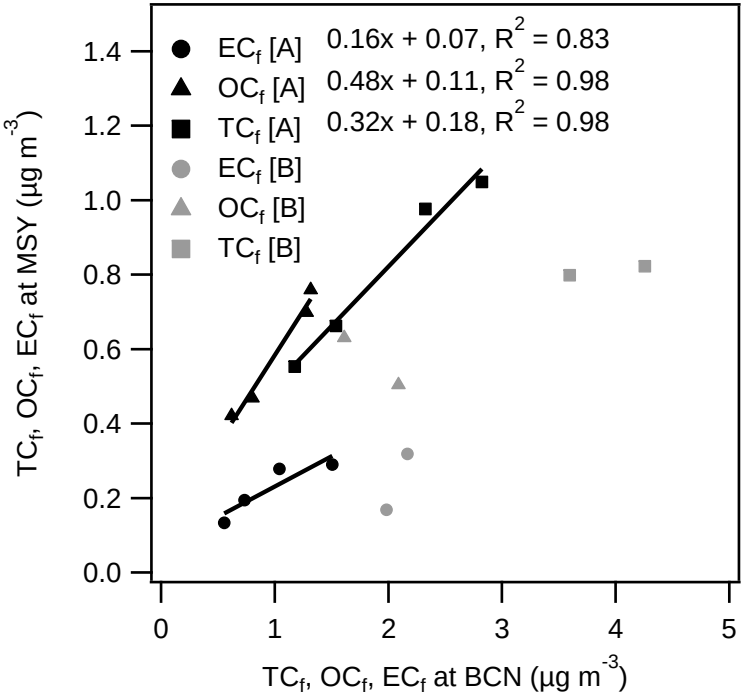

Fig. 5. TC_f, EC_f and OC_f contributions at MSY vs. TC_f, EC_f and OC_f contributions at BCN during scenario [A] and during scenario [B]. Lines and equations correspond to orthogonal distance regressions.

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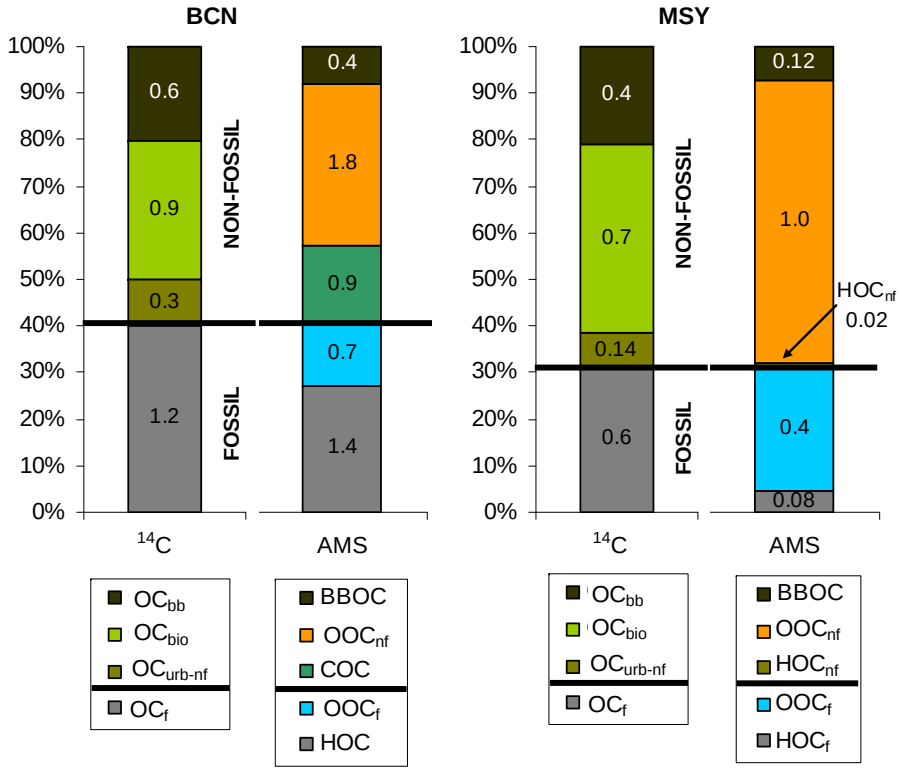

Fig. 6. Relative source apportionment to organic carbon during DAURE-W according to the ^{14}C technique and PMF results of AMS measurements. Numbers indicate the absolute concentrations in μg m^{-3}. BCN averages exclude 1 March–3 March and 13 March–15 March samples because of low availability of AMS data. HOC: hydrocarbon-like organic carbon; OOC: oxygenated organic carbon (secondary); COC: cooking organic carbon; BBOC: primary biomass burning organic carbon; OC$_{urb-nf}$: urban non-fossil organic carbon.

