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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sources and mixing state of size-resolved elemental carbon particles in a European megacity: Paris" *by* R. M. Healy et al.

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The authors would like to thank the reviewers for their analysis and very useful comments. Each general and specific comment has been addressed in detail below, and appropriate additions and changes have been made to the manuscript, figures and the Supporting Information. New versions of the manuscript figures and Supporting Information have also been uploaded.

Reviewer 1, Gary Fuller

General Comment: The discussion paper reports and analyses measurements of ambient carbon particles during the MEGAPOLI campaign in Paris in 2010 using a range

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of measurement techniques. The paper is clearly written and offers useful conclusions regarding the sources and concentrations of carbon PM in the city. The Paris city network, Airparif has recently completed a year-long PM source apportionment study to provide an evidence basis for the development of PM abatement polices. The results of this paper will make a very valuable contribution to this initiative. In addition to quantifying PM carbon and its sources in the city the paper also provides valuable data to help interpret measurements from different techniques adding to the growing body of data on aethelometer measurements for instance.

Specific Comment: P 30335 line 25: Soil scientists frequently separate carbon particles into soot and char depending on their physical properties, See Y. Han et al. / Chemosphere 69 (2007) 569–574. And Han et al 2010 www.atmos-chem-phys.net/10/595/2010/

Response: This is a good point. In the absence of any interdisciplinary "standard" terminology BC, soot, and even EC are often used interchangeably in scientific literature. The separation of soot and char is indeed well established and the references above have now been included in the manuscript to reflect this. The latter reference in particular provides a very useful discussion of terminology and definitions relating to BC, EC, soot and char.

Specific Comment: P30336 line 1: It would useful to refer to the UNEP 2011 report on short lived climate forcing agents which includes black carbon. The report which is aimed at policy makers provides a very valuable context to this work, see http://www.unep.org/dewa/Portals/67/pdf/BlackCarbon_SDM.pdf

Response: This report is very relevant for BC climate forcing and the following sentence has now been included in the manuscript: "Reducing emissions of BC has been identified as a potential means for decision makers to simultaneously mitigate against global warming and poor air quality due to its relatively short atmospheric lifetime (UNEP, 2011)"

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Specific Comment: P30336 line 13: Strictly speaking low emission zones focus on PM reduction as their objective rather than BC. I agree that the focus of LEZ measures on tailpipe emissions should lead to decreases in BC.

Response: BC has now been replaced with PM in the manuscript

Specific Comment: P30342 Line 5: Would it be useful to explore different assumptions of particle density in a sensitivity analysis?

Response: This is also a good point; although a density of 1.5 g cm-3 was chosen in this case (based on the chemical composition of PM1 provided by the MAAP and AMS instruments), assuming different densities will result in different scaled mass concentration values. Densities of 1.3 and 1.7 g cm-3 have now been explored and the resulting mass concentrations for the 4 EC particle types, and the resultant total scaled ATOFMS EC mass concentration compared with the results obtained using a density of 1.5 g cm-3. In brief, using either 1.3 or 1.7 g cm-3 results in very little change to the temporality of the total scaled EC mass (R2 = 0.97 and 0.98 respectively when compared to using a density 1.5). However, the slope and therefore the mass concentration values are affected (slope = 1.02 and 0.78 for 1.3 and 1.7 g cm-3 respectively, when compared to a density of 1.5 g cm-3). Slightly higher mass concentrations are observed using a density of 1.3 g cm-3, and lower mass concentrations are observed using a density of 1.7 g cm 3. This effect arises because the density value is used to "convert" the vacuum aerodynamic diameter (dva) to a corresponding mobility diameter (dm) in order to scale the particle counts to the TDMPS data. For example, employing a higher density (1.7 g cm-3) requires the use of lower mobility diameter bins from the TDMPS compared to those used for a density of 1.5 g cm-3. The centroids of those smaller dm bins are also used to estimate particle volume (assuming spherical shape), and thus the particle volume estimate for a density of 1.7 g cm-3 is lower than that obtained for a density of 1.5 g cm-3. When converting from volume to mass concentration, the volume is multiplied by the density and this offsets the effect of using smaller diameter bins for the volume calculations to some extent, but not completely. In an

