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Effects of aging on organic aerosol from open biomass burning smoke in aircraft and lab studies

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Abstract

Biomass burning (BB) is a large source of primary and secondary organic aerosols (POA and SOA). This study addresses the physical and chemical evolution of BB organic aerosols. Firstly, the evolution and lifetime of BB POA and SOA signatures observed with the Aerodyne Aerosol Mass Spectrometer are investigated, focusing on measurements at high-latitudes acquired during the 2008 NASA ARCTAS mission, in comparison to data from other field studies and from laboratory aging experiments. The parameter f_{60}, the ratio of the integrated signal at m/z 60 to the total signal in the organic component mass spectrum, is used as a marker to study the rate of oxidation and fate of the BB POA. A background level of $f_{60} \sim 0.3\% \pm 0.06\%$ for SOA-dominated ambient OA is shown to be an appropriate background level for this tracer. Using also f_{44} as a tracer for SOA and aged POA, a novel graphical method is presented to characterise the aging of BB plumes. Similar trends of decreasing f_{60} and increasing f_{44} with aging are observed in most field and lab studies. At least some very aged BB plumes retain a clear f_{60} signature. A statistically significant difference in f_{60} between highly-oxygenated OA of BB and non-BB origin is observed using this tracer, consistent with a substantial contribution of BBOA to the springtime Arctic aerosol burden in 2008. Secondly, a summary is presented of results on the net enhancement of OA with aging of BB plumes, which shows large variability. The estimates of net OA gain range from $\Delta\text{OA}/\Delta\text{CO(mass)} = -0.01$ to ~ 0.07, with a mean $\Delta\text{OA/POA} \sim 25\%$. With these ratios and global inventories of BB CO and POA a global net OA source due to aging of BB plumes of $\sim 9\,\text{Tg OA yr}^{-1}$ is estimated, of the order of 5% of recent total OA source estimates. Further field data following BB plume advection should be a focus of future research in order to better constrain this potentially important contribution to the OA burden.

1 Introduction

Organic aerosols (OA) are an important subset of the sub-micron aerosol population worldwide (Murphy et al., 2006; Zhang et al., 2007). Despite intensive research, the impacts of OA on climate, human health and visibility are poorly constrained and further understanding of their sources, physical and chemical properties and atmospheric processing is needed. Biomass-burning (BB) aerosols are composed of a large fraction of organic matter (BBOA), and are an important global contributor to the global OA load due to their emissions of primary OA (POA) (e.g. Bond et al., 2004; de Gouw and Jimenez, 2009). Recent studies have demonstrated the semi-volatile nature of BB POA, which can lead to substantial evaporation upon dilution of BB plumes (Robinson et al., 2007; Huffman et al., 2009a, b). BB emissions have been recently confirmed as a potentially large source of secondary OA (SOA), at least some of which may be formed from reactions of evaporated POA (Grieshop et al., 2009a, b). The net enhancement of the OA mass after evaporation and SOA formation in BB plumes has only recently been quantified in several recent field studies using fast instrumentation, and has sometimes been substantial (e.g. Yokelson et al., 2009) and other times negligible (Capes et al., 2008; Hecobian et al., 2011). Results from laboratory studies of the aging of open BB emissions mirror these findings, demonstrating a wide range of measured net OA production depending on, among other factors, the fuel and burning conditions (Hennigan et al., 2010b; Ortega et al., 2010). Further understanding of the magnitude and extent of both the primary and secondary components of BBOA is required to fully assess the impacts from local to global geographical scales.

The chemical aging of BB POA and formation of oxygenated organic aerosol (OOA) due to photochemistry has been observed in both chamber (Grieshop et al., 2009b; Jimenez et al., 2009) and field studies (DeCarlo et al., 2010). Following from the study of Alfarra et al. (2004), the changing oxidation of OA under the influence of photochemical processes has been extensively described in the literature using the parameter f_{44}, the fraction of the OA mass spectrum signal at *m/z* 44 in Aerodyne Aerosol Mass

Spectrometer (AMS; Canagaratna et al., 2007) data. (Additional ratios for other *m/z* i, f_i, are similarly defined for other integer mass signals). Higher f_{44} values represent higher fractions of OOA and/or more-oxidised OOA, which has been shown to be a surrogate for SOA under most conditions (Volkamer et al., 2006; Jimenez et al., 2009). Some OOA can be formed via heterogeneous aging of POA, although this process is slower than SOA formation (Jimenez et al., 2009; George and Abbatt, 2010). f_{44} has also been shown to be linearly correlated with the elemental oxygen/carbon ratio (O:C) of ambient OA (Aiken et al., 2008). Higher f_{44} and O:C are also associated with decreasing volatility of the OOA, giving rise to the lumped OOA subtypes semi-volatile-OOA (SV-OOA) and low-volatility-OOA (LV-OOA) (Huffman et al., 2009; Jimenez et al., 2009; Cappa and Jimenez, 2010). All of the previously reported systems in the literature have shown chemical transformations that push the measured OA toward LV-OOA, independent of the original OA source (Jimenez et al., 2009; Ng et al., 2010), with an endpoint in f_{44} space at ~0.27. Beyond this point, it has been suggested that further chemical transformations are either slow or result in OA loss through volatilisation (Jimenez et al., 2009; Kessler et al., 2010; Kroll et al., 2011).

Estimates of BB aerosol concentrations from field data (containing OA also from various non-BB sources) have been traditionally based on tracer species. The two most commonly used tracers are potassium and levoglucosan. Potassium (K) is not reactive, but Zhang et al. (2010) report poor correlation between K and fire counts in the Southeast US, which they attribute to the influence of other K sources such as soil dust, sea salt, vegetation and meat cooking. A high K background due to non-BB sources was also reported by Aiken et al. (2010) for Mexico City. Levoglucosan is an organic molecule formed in the pyrolysis of cellulose that is emitted in substantial amounts by BB sources (Simoneit et al., 1999), but it has been shown in recent studies to degrade during photochemical aging (Hennigan et al., 2010a).

