

Interactive comment on “Comparison between simulated and observed chemical composition of fine aerosols in Paris (France) during springtime: contribution of regional versus continental emissions” by J. Sciare et al.

J. Sciare et al.

jean.sciare@lsce.ipsl.fr

Received and published: 14 October 2010

Author's final response

First, we do thank the two reviewers for having provided very fruitful comments and constructive remarks on the manuscript.

Important efforts have been put (supplemental material with 11 Figures and Author's final answer of 15 pages) to fulfil the comments of the 2 reviewers. A point-by-point answer has been given in the following for each reviewer's comments providing (when

C8659

possible) several references to support our statements.

All the points raised by these 2 reviewers have been considered and taken into account in the revised MS. Some of these points have brought new lights on our experimental results, strengthening the general conclusions provided in the manuscript on the factors controlling PM concentration and composition in the region of Paris.

Anonymous Referee #1 Received and published: 7 August 2010 The paper presents a 3-week intensive measurement study in the city of Paris, from which the OC/EC profiles were analyzed and compared with regional model simulations. Except OC/EC, total ion concentrations are estimated from previous studies' correlations, as well as SOC/OC, based on two independent approaches. Finally, a source attribution is presented, based on back trajectory analysis, supported by model results. The results in general are adequately explained and the assumptions made are clearly mentioned. The manuscript is clearly written and the conclusions are most of the time convincing. The methods used are explained in great detail, except an important part missing from the model description that will be addressed below (comments #5 and #13). I suggest the work to be considered for publication in ACP, after addressing the following minor issues.

1) A plot showing the mean diurnal profile of the aerosols studied during the three periods can be very useful, since it might support the idea that ions originate from far away, thus do not present the expected diurnal variation of an urban site, while the carbonaceous aerosols do. This was shown in general in figure 9a, but the inclusion of ions and the separation in the three periods might provide useful additional information.

Authors: The reviewer raised an important point here regarding the factors controlling the ions concentration at our background urban site in Paris. Long-range transport

C8660

should be poorly affected by local emissions and would be less affected by the diurnal development of the PBL by comparison with C aerosols. Consequently a poorly pronounced diurnal variation for ions would bring further indications on their long range transport origin. Following the comments made by the reviewer, we have reported diurnal variations for ions & carbonaceous species for 2 cases (continental air masses -periods 1&3- and marine air masses -period2-). These figures are reported in the supplemental material (Figure 11 (A), (B), (C), (D)). They will be inserted in the revised MS together with a discussion on the factors controlling the diurnal levels of ions and carbonaceous material (see below). From these figures, it can be seen that BC diurnal profile is poorly affected by the shift from continental to marine air masses. The diurnal variation of OC is different for the 2 cases but still presents an increase during daytime (probably linked with photochemical production) and another maximum during nighttime. The diurnal variability of ions for continental air masses is important with a constant rise during nighttime (from 0:00 to 8:00 LT) when local (traffic) emissions are at their lowest. This increase is followed by a regular decrease observed during daytime (from 08:00 till 17:00 LT). This pattern is somewhat unexpected if we consider that ions are mainly governed by long range transport. On the other hand, one must keep in mind that semi-volatile ammonium nitrate is a major component of these ions and should be affected by local thermodynamic equilibriums. This is confirmed by the diurnal variations of Relative Humidity which shows values below 65% during daytime (from 08:00 till 22:00). This RH value of 65% stands for the typical limit value above which an inorganic salt (ammonium sulfate, ammonium nitrate) becomes hydrated (Wexler & Clegg, 2002). Then it can be reasonably hypothesized here that the diurnal profile of ions (during continental air masses periods) is mainly governed by the diurnal variation of semi-volatile ammonium nitrate; accumulating during nighttime under favourable thermodynamic conditions (wet aerosols) and evaporating during daytime when aerosols become dry. This RH dependence of Ammonium nitrate has been often referred in literature (Ansari & Pandis, 1999; Charron et al., 2004; Sciare et al., 2007). Note also that formation of ammonium nitrate of local/regional origin cannot

C8661

be excluded here as shown from modelling results (Figure 8a).

2) Page 16865, lines 3 and 20: artifact-free measurements: this is a very strong statement and I heavily doubt that it is correct. Maybe the new measurements are much better, but artifact-free?