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effort to demonstrate the effect of varying the particle density, a new section has been added to the Supporting Information, including a discussion of the density effect along with 4 new figures (Figs. S15-18) depicting the resulting mass concentrations calculated. The following line has also been added to Section 2.2: "The effect of varying the assumed particle density is also included in the Supporting Information." Ultimately, no single density value is entirely suitable for such a calculation because different particle types will exhibit different particle densities. Although single density values have been demonstrated to work reasonably well for converting ATOFMS data to PM1 mass concentrations (Qin et al., 2006), simultaneous measurement of dva and dm, or an optical scattering measurement of effective density for each particle remains the best way to tackle this problem, especially for non-spherical soot particles (DeCarlo et al., 2004; Moffet and Prather, 2009). In the absence of such measurements, the value of 1.5 g cm-3 has been chosen because it corresponds to the best estimate available for the bulk density of the particle ensemble for this campaign.

Specific Comment: P30342 Line 28 (and elsewhere, including figures): It may be clearer to refer to the PM2.5 measurements technique as FDMS-TEOM to distinguish from the older style TEOM.

Response: The text and figures have now been amended to reflect this suggestion.

Specific Comment: P30344 Line 12 Where is the SITA site relative to LHVP?

Response: The following has been added to the manuscript: "These factors were compared with those obtained from a similar aethalometer instrument running at the suburban SIRTA site (48.71° N, 2.02° E, approximately 20 km SW of the LHVP site) during the MEGAPOLI campaign, exhibiting very good consistency (slope of 1.00: r^2 = 0.87; N = 7)."

Specific Comment: P30346 Section 2.4: I think that this needs to be re-written in the past tense.

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Response: This section has now been re-written in the past tense.

Specific Comment: P30346 Line 23: What is the lowest layer of the model and how does this compare with typical boundary layer heights for February?

Response: The lowest layer of the model is 50 m and is thus representative of the boundary layer. This detail has been added to Section 2.4: "Most emissions occur at ground level and therefore high PES values in the lowest model layer (50 m) were most important when considering transported aerosol input."

Specific Comment: P303347 line 9: It may be good to reference a study that has used K+ as a tracer for wood burning EC.

Response: Although the section includes single particle references that use potassium content in soot particles to assign a biomass combustion source, other references are also very suitable. The following sentence has now been added: "Potassium-containing soot is a well-established tracer for biomass combustion (Andreae, 1983; Soto-García et al., 2011)."

Specific Comment: P30347 line 14, P30348 line 9 and Figure 2: I am concerned that the diurnal profile for EC biomass looks almost identical to ECtraffic, with the sole exception of the morning peak around 8h for ECtraffic which is not reflected in ECbiomass. EC from both sources would be affected by the same urban dispersion processes before arriving at the measurement site but the data in Fig 2 raises questions about the separation of these sources. Could day of week day results be shown also? The weekday/ weekend profiles for ECtraffic and ECbiomas may show greater differences than those shown in Fig 2.

Response: While the diurnal trends are relatively similar, this effect can be explained by the diurnal activity in Paris. In the winter months, domestic wood burning starts in the early evening, when traffic activity is still relatively high. EC arising from both processes can thus accumulate in the evening before dispersion at night. The main differ-

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ence can be observed between 05:00 h and 10:00 h, when the morning ECtraffic spike is not reflected in the ECbiomass diurnal profile. A similar pattern is observed for the aethalometer BCff and BCbb fractions. One advantage of the mass spectral clustering analysis used here is that it is objective with respect to temporality; only mass spectral characteristics are used to separate the different ATOFMS particle types. The mass spectra for these 2 sources are very different and separated relatively easily through clustering. The mass size modes for these 2 particle classes are also quite different, with ECtraffic particles exhibiting a smaller mode than ECbiomass particles (210 and 280 nm respectively). A previous article using the same clustering methodology describes diurnal profiles for EC particles arising from traffic and domestic combustion sources in Cork Harbour, Ireland with very similar mass spectra to those described here (Healy et al., 2010). That site was characterised by relatively consistent marine air masses resulting in faster dispersion of freshly emitted EC particles, and the campaign was performed in the summer months. Thus, the evening domestic combustion and daytime traffic sources exhibited more distinct diurnal profiles. Regarding the weekday/weekend comparison, this data was explored but no obvious conclusions could be drawn because input from traffic and biomass combustion both persisted at weekends and the regionally transported EC also influences the results. Transported EC was not an issue for the Cork Harbour study, resulting in more distinctly different diurnal profiles for EC from traffic and domestic combustion sources. Those results indicate that the designation of ECtraffic and ECbiomass are relatively robust. Ca-containing EC arising from traffic was also found to dominate during the early daytime in Mexico City using ATOFMS while K-containing EC arising from biomass combustion was found to dominate in the evening hours (Moffet et al., 2008).