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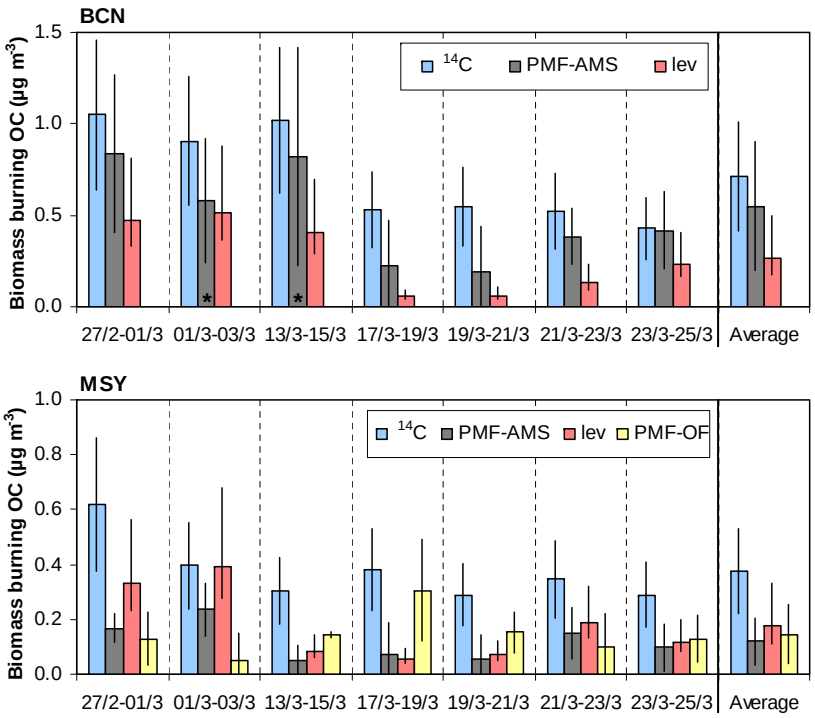

Fig. 7. Concentrations of OC due to biomass burning (µg m^{-3}) estimated with different methods: the ^{14}C technique, PMF-AMS, levoglucosan-tracer method, and PMF-OF. * low AMS data availability for the 48 h period. Error bars in the ^{14}C technique account for the uncertainty of the ^{14}C method and the uncertainty of the $(EC/OC)_{bbe}$ ratio (from 0.2 to 0.4); error bars in the PMF-AMS are an estimation of the uncertainty of the biomass burning contribution; error bars in the levoglucosan-tracer method reflect the variability of the $(lev/OC)_{bbe}$ ratio from 0.07 to 0.17; error bars in the PMF-OF are standard deviation of the four 12 h samples included in each of the 48 h average periods. Date format: dd/m.

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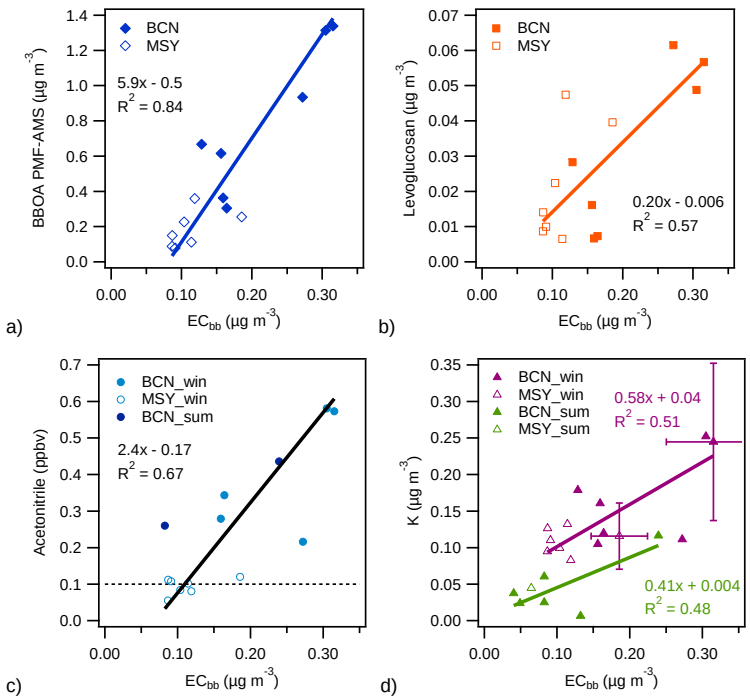

Fig. 8. Scatter plot of **(a)** biomass burning organic aerosol contribution estimated from PMF-AMS vs. biomass burning elemental carbon estimated by ^{14}C method (EC_{bb}) in DAURE-W; **(b)** levoglucosan concentrations (average of lev-HAS and lev-ISAC measurements) vs. EC_{bb} in DAURE-W; **(c)** K concentrations vs. EC_{bb} in DAURE-W (purple) and DAURE-S (green), error bars indicate measurement uncertainty, only shown for two data points for clarity; **(d)** acetonitrile concentrations vs. EC_{bb} in DAURE-W; dotted line indicates typical continental background acetonitrile concentrations (although lower background values are possible for air with recent contact with the ocean). Correlation coefficients were calculated using all data points shown in the plots. Regression lines were calculated with orthogonal distance regressions.

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