Authors: We do agree with the reviewer. This is not a correct statement. Indeed the TEOM-FDMS is affected by filter sampling artefacts, but, using SES & FDMS modules, it can properly correct these artefacts making possible a quantitative determination of semi-volatile material (SVM). Since the role of SVM (incl. NH_4NO_3) is a major concern in this study, it is important to clearly state in the MS that the TEOM-FDMS is able to properly determine this fraction. We will emphasize this point in the revised MS mentioning that this instrument has shown to compare very well with other real-time measurements obtained from other analyzers taking into account semi-volatile material (Grover et al., 2005). Also, it has been widely used to investigate the role of SVM in contrasted urban areas (Sciare et al., 2007; Favez et al., 2007). Following the recommendation of the reviewer, we will replace "artifact-free" by "reliable" (PM_{2.5} measurements) in the revised MS.

3) Page 16869, lines 2-5: Sea-salt is very low even when marine air masses arrive in Paris? How low (in order to be considered negligible) are sea-salt concentrations?

Authors: Most of the mass of sea salts is located above $2.5\mu\text{m}$ and, for that reason, is not accounted by our instruments. Low concentrations of chloride were detected from the manual filter sampling during the campaign (typically below $0.5\mu\text{g}/\text{m}^3$; the highest levels being observed for marine air masses). An estimate of maximum $1\mu\text{g}/\text{m}^3$ of sea salt can be given for the second period (and concentrations of about 10 times less $-0.1\mu\text{g}/\text{m}^3-$ for the first/third periods). Sea salt may contribute at most to 15% of PM_{2.5} during the period with the lowest PM_{2.5} concentrations (second period). This

C8662

contribution is falling below 1% for the continental air masses. Few lines will be added in the revised MS about the contribution of sea salts.

4) Page 16870, lines 16-17: The domain covering the north part of France does not appear in figure 2.

Authors: This is right. This domain is not discussed anymore in the MS. This line was then suppressed in the revised MS.

5) Section 3: a description of how the emissions are distributed between hydrophobic and hydrophilic should be included, as well as a description of the aging of carbonaceous aerosols. These are necessary in order to interpret the model's results.

Authors: The model does not provide information on hydrophobic/hydrophilic fractions of organic aerosols. It simply differentiates between primary and secondary organic aerosol. Comparison between experimental and modelled SOA is using experimental estimates of SOA from 2 different methods: the EC-tracer method and the use of WSOC (being proposed here as the major component of SOA). We are aware that these 2 estimates of SOA have a lot of limitations. More efforts will be put in the revised MS to underline these limitations. In particular, the "strong" statement (WSOM = SOA) will be discussed in more details in the revised MS. This discussion is reported below: There are many known sources for organic compounds that are soluble in water. These include both primary emissions and secondary products from both biogenic sources and anthropogenic sources. (see for instance Forstner et al., 1997; Seinfeld and Pandis, 1998; Kroll et al., 2005). Many of the biomass burning compounds are also watersoluble (Novakov and Corrigan, 1996; Narukawa et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002). During our study, biomass burning contribution to carbonaceous aerosols is considered as negligible. This is supported by co-located VOC measurements showing a very low contribution (2%) of the wood burning source

C8663

(Gaimoz et al., 2010). This is also supported by an averaged angstrom exponent value (deduced from the 7-wavelength aethalometer) close to 1.0, a value which is characteristic for fossil fuel absorbing aerosols (Sandradewi et al., 2008). In the absence of biomass burning, the major WSOC source is thought to be from secondary organic aerosol (SOA) formation in which the oxidation of carbonaceous gases leads to low volatility products that may condense (Saxena and Hildemann, 1996). A large amount of studies have reported the strong connection between WSOC and secondary organics – possibly of biogenic origin – and have concluded that SOA could be approximated by WSOC (Sullivan et al., 2004; Heald et al., 2006; Myazaki et al., 2006; Kondo et al., 2006; Sullivan et al., 2006; Weber et al., 2007; Hennigan et al., 2008a, 2008b). Based on these studies and the poor contribution of biomass burning aerosols, our WSOC data using in the following have been considered as a good surrogate for SOA.