Specific Comment: P30349 Line 8: EU fuel quality regulations required the transition to < 10 ppm sulphur in road fuels by the time of the study. With little diurnal variation in ECOCSOx is it safe to assume a road traffic linkage? A small number of studies have found very large changes in particle number emissions with the transition to so-called ultra-low diesel, in the EU and US (I can send these by email if you wish). It

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would be worthwhile checking the S in road fuel in Mexico (and Tokyo?) before drawing comparison to the Paris measurements. Are there industrial sources in the Paris region that emit large amounts of SO2?

Response: The authors would like to thank the reviewer for these useful articles. The diurnal trend for ECOCSOx particles does indeed make it difficult to assign a specific local source. The relatively flat profile does not immediately point to a fresh diurnal source pattern such as traffic, for example. EC particles that have undergone some chemical processing remain a possibility, and this processing may explain the presence of sulfate and ammonium in the mass spectra. The presence of sulfate does not necessarily point to primary sulfate, from sulfur content in the fuel itself for example, and it must be emphasised that a signal for sulfate does not necessarily mean that a high mass loading of sulfate is present in these particles because the ATOFMS is quite sensitive to this species. The absence of a strong peak for potassium suggests that these particles do not represent processed biomass combustion EC. Upon examination of the mass spectra they are much more similar to ECtraffic than ECbiomass, but with additional signals for ammonium and sulfate (Fig. 1). ECOCSOx particles are relatively small with a mass size mode very close to that of ECtraffic (215 nm). These findings suggest a more efficient combustion source than domestic wood burning, with industry or traffic-related fossil fuel combustion remaining as possible sources. It is also worth noting that the temporality of ECOCNOx particles < 400 nm is similar to that observed for ECOCSOx (Fig. 6) and ECOCNOx may thus represent processed EC particles that have accumulated both ammonium nitrate and ammonium sulfate (Fig. 1). Local sources of SO2 have been estimated to contribute very little (approximately 15%) to sulfate concentrations in Paris (Sciare et al., 2010), however under certain meteorological conditions local contributions can become important. A discussion of local contributions of ammonium sulfate and nitrate and potential sources of ECOCSOx particles, along with relevant additions to the manuscript and Supporting Information, are provided in response to Reviewer 2 below. The following line has also been removed from the manuscript because it is not necessarily relevant: “Coated BC particles de-

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tected in Tokyo using a soot photometer, were also found to contain internally mixed sulfate and OC, although this finding was inferred from concurrent measurements using an AMS (Shiraiwa et al., 2007)."

Specific Comment: P30354 Line 11. The ATOFMS measurements differ from the Sunset during period IV as shown in Fig 5 and stated in the text. Looking at the supplementary material it appears that the ATOFMS also departs from the MAAP and aethalometer during this time, perhaps adding weight to the suggestion that this is an ATOFMS artefact.

Response: The enhanced mass concentration observed during Period IV for the ATOFMS scaled EC-containing particle mass is expected to be due to internally mixed OC and ammonium nitrate. The discrepancy between the ATOFMS EC total mass and the Sunset EC thermal/optical EC mass concentration is also observed in the aethalometer and MAAP BC datasets. The following line has now been added to the manuscript: "The same discrepancy observed between the ATOFMS EC particle mass and the Sunset EC is also apparent in the MAAP and aethalometer BC datasets during Period IV (Figs. S11 & S13)."

Specific Comment: Regarding the figures in general it might be good to increase the font size for some of the index labels. I did have trouble reading them clearly. This is especially the case with Fig 5. I hope that these comments are useful.