Recently BBOA has also been identified in a range of environments through deconvolution of OA mass-spectra from the AMS (e.g. Alfarra et al., 2007; Jimenez et al., 2009; Aiken et al., 2009, 2010). Fresh BBOA observed with the AMS has been shown to correlate well with well-known gas-phase markers of BB activity such as acetonitrile, in addition to a number of other metrics for BB (Aiken et al., 2010). Key tracers of BBOA in AMS spectra are the enhanced signals at *m/z* 60 and 73 from the ions $C_2H_4O_2^+$ and $C_3H_5O_2^+$ (Schneider et al., 2006; Alfarra et al., 2007). Levoglucosan and similar species (mannosan, galactosan) produce an enhanced signal at *m/z* 60. For example, f_{60} for levoglucosan is 13% (Schneider et al., 2006; Aiken et al., 2007). However the total signal at *m/z* 60 in BBOA is 3–10 times larger than would be expected from levoglucosan, mannosan, or galactosan, indicating that most of it arises from different molecules that fragment in a similar way as levoglucosan in the AMS (Aiken et al., 2009; Lee et al., 2010). As levoglucosan is a monomer arising from the pyrolysis of cellulose, it is possible that species such as dimers and trimers of similar molecules account for the rest of the signal at *m/z* 60 in BBOA. We define such species here as "levoglucosan-like" species.

In addition, it is known that signal at *m/z* 60 is also observed from carboxylic acids from SOA (DeCarlo et al., 2008; Docherty et al., 2008; Ulbrich et al., 2009a; Aiken et al, 2010) and fatty acids in cooking POA (Mohr et al., 2009), while motor vehicle exhaust produces very low levels of this tracer (Mohr et al., 2009). Typical gas-phase electron ionisation of carboxylic acids produces major ions at *m/z* 60 and 73 (see NIST database, http://webbook.nist.gov/chemistry/) but, in the AMS, these acids produce ions mostly at *m/z* 44 due to thermal decomposition on the vapouriser, and only produce minor signals at *m/z* 60 and 73. In ambient observations at several locations, f_{60} of ~0.3% has been observed as a background level in air masses not impacted by active open biomass burning, as characterised by fire counts and other BB tracers such as acetonitrile (Docherty et al., 2008; DeCarlo et al., 2008; Aiken et al., 2009). This background level needs to be taken into account in any attempt to infer BBOA impact from ambient AMS observations of f_{60}.

The persistence of atmospheric markers is a required assumption for standard receptor model studies (Schauer et al., 1996), but recent studies have shown that organic molecular tracers can decay in the atmosphere due to photochemical processing (e.g.

Robinson et al., 2006). Levoglucosan is known to oxidise in the atmosphere and the pathways and rate of its oxidation have been the subject of recent research (Hoffman et al., 2010; Kessler et al., 2010; Hennigan et al., 2010a). These laboratory-based studies have estimated a range of lifetimes for levoglucosan under typical atmospheric conditions of 15 h to 10 days. However, the extent of levoglucosan or f_{60} degradation after long aging times is difficult to assess from chamber measurements owing to the finite measurement period due to wall effects. Differences in phase and morphology between laboratory and ambient particles may also result in differences between oxidation lifetimes. For example, previous studies showed that oleic acid survived in the atmosphere much longer than expected based on its pure-component reactivity (Ziemann, 2005), potentially due to being trapped on a solid or glassy phase (Katrib et al., 2005; Hung and Tang, 2010). Such glassy organic phases are thought to be common in the atmosphere (Virtanen et al., 2010; Vaden et al., 2011) and similar effects may play a role for levoglucosan and other levoglucosan-like species.

AMS f_{60} has also been reported to decrease during photochemical processing of BBOA, due to both addition of SOA and evaporation/reaction of POA species. Huffman et al. (2009b) reported that f_{60} showed a volatility slightly higher than the bulk primary BBOA for many different biomasses, so it is likely that evaporation plays a role in the evolution of this tracer. However, it remains unclear whether f_{60} will persist sufficiently in aged BBOA to serve as a marker, especially for BBOA plumes advected on a continental or global scale where the transport times are multiple days.

In this study, the physical and chemical aging of BBOA were studied in the field and compared to laboratory results. The decay of the AMS f_{60} marker of primary BBOA and the increase of the f_{44} marker of secondary BBOA were investigated. Through comparison of BBOA-dominated measurements with those known to be free of BB influence, the chemical evolution of BBOA can be assessed. The net effect of BB plume aging on OA mass is also summarised, and a first global estimate of the net OA source is presented.

2 Methods

The OA measurements presented here have been obtained, unless stated otherwise, using the University of Colorado Aerodyne high-resolution time-of-flight mass spectrometer (HR-ToF-AMS, DeCarlo et al., 2006). The AMS vapouriser temperature was 600 °C for all studies. All data were analysed in high-resolution (HR), but are mostly reported here at unit-mass-resolution (UMR) for simplicity. The AMS UMR signal at *m/z* 60 and the high-resolution $C_2H_4O_2^+$ AMS ion signal are tightly correlated for data from two ARCTAS flights (Fig. S1). This correlation spans three orders of magnitude and demonstrates the the negligible contribution of other ions in the ambient AMS spectrum to the unit mass integration at *m/z* 60, validating the application of the UMR ratio f_{60} in use as a tracer. A similar analysis as to that presented in this work could also be conducted using f_{73}, which shows well-correlated, but different, linear relationships with f_{60} in the ARCTAS measurements and data from the AMS database (Fig. S2). However, the signal at *m/z* 73 is lower and more variable than at *m/z* 60, so somewhat larger constraints would be required on the signal-to-noise ratios in order to draw similar conclusions.

Measurements with negligible BB influence were acquired during three ground-based field campaigns. Two urban datasets are presented, from Pasadena, CA, during the CalNex-LA campaign of 2010 (Hayes et al., 2010), and Riverside, CA, during the Study of Organic Aerosols at Riverside (SOAR-1) in 2005 (Docherty et al., 2008, 2011). In addition, measurements are presented from a remote site at Blodgett Forest, CA, during the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX) of 2007 (Farmer et al., 2010). A period with variable BB impact as determined by several tracers has been removed from the BEARPEX dataset. Together, these measurements represent organic mass loadings from nearly zero to tens of µg m^{-3}, and from urban- to biogenic-dominated OA. They provide a wide range of airmass and OA characteristics over which to assess marker levels in the absence of biomass burning plume impacts.