6) Page 16875, line 8: How about the local and regional sources of NH₃, NO_x and NO₂?

Authors: This is right. Local emissions may also represent a significant source of ammonium nitrate in the region of Paris. This is verified by the model results which shows in Figure 8 that ammonium nitrate of local origin is significant for continental periods (under favourable thermodynamic conditions). This is also supported by the diurnal variations of ions reported in Figure 11 (supplemental material). Changes are made in the revised MS.

7) Page 16878, lines 11-14: How does the model perform the resto of the studied period?

Authors: The model performance for the whole period is described on page 16878, lines 2 to 26. The comparison for May 25 is mentioned explicitly, because it is the day with the largest model overestimation of carbonaceous aerosol. We reformulate in the

C8664

revised MS : “Especially on May 25,”

8) Page 16878, lines 17-21: Why these issues, and especially the numerical diffusion, are not present during the rest of the studied period?

Authors: The misidentification of a rain event has been made evident during the particular period between June 8 to 10. The other reasons given are (potentially) general ones. No particular analysis was performed to evaluate simulated cloud water content or humidity. Additional analysis shows that a fraction (up to a third) of ions is simulated in particles larger than PM_{2.5}, probably due to problems in the coagulation or condensation scheme. These ions should, in principle, appear in particles with diameter below 2.5 μm , which would improve the model observation – comparison.

9) Page 16879, line 2: The simulation labeled “impact of regional emissions” is in reality an “impact of local emissions” study, and should be named as such.

Authors: Changes are made in the revised MS. The first scenario is the base case with zero local emissions. The second scenario is the base case with zero EU emissions. Scenarios have been modified accordingly. Figures 8(A) and 8(B) have been modified accordingly.

10) Page 16879, lines 8-19: The discussion, in conjunction with figure 8, is confusing. Adding the red and grey lines is not expected to give the blue line, mostly because the sources are not exclusively local and EU (based on the authors’ EU definition), but also from elsewhere, sources that are accounted for in both the two sensitivity simulations. In addition, when a simulation is being called e.g. “impact of EU emissions”, one would expect to see how much the emissions of EU contribute. Instead, the grey line shows the impact of all sources, excluding EU.

C8665

Authors: Changes are made in the revised MS following the recommendations of the reviewer. The 2 scenarios mentioned above (one with zero local emissions and one with zero EU emissions) simplify the discussion on the local vs EU contributions to fine ions and carbonaceous material.

11) Page 16879, lines 20-25: Inorganic thermodynamic equilibrium includes also NH₄. The changes of NO₃ are also being affected by changes of NH₄ (thus NH₃ emissions) and have to be taken into account in the discussion.

Authors: Few lines will be added in the revised MS on that. By contrast with many studies (reported in US), ammonia emissions are not expected to represent a major role in controlling the levels of ammonium nitrate in Northern Europe (incl. northern France) as shown by EMEP NH₃ emission maps (see also Jonson et al., 1998). Simulated NH₃ and HNO₃ concentrations at the Paris urban site confirm HNO₃ limitation for the local influence period (II), and during night time for the continental advection periods (I,III). For these periods and during midday, both NH₃ and HNO₃ are limiting. These statements will be included in the revised MS. The fact that HNO₃ is more likely to be the limiting factor in the formation of ammonium nitrate is supported by recent field results (Favez, 2009; unpublished results from the summer/winter EU-MEGAPOLI field experiments; unpublished results from the French PRIMEQUAL-FRANCIPOL program providing 1 year measurements of NH₃, HNO₃, SO₂, NH₄, NO₃, SO₄ in Paris).

12) Section 5.4: The definition of SOA is missing. Do the authors mean by SOA the organic aerosol mass produced by gaseous precursors, or also the aged primary organics as well? This definition is crucial for the understanding of the whole discussion.

Authors: SOA only refers to OA produced from gas-to-particle condensation. This definition will be reported in the revised MS.

C8666

13) Page 16880, line 26, to page 16881, line 5: This part cannot be evaluated without knowing the amount of WSOC vs. WIOC emitted, and the conversion of one to the other via aging. See also comment #5.