Response: Several of the figures have now been improved in the amended manuscript. The labels and text in Figs. 1,2,3,5,7 and 8 have all been increased in size in order to be easily legible upon printing. Figs. 7 and 8 have also been combined into a single figure as suggested by Reviewer 2. Fig. 5 in particular has been redesigned completely. New, higher resolution FLEXPART PES plots have now been generated and increased in size in order to demonstrate the air mass origins in a much clearer way. The authors would like to thank the Reviewer for these comments, which have been very useful.

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Reviewer 2, Andrew Ault

This paper investigates black carbon mixing state and concentrations from a single particle (ATOFMS) and bulk perspective (aeth, MAAP, sunset ECOC, etc.) for the purpose of source apportionment in Paris during the MEGAPOLI campaign. The authors have drawn substantial conclusions regarding the properties and origins of black carbon through comparison with meteorological conditions and FLEXPART Lagrangian modeling. The paper thoroughly documents the analysis and scaling decisions made regarding the different data sets, which helps explain where the correlations are strong (or not strong in places). There are a few areas within the paper that could use revision or further analysis (discussed below) regarding aging and scaling. However, overall this paper is a solid contribution to the literature regarding sources and aging of black carbon and should be accepted after minor revisions. I hope the comments below are helpful.

Specific Comment: The paper makes the assumption in a number of places that intense peaks of 46NO2- and 62NO3- in the negative mass spectrum are ammonium nitrate. I am not sure the data supports being this definitive given the weak 18NH4+ signal and other potential cations for nitrate in the aerosol phase. This argument could be strengthened by showing that high ECOCNOx time periods have increased NH4+ from the HR-AMS relative to ECOCSOx time periods or through the comparison of m/z 18 intensities for the EC particles themselves for the 4 different EC types discussed in the paper. Absent that, the label could be changed to “nitrate” instead of “ammonium nitrate” or a more thorough qualifier could be added.

Response: This is a good point. Upon reflection it was an oversight not to include the AMS data for the inorganic ions, as this data supports the ATOFMS results quite well. A new figure has now been included in the Supporting Information comparing mass concentrations of ECOCNOx, ECOCSOx with ammonium, nitrate and sulfate mass concentration data for PM1 from the AMS (now Fig. S4). Periods characterised by elevated ECOCNOx mass concentrations are also characterised by increases in mass concen-

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trations of nitrate and ammonium, suggesting that ammonium nitrate does contribute significantly to the composition of ECOCNOx particles. Condensed ammonium nitrate has previously been observed to be a major component of PM2.5 in Paris (Sciare et al., 2010). However, some neutralisation of nitrate through heterogeneous reaction with other cations such as potassium or calcium cannot be completely ruled out, in particular for ECbiomass particles. Thus the following has been removed from the manuscript: "suggesting the presence of some condensed ammonium nitrate" Increases in mass concentrations of ECOCSOx particles are also coincident with increases in mass concentrations of sulfate and ammonium, most notably on the 18/01/2010 and 11/02/2010. ECOCSOx particles are much smaller than ECOCNOx particles and are expected to be less aged. Potential sources of ECOCSOx are discussed in response to a subsequent comment below. The following lines have now been added to the manuscript: "Examination of the HR-ToF-AMS data for inorganic ions reveals that periods of elevated ECOCSOx mass concentrations are also characterised by elevated ammonium and sulfate mass concentrations (Fig. S4)." "The HR-ToF-AMS data demonstrates that periods of elevated ECOCNOx mass concentrations are also characterised by elevated ammonium and nitrate mass concentrations (Fig. S4)."

Specific Comment: The bimodal nature of the EC particles is a particularly interesting finding. One question regarding these two modes is whether the modes are indicative of two real EC populations (as the authors discuss) or whether these populations are due in part to instrumental effects from the ATOFMS or the scaling methods used to convert from raw ATOFMS counts to mass size distributions? In particular I am curious as to whether the mode below 300 nm may be due in part to non-spherical/fractal soot particles. The increased scattering of these particles relative to their small aerodynamic diameters can lead to a mode at the smallest sizes of the ATOFMS size range. The potential shift from fractal to spherical, even if it cannot be addressed numerically should be discussed to provide context to Figure 3. This issue of sphericity might also impact the assumption of spherical particles used to convert from Dva to Dve. Thoroughly addressing this issue would be beyond the scope of this specific paper, but its

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potential importance could be discussed.