Measurements in BB plumes were taken during research flights of the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) mission of 2008 (Jacob et al., 2010). The ARCTAS data presented here were recorded aboard the NASA DC-8 platform and span locations above the North American continent from 35 to 90 degrees latitude and 150 to 12 000 m in altitude. In addition to BB plumes advected thousands of kilometres from the Asian continent, near-field plumes were sampled from the mid-latitudes of California and the boreal forests of high-latitude Canada. These plumes came from a wide range of source fuels, meteorological and burn conditions, although the observed physical and chemical characteristics of the plumes were remarkably similar in nature (Singh et al., 2010). To ensure the capture of the true chemical nature of the BBOA, the AMS was operated through most plume penetrations in a new "Fast-MS" mode (FMS, Kimmel et al., 2011), with a time resolution of 1 Hz translating to an approximate geographical resolution of 100–200 m. Co-located gas-phase measurements taken on the DC-8 are also used in airmass classification. The University of Innsbruck Proton-Transfer-Reaction Mass-Spectrometer (PTR-MS, Hansel et al., 1995; Wisthaler et al., 2002) measured, amongst other species, acetonitrile (CH_3CN) for 1 s in every 5. The same species was also measured by the Trace Organic Gas Analyser (TOGA, Apel et al., 2003) instrument of the National Center for Atmospheric Research (NCAR). The NASA Langley Research Center measured Carbon Monoxide (CO) at a rate of 1 Hz using a tunable diode-laser (Sachse et al., 1987). Ozone (O_3) was also measured at a 1 Hz rate by the NCAR 4-channel chemiluminescence instrument (Weinheimer et al., 1994). As such, the transition from background to plume conditions is apparent in the plume transect and edge effects can be eliminated.

Meteorological support during ARCTAS was led by Florida State University; we present here kinematic back-trajectories for plume transects for which the in-situ data is used in this analysis. The trajectories (http://fuelberg.met.fsu.edu/research/arctas/traj/traj.html) were based upon meteorological data from the Weather Research and Forecasting numerical model (Skamarock et al., 2008); for a detailed discussion the reader is referred to Fuelberg et al. (2010). The geographical extent and chemical evolution of BB plumes during ARCTAS was modeled by the Atmospheric Chemistry Modeling group at Harvard University using the GEOS-Chem chemical transport model v8-02-03 (http://geos-chem.org/), which has been extensively compared to aerosol and gas phase measurements from ARCTAS (Fisher et al., 2010, 2011; Wang et al., 2011). The aerosol optical depth and CO, in particular, are useful tracers within the model outputs for determining expected plume transects and BB vs. non-BB contributions in the in-situ data.

AMS measurements of BBOA from controlled chamber open burning of specimens (~300 g) were taken in the US Department of Agriculture Fire Sciences Laboratory, Missoula, MT, as part of the third Fire Lab at Missoula Experiment (FLAME-3) of 2009 (McMeeking et al., 2009). The BB smoke was diluted in a large chamber (~3000 m^3) where it stayed for ~2 h and was gradually diluted with ambient air with much lower OA concentrations. Smoke from the chamber passed through an in-line photochemical reaction flow tube (a fourth generation Potential Aerosol Mass flow tube, or PAM, Kang et al., 2007; 2011) and was exposed to high concentrations of OH, such that the integrated exposure was equivalent to hours to days of aging for typical atmospheric oxidant concentrations. With a residence time of ~5 min., the PAM flow tube allowed the study of aged POA and SOA in each burn for several "equivalent atmospheric ages", calibrated against SO_2 decay, simulating the aging that may occur during advection from an ambient BB plume source region. Recent results indicate that the composition and hygroscopicity of the SOA produced by the PAM chamber resemble atmospheric OOA of variable to high aging (Kang et al., 2011; Massoli et al., 2011). We present here lumped measurements of the unprocessed POA and the photochemically processed POA/SOA mixture, for four different fuels in the fire chamber (Ortega et al., 2010).

Finally, data are presented from multiple mass spectra from the AMS Spectral Database (Ulbrich et al., 2009b). These data were acquired by a number of groups, predominantly with the quadrupole version of the AMS. In particular, the measured spectra are presented from traditional environmental chamber studies of (a) SOA formed from exposing VOC precursors to oxidants (Bahreini et al., 2005; Liggio et al., 2005; Sage et al., 2008) and (b) POA from BB (Schneider et al., 2006; Weimer et al., 2008).

To provide context for the BB plumes observed over the Arctic in spring-time, an "Arctic-background" dataset was defined for ARCTAS-A, using co-located measurements to remove periods in intense biomass-burning plumes. Following the methodology of Wisthaler et al. (2009), the correlation of gas-phase acetonitrile to carbon monoxide was used in assessment of the different air mass types encountered (see Fig. S3 for further detail). In this study, the background data are accumulated after conservatively eliminating measurements according to a number of criteria. Data with $\mathrm{CO} > 180\,\mathrm{nmol\,mol^{-1}}$ were eliminated, as CO is a known long-lived tracer for incomplete combustion of all kinds. Data with acetonitrile $>160\,\mathrm{pmol\,mol^{-1}}$ were eliminated. Values below this were determined by Wisthaler et al. to be "out-of-plume", and comfortably below the marked increase in concentrations noted in the upper quartile of the cumulative distribution functions for both the PTR-MS and TOGA instruments (shown in Fig. S4). To further filter out clear BB plumes, periods where the OA mass loading exceeded that of the omnipresent background sulphate are also removed, although this has little influence after application of the acetonitrile filter. To help reduce scatter in the data, all points with OA mass loading $<1\,\mu\mathrm{g\,s\,m^{-3}}$ are eliminated. Finally, those data in the stratosphere (defined by $\mathrm{O_3/CO} > 1.25\,\mathrm{mol\,mol^{-1}}$, Hudman et al., 2007) and marine boundary layer (based on altitude) are eliminated. The remaining 252 measurement points, representing ~250 km of aircraft flight range, were used to construct a so-called "Arctic background" dataset. The average parameters of interest were constructed for only four flights during ARCTAS-A because the rigorous screening process did not leave sufficient data in the rest of the flights to compose a meaningful average.

3 Results and discussion

3.1 Levels of f_{60} in air without biomass burning influence

Figure 1 shows f_{44} as a function of f_{60} for the data of negligible BB-influence from SOAR-1, BEARPEX (BB-impacted period removed) and CalNex-LA, binned into quintile plots to exemplify the observed variations. The continuum of observed f_{44} values suggests a range of oxidation states in the measured OA for these three campaigns, due to both coexistence of POA and SOA in air, as well as a variable degree of OOA oxidation (Jimenez et al., 2009; Ng et al., 2010). The representation of photochemical aging of SOA in a f_{44} vs. f_{43} diagram, in which f_{44} increases and f_{43} decreases with aging (the so-called "triangle plot", Ng et al., 2010, e.g. Fig. S5) allows a simplified description of SOA aging and comparison across studies. Similarly, the f_{44} vs. f_{60} plot is introduced here to map the formation and transformation of primary and secondary BBOA as BB plumes are advected from source to background regions. Figure 1 shows that for a wide range of states of oxidation, the measurements in air masses with negligible BB influence exhibit only a very small range in f_{60}, from about 0.2 to 0.4% of total OA. Such data form a broad vertical line in the f_{44} vs. f_{60} plot; the histograms for each of these three datasets are shown on the bottom panel of Fig. 1, and give median values of 0.25, 0.27 and 0.33% for SOAR-1, BEARPEX and CalNex-LA, respectively.