Authors: As mentioned in the comment #5, it is assumed here that WSOM can be used as a surrogate for SOA (assuming that SOA is defined as being exclusively produced via gas-to-particle formation). Justification is given in the revised MS. Based on this assumption, it is proposed here that WIOM can be used as a surrogate for POA. Although ageing may significantly affect the partitioning of WSOC vs WIOC, it remains unclear from literature data in which way the ageing will act (producing more WSOC or more WIOC). It remains also unclear whether this process will be more important than the gas-to-particle formation of watersoluble OA. For all that reasons, we have decided to stick to the large number of references cited in comment #5 proposing WSOC as a surrogate for SOA.

14) Page 16882, line 20: This does not make sense. The model does not have dedicated BC emissions, but has a scaling factor based on OC emissions?

Authors: This sentence is misleading. In fact, the ratio of 1.35 can be derived from the POA / EC concentration ratio. In the study, this ratio is on the average 1.35, with values ranging from 1.2 to 1.5. This ratio is NOT fixed in the model. POA and EC are emitted independently, as explained in section 3. POA and EC are considered as chemically inert, non-volatile, and loss processes are similar. This is why the POA/ EC ratio in the model is not quite stable. Recent studies have shown that POA could present a semi-volatile pattern (Robinson et al., 2007). The fact that POA is considered as non-volatile in the model might contribute to the fact that the simulated POA/EC ratio is larger (by about a factor 2) than that derived by the EC tracer method. The misleading sentence will be removed in the MS and replaced by the arguments given above.

C8667

Technical corrections

15) Page 16878, lines 10 and 16: 8-10 of June should be 7-9, based on figure 7.

Authors: Changes are made in the revised MS.

16) Page 16883, line 23: "more stable" should read "less variable".

Authors: Changes are made in the revised MS.

17) Figure 8: The colors in the figure and the text do not correspond with the colors in the legend. My guess is that the legend is wrong, otherwise the whole discussion is off.

Authors: Changes are made in the revised MS.

Anonymous Referee #2 Received and published: 20 August 2010 This paper describes an experimental and modeling study of fine particle pollution in Paris. The paper reports high time resolved data for Paris from a three week period in the spring of 2007. Data analysis is presented that quantifies the relative importance of more local (called regional) versus continental emissions. The data are also used to evaluate the chemical transport model CHIMERE, which is then used to examine sources of pollution in Paris. The paper concludes that the high fine PM concentrations in Paris are associated with ions and emissions in northern Europe. This has important implications about the potential effectiveness of local emissions controls, a point made in the conclusion of the paper.

The paper is of interest to readers of ACP. Below I have outlined some con-

C8668

cerns with the experimental work and model evaluation that need to be addressed.

Major concerns OC measurements – The paper compared manual filter sample measurements with those taken using an in situ or field OC/EC analyzer to validate the OC EC data. The OC data from the two approaches are highly correlated with a slope of 1 but there was an offset of 3 $\mu\text{g}/\text{m}^3$. My understanding is that the in situ instrument was higher than the manual sample (is that correct?). That is a very big number given that the ambient carbonaceous (OC+EC) concentration during the study was typically less than 10 $\mu\text{g}/\text{m}^3$. For their analysis they simply subtracted off this 3 $\mu\text{g}/\text{m}^3$ claiming that it is a sampling artifact. However, both the manual sampler and the in situ instrument had denuders so the source of such a large positive artifact seems very unclear. This is a big correction (30-60% of ambient) which potentially has important implications on some of the conclusions of the work. The authors appear to be assuming, without any justification/discussion, that the manual filter samples are correct. It is not clear to me that that is necessarily the case. Although this correction will likely not influence conclusions regarding the contribution of OC to the large spikes in PM it will alter the overall PM mass balance and affect conclusions regarding the model performance for OC. The authors need address this issue, especially since the OC data are key to deriving all of the high time resolved ion concentrations.