Response: It is expected that ECtraffic particles in particular will exhibit non-spherical shape, and thus an assumed density is admittedly less satisfactory for these particles. Furthermore, the assumed density is used to estimate mass concentration assuming spherical shape for all particles. The effect of changing the particle density used for the scaling calculations has now been explored in response to Reviewer 1 and a new section and new figures have been added to the Supporting Information. Part of that section is also relevant here: "Ultimately, no single density value is perfectly suitable for such a calculation because different particle types will exhibit different particle densities. Although single density values have been demonstrated to work reasonably well for converting ATOFMS data to PM1 mass concentrations (Qin et al., 2006), simultaneous measurement of dva and dm, or an optical scattering measurement of effective density for each particle remains the best way to tackle this problem, especially for non-spherical soot particles (DeCarlo et al., 2004; Moffet and Prather, 2009). In the absence of such measurements, the value of 1.5 g cm-3 has been chosen because it corresponds to the best estimate available for the bulk density of the particle ensemble for this campaign."

Fresh ECtraffic particles are expected to be fractal aggregations with an overall non-spherical shape. Processed EC-containing particles, however, have been demonstrated to possess a collapsed fractal EC core surrounded by a spherical coating of OC and inorganic ions (Moffet and Prather, 2009) and references therein. Thus the volume and mass scaling calculations used in this work are expected to be most accurate for larger, more aged ECOCNOx particles and least accurate for smaller ECtraffic particles. However the agreement between the aethalometer BC fossil fuel fraction mass concentration and the ATOFMS EC fossil fuel mass concentration (Fig. 7) is encouraging despite these errors. The calculations are also based on the assumption that all particles in each dva size bin are detected by the ATOFMS with equal efficiency. As suggested by Reviewer 2, this may not be the case if certain particle classes exhibit

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more efficient light scattering than others. Fractal particles such as soot are also susceptible to perpendicular drag forces, reducing transmission efficiency in the ATOFMS. The explanation of these effects is now revised in the text in Section 2.2: "This may introduce error in the scaled counts for the different particle classes, as different detection efficiencies are observed for particles of differing composition (Kane et al., 2001; Wenzel et al., 2003; Gross et al., 2006). Non-spherical particles such as fractal soot are also more susceptible to divergence from the particle beam due to perpendicular drag forces, and thus may be detected less efficiently than spherical particle types (Moffet and Prather, 2009)." Despite these problems, the smaller and larger EC modes do exhibit different aerodynamic diameters, exhibiting well defined modes even prior to scaling with the TDMPS data. The appearance of the larger mode does consistently coincide with a shift to air masses originating in North Eastern and Eastern Europe, and is relatively unimportant when marine air masses dominate, particularly during Period III (Fig. 5). This finding suggests that EC particles of different aerodynamic diameters detected in Paris do have different sources. Thus, the potential for future size-resolved aethalometer measurements of BC in Paris remains promising. Although Section 2.2 includes a discussion of the potential errors associated with the scaling procedures used, the following lines have also been added to Section 3.3 to reinforce the point: "Non-spherical fractal particles exhibit different shape factors and particle densities to spherical particles, and perpendicular drag forces impact upon the transmission efficiency of the former through the instrument (Moffet and Prather, 2009). The largest, most sustained discrepancy is the overestimation of the ATOFMS EC particle mass relative to the Sunset EC during period IV (Fig. 5), which is also characterised by a much lower r2 value of 0.30. A significant fraction of the ATOFMS EC-containing particle volume for this period is expected to be ammonium nitrate and OC (Fig. S8), thus the ATOFMS EC particle mass is significantly higher than the Sunset EC mass."

Specific Comment: Figure 4: The very tight and strongly westerly PES for Period 1 is quite interesting. Could the oceanic time period here (and in period 3 to a lesser degree) be influenced by ship emissions, specifically those leaving the English Channel?

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Would that help explain the higher ECOCSOx/ECOCNOx ratio during this time period?