In addition, data are also shown in Fig. 1 for five distinct periods during the California segment of the ARCTAS mission (ARCTAS-CARB), representing flyovers of Los Angeles, Los Angeles International Airport, Sacramento and the California Central Valley during periods without forest fires. Several µg m^{-3} of OA loading were observed at all these locations, but low average f_{60} ratios are observed, in the range 0.1 to 0.4%.

Thus, the f_{60} tracer does not fall to zero for air without apparent BB influence, owing to the contributions at *m/z* 60 from non-BB sources. Figure 1 demonstrates that, for the entire range of previously reported values of f_{44}, over a wide variety of atmospheric conditions, the previously applied metric of background $f_{60} = 0.3\%$ of OA is indeed appropriate.

3.2 Observation of elevated f_{60} in BB plumes transported thousands of km

The persistence of f_{60} over long timescales is investigated looking at two separate BB plume case-studies from ARCTAS. Firstly, from spring 2008, for the inter-continental transport to Alaska of BB plumes from fires burning in southern Russia, a straight-line distance of ~6000 km, although the actual eastward transport path was in fact fairly complex and thus likely covered a substantially longer distance (Fuelberg et al., 2010). Secondly, in summer 2008, a separate case of inter-continental transport, from fires burning near and west of Beijing to western Canada, a straight-line distance of ~8000 km. These summer plumes followed a looped path across the Pacific, at much lower latitudes than the spring-time event. Figure 2 shows the time-series of f_{60} together with co-located gas-phase measurements across these plumes. The independent gas-phase tracers provide evidence that the intersected plumes are impacted by BB smoke, due to high levels and high correlation of BB tracers such as acetonitrile and CO. The in situ time-series data is also consistent with the model predictions of the BB plume transport shown on the left panels of Fig. 2. Back-trajectories from the plume transect points suggest that the sampled air-masses originated over the Asian continent in both cases; for a detailed discussion on the long-range transport of these, and other, plumes sampled during the ARCTAS mission, including parcel dispersion model output, see Fuelberg et al. (2010, their Figs. 12, 13, 23, 24).

The scatter in f_{60} apparent in the low-loadings out-of-plume contrasts with the more consistent values, elevated above the 0.3% of OA background level, observed in the plumes (cf. Fig. 2, top panel). A key question for the usefulness of the f_{60} tracer and the ability of the AMS to identify BB plumes in ambient air is "Does the oxidation of levoglucosan-like species in ambient BB plumes occur at a sufficient rate so as to decrease f_{60} to background values before f_{44} reaches the LV-OOA range? Or, does it persist for even very oxidised OOA?" Component deconvolution methods such as PMF may identify subsets of OA if they comprise a sufficient fraction of the total, but their identification as BB plumes requires that f_{60} of those components persists above background levels. In the cases presented in Fig. 2, the f_{60} tracer indeed appears to persist after long advection and aging times in the atmosphere.

3.3 Tracer evolution with aging for ambient BB plumes

Hecobian et al. (2011) identified and classified 245 BB plumes intercepted by the NASA DC-8 aircraft during ARCTAS-B, representing a wide range of source locations, fuels and meteorological conditions. Despite these differences, the variation in f_{60} and f_{44} as a function of transport time of the plume from source is sufficiently strong so as to indicate trends in the data, as shown in Fig. 3. The plume f_{60} values are in all cases substantially larger than the measured ratios during the campaigns unaffected by BB also shown on the plot. The observed f_{44} in the plumes appears to increase into the LV-OOA range on the timescale of approximately a day and, although the plume aerosol is a combination of primary and secondary components, the progression of its evolution in the f_{44} vs. f_{43} space falls within the expected range for ambient OOA (Ng et al., 2010) (Fig. S5). However, despite the increasingly oxygenated nature of the aged BBOA, f_{60} remains above background levels for all the measured plumes. There is a clear contrast of the f_{60} values measured in the ARCTAS plumes to those recorded during the BEARPEX and CalNex-LA campaigns; the latter measurements lie on the background 0.3% line and show little deviation from this value when compared to the difference with the BB-influenced values. Thus for ambient BB plumes less than or around one day in transport time from the source region, Fig. 3 suggests that f_{60} may be a robust tracer for BB.

The decay of f_{60} in ambient plumes from source to transport times of multiple days is represented in the f_{44} vs. f_{60} space in Fig. 4, showing the long-range plumes introduced in Fig. 2 together with all of the previously-discussed ambient BB plumes, and measurements of tropical agricultural residue BB plumes over the Yucatan peninsula reported in Yokelson et al. (2009). All the BB plume measurements exhibit a trend toward higher f_{44} and lower f_{60} values with age, although the direction of the trends in the f_{44} vs. f_{60} space varies. The representation of the measurements in f_{44} vs. f_{60}

space facilitates a direct comparison with the measurements from campaigns free of BB influence; this concept is mapped in the inset of Fig. 4. Despite the widely varying conditions and number of BB plumes presented here, all exhibit a negative slope in this space upon aging. Given that the levoglucosan-like species that give rise to f_{60} are much less-abundant than the bulk oxidised OA mass and may not oxidise directly to increase f_{44}, the two parameters are effectively independent. Thus, the relative slopes of the different plume data facilitates a comparison of the rates of oxidation of the OA as a whole to those of just the levoglucosan-like species. Consider m, the absolute slope of decay observed in the f_{44} vs. f_{60} space for a given set of measurements (i.e. $\delta f_{44}/\delta f_{60}$). In the extreme cases we have $m = \infty$ for the data with negligible BB influence, and the lowest values for the near-field data in the Lake McKay plume. This plume was followed downwind, exhibiting a similar value of m to that for the lumped BB plumes observed during ARCTAS. Both show a similar increasing progression of f_{44} during advection, but the Lake McKay plume was the most intense of those sampled on the project, and the levoglucosan-like content of the aerosol in the plume was the highest of all the ambient plumes. Notably, the tropical plumes from Yokelson et al. (2009) show a lower initial f_{60} and a higher m, whilst still tending towards the same point in the f_{44} vs. f_{60} space as the boreal data. The endpoint for the most oxidised plumes within these data appears to be $f_{44} \sim 0.20$–0.22.