Authors: We do agree with the reviewer that this “blank” value of 3 $\mu\text{g}/\text{m}^3$ is a large number that will require more explanations in the revised version. Such blank issues with the sunset field instrument have been widely reported in literature and associated with a breakthrough of the VOC denuder (Bae et al., 2004; Arhami et al., 2006; Polidori et al., 2006; Offenberg et al., 2008; d’Argouges, 2009). Using the same methodology as ours (off-line filter sampling with VOC denuders), Bae et al. (2004) have reported constant blank values of $\sim 1 \mu\text{gC}/\text{m}^3$. Blanks can be also performed using a Teflon filter upstream of the VOC denuder. Doing so, Arhami et al. (2006) have reported for an urban site in Los Angeles a constant off-set for OC of $0.82 \pm 0.31 \mu\text{gC}/\text{m}^3$ unrelated to OC concentrations. Using the same methodology (total filter upstream of the VOC de-

C8669

nuder), we have been running our Sunset Field Instrument continuously for 1 week in the region of Paris during the spring period (d’Argouges, 2009). An averaged EC value of $0.01 \pm 0.01 \mu\text{gC}/\text{m}^3$ (N=150 data points) was obtained here demonstrating the efficiency of the total filter and the lack of leaks in our sampling system. An averaged OC value of $1.46 \pm 0.40 \mu\text{gC}/\text{m}^3$ (N=150 data points) was then obtained, bringing further evidence of the existence of absorbed VOC onto the filter matrix within the instrument. The influence of this off-set given by the Sunset Field instrument has been investigated in a more systematic way by Offenberg et al. (2008). These authors have shown that this off-set (ranging from 0.5 μgC to 2.0 μgC) was strongly dependent on the sampled air volume; more air being needed to minimize the off-set. During our study, the averaged OC filter loading in our Sunset field instrument was typically of $2.63 \pm 0.56 \mu\text{gC}$ (without blank correction); $1.33 \pm 0.56 \mu\text{gC}$ once the VOC adsorption correction is made. Our blank correction (due to VOC adsorption) of 1.3 μgC is not an uncommon value (Offenberg et al., 2008). A simple sensitivity test can be performed here using field OC concentrations not corrected from this 3 $\mu\text{gC}/\text{m}^3$. Doing so, the concentration of carbonaceous aerosols (EC+1.6*OC) for the second period of the campaign is on average $9.4 \pm 1.5 \mu\text{g}/\text{m}^3$ which is systematically higher than PM_{2.5} (TEOM-FDMS) which is on average $7.4 \pm 2.5 \mu\text{g}/\text{m}^3$ during the same period. Using an OC-POM of 1.4 during this second period brings EC+POM to $8.4 \mu\text{g}/\text{m}^3$ which is still significantly higher to PM_{2.5}. These results are consistent with our results suggesting that OC is overestimated within the ECOC Sunset Field Instrument. We do agree with the reviewer that this OC correction will alter the PM mass balance (Figure 1 of the ACPD paper). The absence of such OC correction will lead to similar slope (0.93) and correlation coefficient (0.96) between reconstructed and measured PM_{2.5}. On the other hand, it will increase the intercept (from -1.67 $\mu\text{g}/\text{m}^3$ to -3.18 $\mu\text{g}/\text{m}^3$) pointing out an increasing role of a constant bias in the reconstructed PM. Again, this is consistent with the idea that OC field measurements are affected by a constant bias (due to VOC adsorption). In conclusion, several studies have clearly shown that the existence of a sampling artefact (VOC adsorption onto the filter matrix) within the Sunset Field Instrument. This

C8670

artefact will play an important role if the sampling time is reduced and/or particulate OC are low (which is the case for our study). We do believe that the intercept between the OC dataset (field instrument and manual filter sampling) can be explained by such sampling artefact observed for the field instrument. More explanations will be given in the revised version of the manuscript (MS) to justify the reason of this correction of Field OC concentrations of $3\mu\text{gC}/\text{m}^3$. The figure reporting the temporal variations of OC (Sunset Field Instrument and manual filter sampling) will be added in the revised MS to better illustrate the good agreement between this 2 dataset (Figure 1 of the supplemental material).

Intercomparison of samplers – In section 2.3 the authors report results from linear regressions of manual and field samplers to validate these data. Given that regressions can be strongly influenced by outliers the authors should present scatter plots of the actual data. These could be put in the supplemental material. This seems particularly important for the OC measurements given the large intercept and lower R2 value (0.76). For example, are there any trends in sampler performance with levels – e.g. could the field measurement not be capturing the high spikes for some reason.