Response: This response also covers Reviewer 1's comment regarding potential sources of ECOCSOx particles. The temporal trend for ECOCSOx particles is quite interesting, particularly the event on the 18/01/2010. This day was characterised by very low wind speed. The Eulerian regional chemistry transport model CHIMERE, described in detail elsewhere (Sciare et al., 2010), estimated a relatively low contribution (15%) of local emissions from within the Greater Paris (Ile de France, IDF) region to levels of particulate phase sulfate at the LHVP site during a campaign in Spring 2007. However, under low wind speed conditions, local contributions can dominate. This provides further support that the sulfate content in ECOCSOx particles can be partly attributed to a local source. However, emissions from coastal cities and ports to the West and North of Paris cannot be completely ruled out as a potential source of ECOCSOx particles. Although fresh ship exhaust particle mass spectra detected in Cork Harbour using ATOFMS were found to consistently contain vanadium, iron and nickel, these metals are not observed in ECOCSOx particles (Healy et al., 2009; Healy et al., 2010). A previous ATOFMS study performed in the Port of Los Angeles demonstrated that not all ship plume combustion particles contain vanadium signatures, because not all ships are using residual fuel oil (bunker fuel) (Ault et al., 2010). The soot particles assigned to ship plumes from vessels using cleaner distillate fuel by Ault et al do exhibit similar positive ion mass spectra to the ECOCSOÂňx particles observed in this work, however there was little or no sulfate signal detected in the Los Angeles case. While this comparison suggests that ECOCSOx particles are processed locally in the IDF region, it is admittedly difficult to be sure of their specific origin. A year-long source apportionment study of PM2.5 chemical composition for Paris has enabled the identification of an oil combustion factor that contributes an estimated 12% of the measured PM2.5 mass concentration (Bressi et al., 2011). The oil combustion factor is associated with Northerly wind direction, although there is some input from the Northwest. This suggests that oil combustion sources such as shipping traffic in the English Channel or petrochemical industrial activity can contribute to PM2.5 mass concentrations

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in Paris. However, in the absence of a useful internally mixed metal as a marker ion for a specific combustion source, the best assignment for ECOCSOx particles in this case remains as fossil fuel combustion followed by chemical processing in the IDF region. The manuscript has now been expanded as follows: Section 3.1: "The highest concentrations of these particles were observed during a low wind speed fog event, as described in detail in Section 3.2, indicating that ECOCSOx particles are at least partly formed through heterogeneous processing of locally emitted EC particles. Identifying a specific source for these particles is difficult and is discussed below in Section 3.2." Section 3.2: "A distinct fog event was identified during Period I. As shown in Fig. 4, denoted by a red asterisk, a significant increase in mass concentration is observed for ECOCSOx on 18/01/2010. A corresponding increase in sulfate mass concentration is also observed in the HR-ToF-AMS data (Fig. S4). There is no significant shift in air mass origin from 17/01/2010-18/01/2010 (Figs. 5 and S5). Instead, this day was characterised by the lowest average wind speed of the campaign, coupled with high relative humidity (Fig. S6). The Eulerian regional chemistry transport model CHIMERE, described in detail elsewhere (Sciare et al., 2010), estimated a relatively low contribution (15%) of local emissions from within the Greater Paris (Ile de France, IDF) region to levels of particulate phase sulfate in Spring 2007. However, under low wind speed conditions, local contributions were predicted to dominate. The low wind speed suggests that ECOCSOx particles arise at least partly from local processing of EC. In fact, the highest mass concentrations of ECOCSOx particles for the entire measurement period are observed during this event. Emissions from coastal regions to the West of Paris cannot be completely ruled out as a potential source of ECOCSOx particles, however. Shipping and petrochemical industry sources are present along the Channel, and air masses arriving at the site on 18/01/2010 are susceptible to ground level emissions along the Northwest coast of France (Fig. S5). Although fresh ship exhaust particle mass spectra detected in Cork Harbour using ATOFMS were found to consistently contain vanadium, iron and nickel, these metals are not observed in ECOCSOx particles (Healy et al., 2009; Healy et al., 2010). A previous ATOFMS study performed in the

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Port of Los Angeles demonstrated that not all ship plume combustion particles contain vanadium signatures, because not all ships are using residual fuel oil (bunker fuel) (Ault et al., 2010). The soot particles assigned to ship plumes from vessels using cleaner distillate fuel in Los Angeles do exhibit similar positive ion mass spectra to the ECOC-SOÂňx particles observed in this work, however there was little or no sulfate signal detected in the Los Angeles case. The specific origin of ECOCSOx particles remains difficult to confirm, however the processing of these particles can be demonstrated to occur at a local level."