From Fig. 4, it appears as though m increases slightly for more oxidised aerosol (so f_{60} appears to change less for the same change in f_{44}). This increase is perhaps due to the combination of a near exponential decay of levoglucosan-like species (Hennigan et al., 2010a; Hoffmann et al., 2010) with the more linear increase in f_{44} with age. The potential elevation of the endpoint in f_{60} above background levels will be discussed later.

3.4 Tracer evolution in laboratory aging of BB emissions

We investigate here the evolution of f_{44} and f_{60} in mass spectra of fresh and aged OA smoke from controlled burns during the FLAME-3 campaign, after aging in the PAM photochemical oxidation flow tube. The progression of these metrics as a function of the equivalent atmospheric age is shown in Fig. 5. The trends are very similar to those observed for the field data in Fig. 4. f_{44} increases with aging, as oxidation of the BB-POA and/or SOA formation in the PAM flow-tube trends the overall OA oxidation state into the SV-OOA range. f_{60} is reduced by oxidation in most cases, although all the measurements lie well above the 0.3% background level, but the different fuels also exhibit very different degrees of change and trajectories (slopes) in f_{44} vs. f_{60} space. The direction of the trends, however, is similar to the field data and always toward the top-left corner of the plot, a progression of BBOA oxidation toward the SV- and LV-OOA range.

The timescales of oxidation observed here are considerably slower than those reported by the lab study of Hennigan et al. (2010a) for levoglucosan. For a constant OH concentration of 1.5×10^6 molecules cm^{-3}, Hennigan et al. report a mean 1/e lifetime for levoglucosan in BB particles of 18 h. Timescales of the same order are consistent with the f_{60} decay for the ARCTAS data shown in Fig. 3. However the fastest f_{60} decay observed in PAM during FLAME-3, that of the Wire Grass, leads to an estimated lifetime of ~5 days under the same conditions. We note that the one case of decay of *m/z* 60 shown by Hennigan et al. (2010a) also shows a timescale much longer than 18 h. The reason for the longer lifetimes observed in our study vs. that of Hennigan et al. are unclear. f_{60} contains contributions from molecules other than levoglucosan (Aiken et al., 2009; Lee et al., 2010), and perhaps other molecules do not decay as fast as levoglucosan does. It is also possible that differences in particle phase between the lab and ambient data, or the higher concentrations used in our experiments, may have also shielded some of the levoglucosan-like species from oxidation, which will be investigated in future work.

3.5 Evaluation of background levels of f_{60} for diluted and aged BB plumes

In this section we evaluate whether an f_{60} signature above background persists for some of the most aged data with biomass burning influence observed in our aircraft studies, those within the “Arctic-background” air-masses of ARCTAS-A. Warneke et al. (2010, their Fig. 2) show single-particle measurements from the NOAA P-3 aircraft during the co-located ARCPAC campaign (Brock et al., 2010), concluding that particles containing BB material dominated the distribution above the boundary layer during ARCPAC. In addition, the air masses transported to the Arctic are known to have been trapped within the polar high and thus exposed to exceptionally long processing times (Fuelberg et al., 2010). As such, the Arctic-background data is highly aged and oxygenated in nature; represented as flight-averages in the triangle space of Ng et al. (2010), it reaches values close to the ultimate state of oxidation observed for ambient data (Fig. S5). Thus, this Arctic-background air, even if not entirely representative of the true Arctic background owing to the targeted nature of the research flights, is nonetheless considered a good example of oxygenated background OA containing a fraction of oxidised BB POA and/or SOA from precursors of BB origin. In the f_{44} vs. f_{60} space of Fig. 4, the Arctic-background OA show high oxidation and relatively low f_{60} values, compared to the long-range plume of flight 9, and can be considered as an endpoint in this space of the evolution in BBOA observed from the near-field data bottom-right. The question pertinent here is “Does this endpoint lie elevated in f_{60} with respect to the 0.3% of OA background level, or is this BB signature completely lost for such intense aging?”

This question is addressed through comparison of the observed cumulative probability distributions (CDFs) of f_{60} in BB plumes, the Arctic-background data and the negligible-BB data from the ground campaigns, as shown in Fig. 6. Combining the measurements from the three ground campaigns, the mean f_{60} value is 0.3% with a standard deviation of 0.06% (absolute); both the mean nominal background value and the three-sigma limits are shown in Fig. 6 . The CDFs of the non-BB data, the two long-range plumes and the combined ARCTAS plume data are distinct in f_{60} space. Virtually all of the measurements of f_{60} from the long-range plumes lie above the average plus 3σ of the background level. f_{60} for near-field, less-oxidised, BBOA measurements, represented by BBOA spectra from the AMS database and the Lake McKay fire plume from ARCTAS-B, are even more separated from the background level.

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Less elevated in f_{60} than the plumes, but with mean values elevated above and statistically separable from that of the ground-campaign data, is the data from the "Arctic-background" dataset. The reader is reminded that "background" in this context refers to the omnipresent, disperse OA observed out-of-plume in the Arctic spring, and the f_{60} exhibited by this dataset is distinct from the f_{60} background level of 0.3% discussed earlier. The statistical separation of the two, although small, suggests consistency with Warneke et al. (2009, 2010), in that BBOA represented a significant fraction of the total OA burden during the 2008 Arctic spring, even outside of the clear BB plumes.

3.6 Net enhancement of OA mass due to BB plume aging: compilation of field data and global budget estimate

We summarise here results from this study and the literature on the measured OA with aging of evolving ambient open BB plumes (Capes et al., 2008; Yokelson et al., 2009; Akagi et al., 2010; DeCarlo et al., 2010; Hecobian et al., 2011). Figure 7 shows that total primary OA (POA) mass, once normalised to excess CO (above background) mass concentration to remove the effect of dilution, is highly variable for the five datasets presented, consistent with the variability in BB POA emissions from previous literature reports (e.g. de Gouw and Jimenez, 2009; Akagi et al., 2010). The variability in POA/ΔCO is not only seen across the different studies, but also within the ARCTAS-B dataset utilised in this work (based on the plume transects classified by Hecobian et al.), for which OA/ΔCO ranges from ~0.02 to 0.25, independent of plume age but highly variable between plumes. The Lake McKay plume sampled on 1 July 2008 was particularly well characterised, exhibiting an invariant linear relationship between OA and CO enhancements of OA/ΔCO ~0.14. In contrast, the data from the Yucatan agricultural fires of Yokelson et al. suggested a substantial enhancement in OA/ΔCO with plume age owing to SOA production. DeCarlo et al. (2010) also quantified an enhancement of OA/ΔCO with aging for forest fire plumes near Mexico City. Finally Akagi et al. (2010) observed a small decrease in OA/ΔCO with aging for brush fires in California. Aging of controlled-burn chamber data during FLAME-3 with two different experimental setups also resulted in a highly variable net OA enhancement, depending (among other parameters) on fuel type and burn conditions (Hennigan et al., 2010b; Ortega et al., 2010), which appears consistent with the large degree of variability observed in the ambient datasets.