Authors: In order to get a better idea of the temporal variations of OC (filter sampling) and OC (Sunset Field Instrument), these 2 temporal variations have been reported in supplemental material (Figure 1). The “horizontal” bars in the filter sampling OC data stand for the sampling interval for each data point. Correlation between this 2 dataset has been also reported as suggested by the reviewer (Figure 2). The secondary Y axis (field measurements) has been shifted by $3\mu\text{gC}/\text{m}^3$ to better characterize the good covariation between the 2 datasets. As it can be seen from these figures, both datasets appear to properly account for the major maximum/minimum values. Given this, there is no clear trend in the sampler performance (concern of the reviewer). The fact that OC concentrations in the filter sampling are not highly variable during the campaign probably prevents probably from better correlation between the 2 datasets. This is

C8671

verified when the 2 datasets are compared in terms of OC (μgC) for the sampling intervals of the manual filter sampling ($r^2=0.80$).

Strong correlation of inferred ions and measured ions. I found this surprising. It was also not clear how much nitrate was in the aerosol. As stated in the paper nitrate is semivolatile and that during episodes (5 to 15 $\mu\text{g}/\text{m}^3$ of aerosol was semivolatile). Samplers that quantitatively measure nitrate usually have denuders to capture volatilized nitrate. However, the sampler used in this study did not. Therefore the strong agreement of inferred ions and measured ions is somewhat surprising. It is not clear to me how they achieved such a high level of nitrate capture using this sampler if there was a lot of nitrate in the aerosol.

Authors: In order to better illustrate the good agreement between measured (filter sampling) and reconstructed ions, we have reported in the supplemental material the temporal variations of both dataset (Figure 3) as well as the correlation between them (Figure 4). In order to better address the role of semi-volatile ammonium nitrate, we have also reported in the supplemental material the ammonium nitrate and ammonium sulfate concentrations obtained from the filter sampling (Figure 5). The “horizontal” bars in the filter sampling ion data stand for the sampling interval for each data point. From these figures, we can see that the good agreement between the 2 ion datasets is well established (and not statistically driven by few outliers). The following explanation can be proposed to interpret the “unexpected” performance our filtration system: It can be seen from Figure 3, that the best agreement between measured and reconstructed ions is obtained when the filter sampling intervals are small (typically 2-4 hours). By opposite, the largest differences in the two dataset are observed with longer sampling intervals (typically 1 day). It can be proposed here that short sampling intervals are expected to cover periods with relatively stable thermodynamic conditions (e.g. no significant change in the equilibrium between gas and aerosol phase of nitrate). Then, ammonium nitrate collected during this period will not volatilize and will be properly

C8672

determined from the filter analysis. In contrast, thermodynamic equilibrium may significantly change for longer sampling periods (of typically 1 day). Semi-volatile nitrate may then evaporate during these periods inducing a significant bias in the determination of ammonium nitrate from the filter sampling. Figure 3 reporting the temporal variations of ions (measured and reconstructed) will be added in the revised MS to better illustrate the good agreement between this 2 datasets. The fact that the best agreement between the 2 ion datasets was obtained for short sampling intervals (probably during periods with stable thermodynamic conditions) will also be added in the revised MS as an explanation for the good agreement between measured and reconstructed ions.

Page 16783 – the paper states that nitrate is main component of SVOC. Another candidate would be semivolatile organics. Do the authors have direct evidence that the SVOC was actually nitrate? Maybe more volatile (semivolatile) OA contributes to high spikes that is removed/evaporated in denuder and therefore not measured. Note that by using the denuder they may be just measuring the low volatility, background OC. See papers by Delbert Eatough and the PC-BOSS sampler.

Authors: Page 16783, line 14; The paper states that ammonium nitrate could be partially inferred from the levels of SVM (and not SVOC). There is no direct evidence in this study that SVM is exclusively composed of Ammonium nitrate although a recent paper by Favez et al. (2007) has shown that SVM (from TEOM measurements) can be mainly explained by ammonium nitrate during wintertime in Paris. Since this point is not an important issue for the paper, we have removed this statement on SVM in the revised MS.