Specific Comment: Page 30348 Line 5: The contribution of other combustion sources is discussed here; I would be interested in a slight expansion of this section to discuss what other sources may be present in the Paris region and how they were determined to have minimal impact.

Response: The year-long source apportionment study mentioned in the last response is relevant here also. In that work, six major sources of PM2.5 were identified by subjecting off-line mass concentration data for a range of cations, anions, metals, and EC/OC to positive matrix fatorisation analysis (Bressi et al., 2011). The sources identified were: Traffic, Wood burning, Oil combustion, Marine aerosol, an NH4NO3 rich source and an (NH4)2SO4 rich source. The two inorganic ion-rich factors were found to have Easterly wind dependence and Marine Aerosol had a Westerly dependence. The Traffic factor was found to be of local origin. Wood Burning was found to be local but also partially imported from the South. The Oil Combustion contribution was deemed to be imported from regions outside the city to the North of Paris. These findings were consistent with the findings of this work, in that the two significant local sources of carbonaceous PM2.5 are traffic and wood burning. The following lines have now been added to Section 3.4, which is more focused on source apportionment than Section 3.1.2: "A recent year-long source apportionment study based on the chemical composition of PM2.5 in Paris resulted in the identification of six major sources (Bressi et al., 2011). The sources identified were: Traffic, Wood burning, Oil combus-

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tion, Marine aerosol, an NH4NO3 rich source and an (NH4)2SO4 rich source. The two inorganic ion rich factors were assigned to regional transport, consistent with the findings of Sciare et al. (2010). The Traffic factor was found to be of local origin. Wood burning was found to be local but also partially imported from the South. The Oil combustion contribution was deemed to be imported from regions outside the city to the North of Paris. The results are consistent with the findings of this work; that the two major local sources of carbonaceous PM2.5 in Paris are traffic and wood burning."

Specific Comment: - Page 30348 Line 11: Given the small number of bins (and likely low counts) at the smallest sizes used for the fit of the mode greater emphasis should be placed on the roughness of this assumption.

Response: It is true that the largest scaling factors are required for the smallest size bin. As discussed earlier, problems associated with assuming particle sphericity and a single density equal to the bulk particle density are more likely to be inaccurate for ECtraffic particles than for spherical, aged EC particles. The following line has now been added to the manuscript: "It must be emphasised that the large scaling factors, assumption of sphericity in the conversion of dva to dÂňve, and the assumption of a single particle density equal to the bulk particle density, are more likely to cause inaccuracy when scaling potentially fractal ECtraffic particles compared to the aged EC-containing particles discussed below (Moffet and Prather, 2009)."

Specific Comment: - Figures 7 and 8: The agreement here is remarkable; an expanded discussion of why there is divergence on Feb 10 between the methods would be of interest.

Response: As discussed in response to Reviewer 1, the divergence here is most likely due to internally mixed OC and ammonium nitrate present in the larger, more aged ECOCNOx particles. The larger diameter of these particles suggests a significant fraction of the particle volume is not EC. Thus the ATOFMS total EC-containing particle mass is higher than the EC and BC mass concentrations provided by the other in-