We can provide a first estimate of the global source of OA due to aging of open BB plumes by combining the average OA/ΔCO and ΔOA/POA from the field data with the IPCC CO emissions for biomass burning (508 Tg CO yr^{-1}) and the corresponding figure for POA (41 Tg yr^{-1}, de Gouw and Jimenez, 2009). The net OA/ΔCO gain during aging of the field data ranges from −0.01 to 0.07, with an average of 0.016. The average ΔOA/POA is 0.25 for the combined six sets of aircraft measurements. These results give an estimated OA burden from BB-SOA of 8–10 Tg yr^{-1}. With respect to the overall global OA budget, estimated at ∼150–300 Tg yr^{-1} (Hallquist et al., 2009; Spracklen et al., 2011), the estimated BB-SOA source is about 5% of the total global OA source. Thus secondary OA production in BB plumes could represent an important global source of OA. However, more field measurements are required to better constrain the magnitude, frequency of occurrence, and controlling parameters of net BB-SOA production.

4 Summary

Using HR-ToF-AMS data of negligible BB influence from three field campaigns, it has been shown that an appropriate background level of the f_{60} tracer is 0.3% of OA. Furthermore, the contribution in signal at unit mass *m/z* 60 arises virtually entirely from a single ion, $C_2H_4O_2^+$, allowing the analysis presented here to be performed using UMR data and thus extended to the lower resolution versions of the AMS or the recently developed Aerodyne aerosol chemical speciation monitor (ACSM, Ng et al., 2011b).

A novel method for representing the aging of BBOA in the atmosphere uses the f_{44} vs. f_{60} space, which shows the increasing oxidation of the OA ensemble in parallel with the oxidative decay of the levoglucosan-like species emitted as primary aerosol during BB. Measurements of several hundred ambient BB plumes exhibit f_{60} levels above background and negative slopes in f_{44} vs. f_{60} space. This behaviour was seen for plumes measured over three continents, with some close to the source and some transported from sources many days away. These measurements contrast with measurements free from BB influence which exhibit a similar progression in oxidation and thus f_{44}, but display uniform f_{60} values close to the 0.3% background level. The relative rate of decay of f_{60} in ambient BB plumes, as compared to the oxidation of the bulk OA, is shown to differ between plumes. Oxidation flowtube data from controlled burns, known to be exclusively BBOA and aged using an in-line reaction flow-tube, resulted in a similar progression of BBOA during aging in the f_{44} vs. f_{60} space. The BBOA was observed in some cases to evolve to f_{44} values associated with the LV-OOA subtype, but in all cases maintained f_{60} values significantly above background for all the flow chamber measurements.

Statistical analysis of the data shows that BB plumes, even those having undergone multiple days worth of atmospheric oxidation, exhibit f_{60} values elevated by a statistically-significant level with respect to the negligible-BB campaign datasets. Whilst consecutive individual measurements may only retain $f_{60} > 0.3\%$ in sampling of clear BB plumes, it is proposed that cumulative distribution functions of f_{60} may be used together with representation in f_{44} vs. f_{60} space to make a general, qualitative, statement about the prevalence of BBOA as a component of OA in AMS mass-spectra. Thus whilst not completely inert, f_{60} appears to be a persistent tracer, and quantitative analysis of its prevalence in sub-groups of OA should be the subject of future research addressing source-receptor relationships.

A first synthesis of the limited field measurements of net OA production in ambient BB plumes was presented. There is large variability in the observed values as normalised to CO or POA emission. Taking a simple average of the five available datasets shows that aging of open BB smoke may produce ~9 Tg OA yr^{-1}, of the order of 5% of the global OA burden, making this a potentially important atmospheric OA source.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/12103/2011/ acpd-11-12103-2011-supplement.zip.

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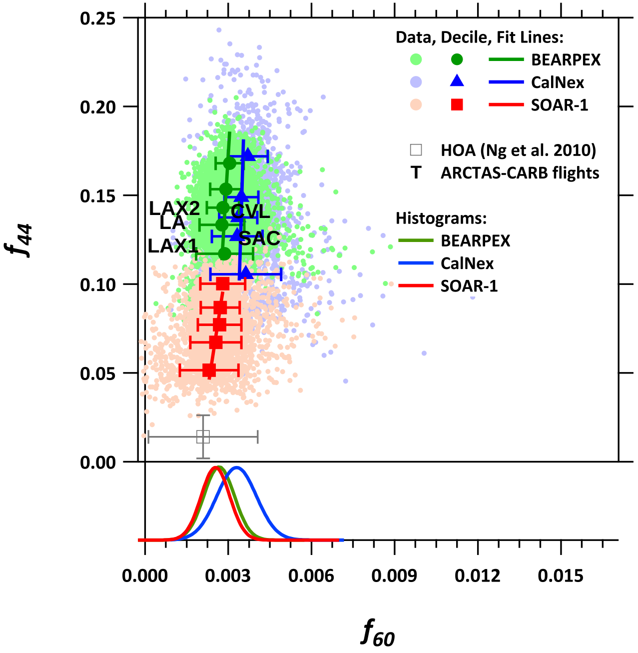

Fig. 1. Upper Panel: f_{44} as a function of f_{60} for measurements with little or negligible BB influence. Coloured points represent data from the ground campaigns SOAR-1, BEARPEX and CalNex-LA, and are also shown binned to quintiles for clarity. Text represents averaged periods from the ARCTAS-CARB mission: LA = Los Angeles overpass, LAX = missed approach on LAX, CVL = San Joaquin valley, SAC = Sacramento overpass. Also shown is the average hydrocarbon-like OA across 15 urban studies (and its variability) from Ng et al. (2011a) for reference. Lower Panel: normalised histograms of f_{60} for the three ground campaigns.