Section 4.3 – In this section the authors compare PM_{2.5} levels at three sites. Based on this comparison they conclude that “most of ion species observed in Paris were transported.” However, this conclusion is completely qualitative. Looking at Figure 5 it appears that levels in Paris are significantly higher than the Bethune site during

C8673

periods 1 and 3. They also seem to be higher than in Paris then in St. Jean. By eye there does seem to be some correlation of the data from the different sites but there are also clear instances when the PM levels at the sites are showing different trends. The authors need to make much more quantitative comparisons. What is the correlation of time series? What are the average levels for different periods? These sorts of comparisons need to be done to quantitatively estimate regional background levels and the Paris urban excess.

Authors: We do agree with the reviewer, the purpose of this comparison is mainly qualitative since quantitative comparison may be hard to achieve considering the sulfate and nitrate gradient concentrations within the plumes from N-E Europe (illustrated in Figure 6). Discrepancies between 2 stations could be also explained by photochemical formation and/or thermodynamic equilibrium (for ammonium nitrate) or even just by transport gradients within the plumes. For that reason, we cannot simply subtract 2 datasets (from 2 different stations) to investigate regional/continental contributions. Only model calculation can take into account these different parameters (diffusion, thermodynamic equilibrium, photochemical processes . . .). This is the main reason why we have decided here to use model results to investigate local/continental contributions. Nevertheless, for the closest stations (Paris & St Jean located at about 100km distance), a comparison can be performed and is reported in Figures 6 & 7 (supplemental material). The best correlation of 0.68 is obtained between these 2 stations when a time shift of 3h is applied for the St Jean dataset. This shift is relatively consistent with the transit time of air masses coming from N-E Europe (Figure 4 of the MS) and reaching Paris about 2-4h before arriving at St Jean. This good agreement is in line with the statement made in the manuscript: “it can reasonably be hypothesized that most of the ion species observed in Paris during our study were transported (or formed during their transport) from continental Europe and were spread over large areas”. This quantitative comparison will be reported in the revised MS to strengthen our qualitative statements on large scale elevated PM episodes. Note that the comparison between Paris (LHVP) and St Jean shows very comparable results for the second period which

C8674

is somewhat surprising considering the fact that St Jean is much less impacted by local (traffic) sources compared to Paris. This would suggest that a major fraction of PM during this period is not local but has a regional (France) origin. This is consistent with our conclusion (page 16885) stating that “regional emissions may have been quite important and/or have reacted quite rapidly, bringing the relative abundance of SOA at similar levels compared to continental aged air masses”.

Section 5.2 – In this section they compare model to measurements, concluding “general good agreement observed in Figure for all chemical constituents.” The authors needs to be much more quantitative on model measurement comparison. Please present scatter plots. Calculate standard performance measures such as error and bias. Although the model appears to reproduce temporal patterns in Figure 6b it clearly is significantly under predicting most peaks in the ion concentrations by 10 ug/m³ or more. The agreement for PM_{2.5} mass seems surprising good given the problems with ion predictions. Some of this is due to compensating errors, for example PM peak on 5/25 is predicted correctly because model is way overpredicting organics but underpredicting ions. The model also seems to be overpredicting the temporal variability of organics. Note that the fact that model captures some of the daily pattern is simply due to boundary layer dynamics so absolute comparisons are important.

Authors: We do agree with the reviewer that the good agreement between measured/modelled PM_{2.5} is partly due to compensating errors between individual fractions (ions, carbon). In the revised MS, we will downsize the conclusion about a general good model to observation agreement and will differentiate our statement for different fractions. Quantitative comparison (includ. scatter plots) will be performed between model and measurements results in the revised MS. They are reported in Figure 8 as scatter plots. Measured and modelled PM_{2.5} have shown to be correlated ($r^2=0.63$; N=354) with a slope of 1.10 (e.g. ~10% underestimation of model results) and intercept of 3.4 μg/m³. The sample-to-sample error is on average 28±18%. Measured

C8675

and modelled ions have shown a correlation coefficient of $r^2=0.59$ (N=354) but showing a net underestimation of more than 60% from the model. Measured and modelled carbonaceous matter have shown to be poorly correlated ($r^2=0.26$; N=354).

Figure 10. & page 16881 paper says that SOA and POA estimates are poorly correlated. This is not clear from figure. Please provide quantitative measures of correlation and comparison of the two estimates.