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struments. Section 3.3 contains the following lines which have now been expanded in response to previous comments: “A comparison of the hourly scaled ATOFMS EC mass concentrations and the hourly averaged Sunset thermal/optical EC data is given in Figs. 7 and S13. The agreement observed is reasonably good (r2 = 0.61, slope = 0.79) considering the possible sources of error associated with the ATOFMS scaling procedures. Non-spherical fractal particles exhibit different shape factors and particle densities to spherical particles, and perpendicular drag forces impact upon the transmission efficiency of the former through the instrument(Moffet and Prather, 2009). The largest, most sustained discrepancy is the overestimation of the ATOFMS EC particle mass relative to the Sunset EC during period IV (Fig. 5), which is also characterised by a much lower r2 value of 0.30. A significant fraction of the ATOFMS EC-containing particle volume for this period is expected to be ammonium nitrate and OC (Fig. S8), thus the ATOFMS EC particle mass is significantly higher than the Sunset EC mass. If period IV is removed, the agreement between the ATOFMS EC particle mass and the Sunset EC mass noticeably improves (r2 = 0.71, slope = 0.88). Good agreement was also observed between ATOFMS EC particle mass and aethalometer BC and MAAP BC mass for the entire measurement period (r2 = 0.65 and 0.68 respectively). The same discrepancy observed between the ATOFMS EC particle mass and the Sunset EC is also apparent in the MAAP and aethalometer BC datasets during Period IV (Figs. S12 and S14).”

Specific Comment: - The supplemental information is a strong aspect of the paper and supports the findings nicely. Technical Comments: - Figure 1: The labels on these peaks are really small in my version of the figure; please increase their size for the next version.

Response: The labels and text in Figs. 1,2,3,5,7 and 8 have all been increased in size in order to be easily legible upon printing.

Specific Comment: - Page 30335 line 27: This sentence might be reworded to clarify that BC has this effect if it is internally mixed.

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Response: The sentence has been reworded as follows: “BC causes positive radiative forcing (RF) through absorption and, if internally mixed, is estimated to be the second most important contributor to global warming through direct forcing after CO2 (Jacobson, 2001).”

Specific Comment: - Page 30340 line 1-2: Was testing done to determine if semi-volatile species such as ammonium nitrate were lost due to the denuder (or controlled RH system described above)? Heating has been shown to drive off nitrate from aerosols in denuder systems, could that help explain lower aeth concentrations?

Response: The sampling conditions were not identical for the aethalometer, MAAP and OCEC instruments. The MAAP was located in a container and sampled from the humidity-controlled PM10 line 6 m above ground level. The OCEC and aethalometer instruments were located on the roof of the LHVP building. A denuder was fitted upstream of the OCEC instrument, but the aethalometer sampled directly (through a cyclone) without a denuder. The most likely reasons for the differences are listed in the manuscript as follows: “Agreement is also very good between the MAAP, aethalometer and Sunset instruments (r2 = 0.86-0.94, Figs. S9-11). Differences between the aethalometer and MAAP BC datasets are expected to be mostly due to differences in the corrections used to account for scattering effects (Petzold and Schönlinner, 2004). The MAAP absorption data is internally corrected for particle and filter scattering, and thus an established MAE637nm value of 6.60 m2 g-1 is used (Müller et al., 2011). The aethalometer absorption data is not internally corrected for scattering and thus a MAE950nm value was derived from comparison with the thermal/optical EC data (5.08 m2 g-1). Differences between MAAP BC and thermal/optical EC mass concentrations have been previously reported in winter intercomparisons influenced by biomass burning, and may be partly due to the presence of light-absorbing brown carbon (Reisinger et al., 2008). Another possibility is that the thermal (NIOSH) program implemented in the OCEC instrument may be inappropriate for the analysis of wood-burning aerosols, leading to an underestimation of EC from this source (Sciare et al., 2003; Sciare et al.,

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2008)."

Specific Comment: - Figure S2: The TEOM mass is often times lower than the AMS mass, even though the AMS does not measure much above a micron and doesn't measure refractory material such as sea salt and dust that contribute to PM2.5-1, is there an explanation for the seemingly low TEOM values?

Response: The TEOM data was plotted using a secondary axis on the right hand side in order to better demonstrate the agreement between the temporality of the different PM mass measurements, despite the different size fractions. The PM2.5 mass concentration data from the FDMS-TEOM are consistently higher than the AMS PM1 and ATOFMS scaled PM1 mass concentration data. The axis labels have been increased in size and the axes are now also described in the figure caption.

Specific Comment: - Figures 7 and 8 could be combined for space considerations at a 3 level plot as they contain similar information.

Response: This is a good suggestion. These figures have now been merged to create the new Fig. 7. The authors would like to thank both reviewers for their comments which have provided some very useful insights and additions to the manuscript.

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