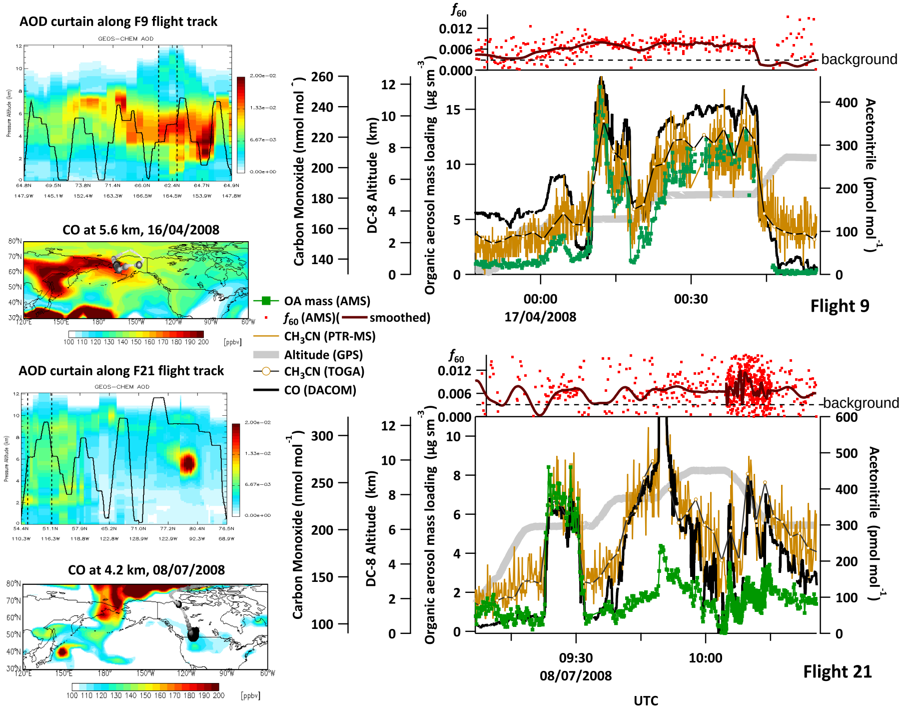

Fig. 2. Two long-range plumes intercepted during flight 9 of ARCTAS-A (top) and flight 21 of ARCTAS-B (bottom). Left panels: GEOS-Chem model output showing the aerosol optical depth curtain along the flight tracks with plume time-frames indicated by dashed lines (top), and global CO at a time and altitude relevant to the plume crossings (bottom). DC-8 flight tracks are also shown on the map, coloured and sized by gas-phase acetonitrile mixing ratio. Right panels: time-series in-situ data for the plume transects aboard the DC-8 aircraft, showing the increase in gas- and aerosol-phase species associated with the plumes predicted by the model.

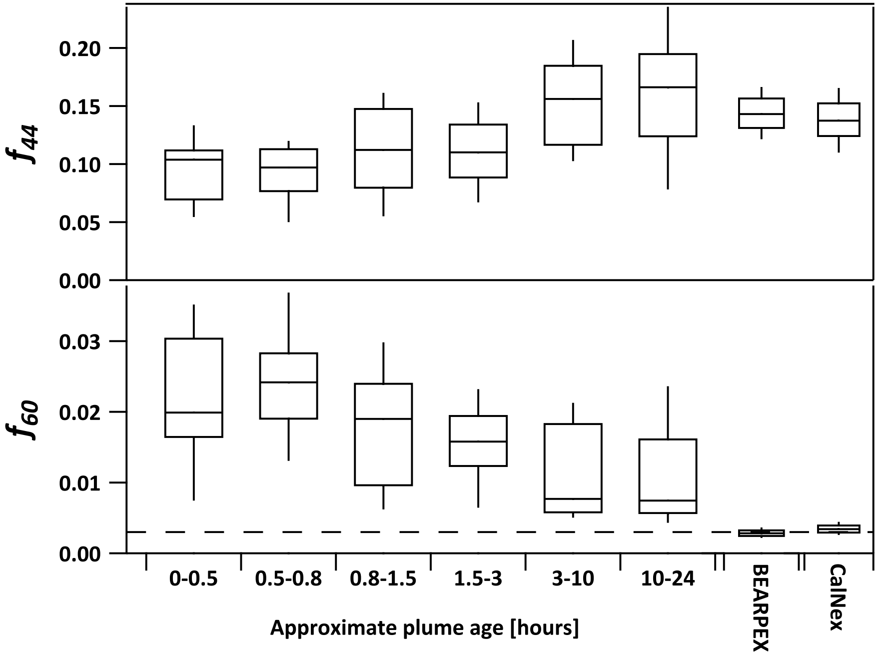

Fig. 3. Box and whisker plots representing the 10th, 25th, median, 75th and 90th percentiles for 245 BB plumes intercepted during ARCTAS. Classification of the plumes, and transport times shown on the horizontal axis, are adapted from Hecobian et al. (2011). Also shown are data from two ground campaigns free of BB influence.

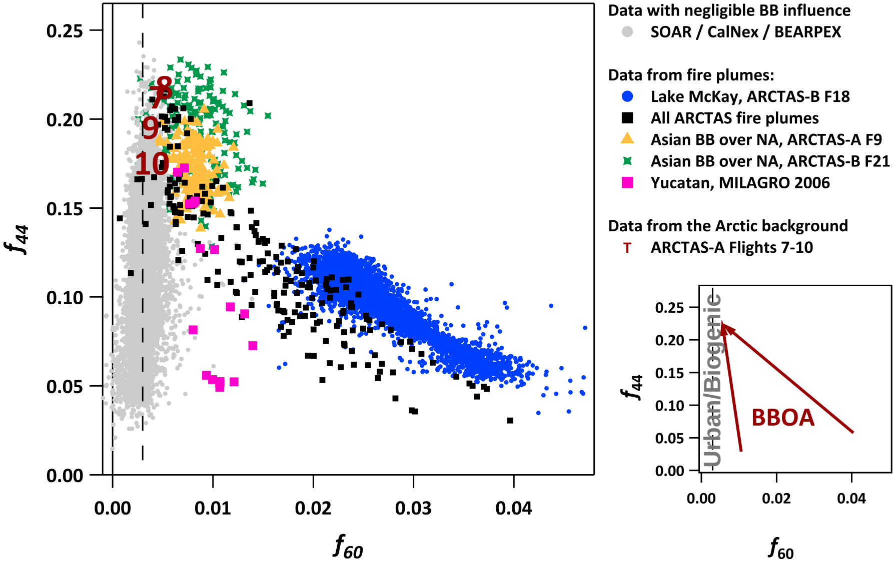

Fig. 4. Summary plot showing f_{44} vs. f_{60} for all the field measurements discussed in the text. The nominal background value at 0.3% is shown by the vertical dashed line. Inset: schematic of the different representations that the non-BB and BB data make in this space.

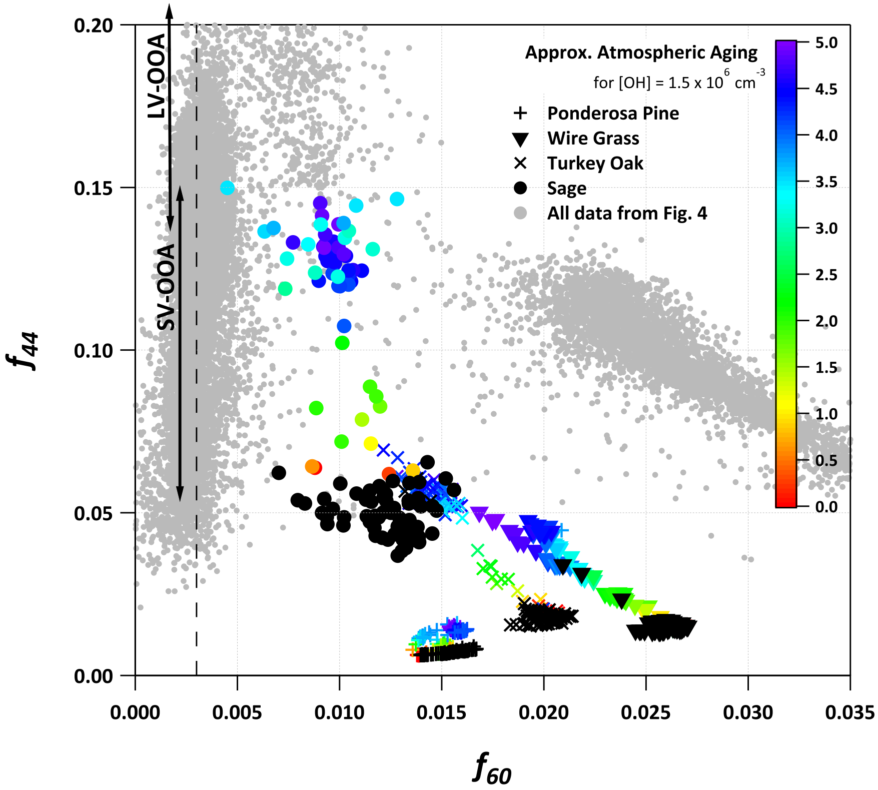

Fig. 5. f_{44} vs. f_{60} ratios for laboratory smoke during FLAME-3, and after processing with the Potential Aerosol Mass (PAM) flowtube. The colour scale indicates the estimated processing time of the aerosol in the flowtube, after normalisation to the stated 1.5 × 10^6 atmospheric [OH] level. The background f_{60} level of 0.3% of OA is indicated by the dashed line in the figure and the data from Fig. 4 are also shown. The typical oxidation range exhibited by ambient SV-OOA and LV-OOA is indicated with the vertical arrows.

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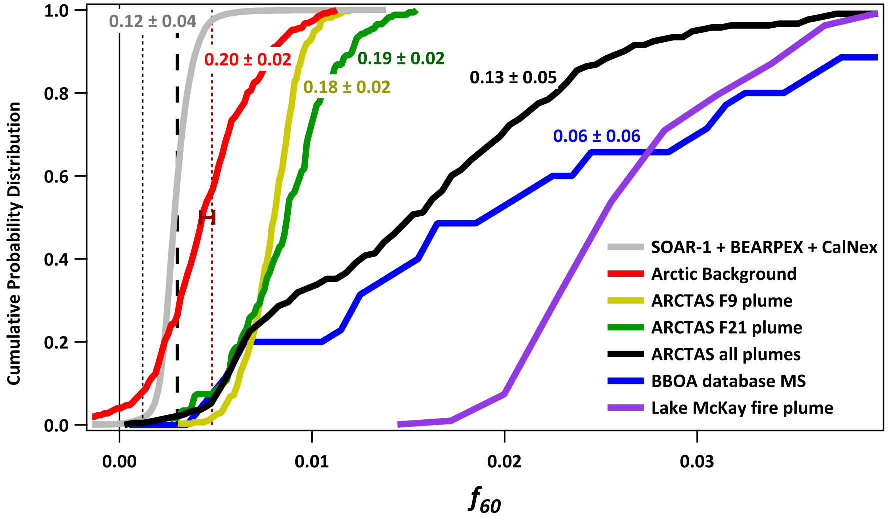

Fig. 6. Cumulative probability distributions of f_{60} from multiple datasets. The nominal background value at 0.3% is shown by the thick dashed line, and the 3-sigma widths of the negligible-BB datasets by the thin dashed lines. The mean ± standard error for the "Arctic-background" dataset are indicated by the horizontal red bar. The mean and standard deviation of the f_{44} value for each dataset is indicated on the plot.

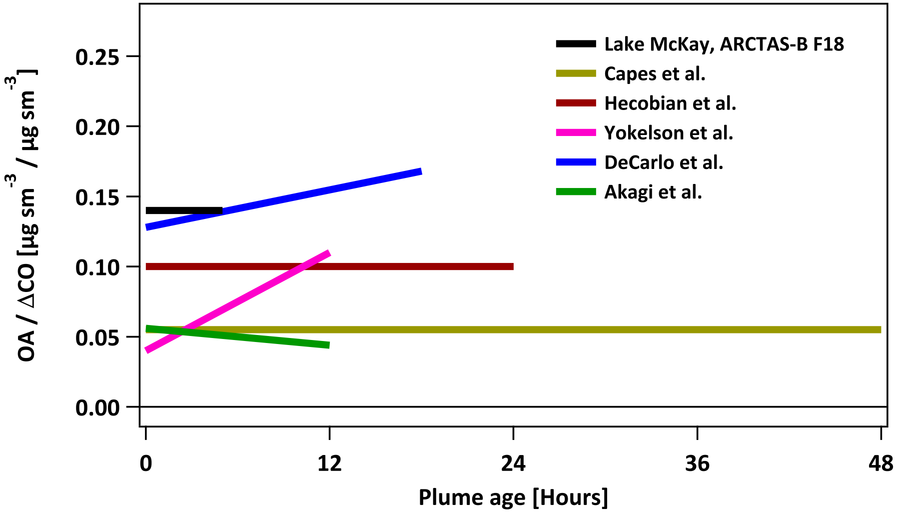

Fig. 7. Schematic summarising, for the available field BB datasets presented here and in the literature, the organic aerosol (OA) concentration observed as a function of plume age, normalised to the enhancement in CO concentration above its background.