Authors: In order to better show that SOA and POA are poorly correlated, we have reported in Figure 9 & 10 (supplemental material) the temporal variation and scatter plot of these 2 datasets obtained from the EC-tracer method. As shown from these figures, there is no correlation between the 2 dataset ($r^2=0.01$). One sentence will be added in the revised MS given the result of this correlation. The small number of data points available for comparison between the 2 methods to estimate POA and SOA (N=18) makes difficult to bring a more definite answer on the discrepancies observed in Figure 10.

Couldn't the SOA in period 2 have been advected into Paris from the marine environment?

Authors: Marine SOA are likely to play a very minor role compared to continental sources (O'dowd et al., 2004; Sciare et al., 2009; Arnold et al., 2009; Myriokefalitakis et al., 2010) and are not considered here as playing a significant role. We will add this sentence in the revised MS.

Is the Primary OC/EC ratio you derive valid for marine air masses?

Authors: Our primary OC/EC ratio was taken from air masses originating from the ocean (MS page 16681, lines11-14), e.g. during the second period of the campaign.

C8676

We will make this more clearly in the revised MS version.

I did not follow the argument for why local SOA formation was important.

Authors: We agree that the statement on SOA formation during the second period reported in the MS is not clear. We will rephrase it in the revised MS. During the second period (with clean air masses originating from the Atlantic Ocean) still elevated SOA levels (EC-tracer method) are observed ($2.7 \pm 1.7 \mu\text{g}/\text{m}^3$). Keeping in mind that the marine SOA source is very weak, most of the SOA signal recorded in Paris should originate from fast processes occurring upwind of the agglomeration (marine air masses arriving in Paris have on average a 10-h residence time above ground level during the second period). Note that these findings are consistent with the results obtained in Paris region during the EU-FP7-MEGAPOLI summer experiment (Sciare et al., IAC, Helsinki, 2010).

Is WSOC all SOA?

Authors: This campaign is not affected by wood burning (cf PTR-MS measurements of methanol and acetonitrile performed in parallel and reported in Gros et al., Environ. Chem., under review). In the absence of wood burning it is reasonable to assume that a large fraction of SOA is oxidised and then water soluble. Report to the authors answer to comment #5 (reviewer #1).

How does the large corrections made to the OC data effect the conclusions reached about model performance with respect to OC, POA and SOA. If the field data are correct (i.e. we should not subtract off $3 \mu\text{g}/\text{m}^3$) would comparisons get better or worse?

Authors: As explained before, such correction of $3 \mu\text{g}/\text{m}^3$ is needed to be consistent

C8677

with PM_{2.5} measurements performed during the second period.

Minor comments

"Measurement uncertainty given by the ECOC analyzer is poorly described in literature and an estimate of 20% for this uncertainty was taken here following Peltier et al. (2007)." I disagree with this statement. There have been numerous studies looking at this issue. Schauer, J. J., B. T. Mader, et al. (2003). "ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon." *Environmental Science & Technology* 37(5): 993-1001. Looks at precision of instruments running same protocol. Judy Chow has written numerous papers on effects of analysis protocol on EC measurements (here is one of Judy's papers. Chow, J. C., J. G. Watson, et al. (2001). "Comparison of IMPROVE and NIOSH carbon measurements." *Aerosol Science and Technology* 34(1): 23-34.) Others have looked at these issues as well Subramanian, R., A. Y. Khlystov, et al. (2006). "Effect of peak inert-mode temperature on Elemental Carbon measured using Thermal-Optical Analysis." *Aerosol Science and Technology* 40(10): 763-780. There have been numerous interlaboratory comparisons of EC measurements with different techniques. There is lots of work on sampling artifacts and OC measurements – see review by Turpin, B. J., P. Saxena, et al. (2000). "Measuring and simulating particulate organics in the atmosphere: problems and prospects." *Atmospheric Environment* 34(18): 2983-3013.

Authors: We thank the reviewer for this detailed review on OC measurement uncertainties. However, it is not our purpose to give in this paper a critical review on the large number of uncertainties related to sampling and analysis of OC. The sentence given in the text (concern of the reviewer) refers to measurement uncertainties given by the instrument "ECOC analyzer" and not by the thermo-optical method implemented in it. To our best knowledge, uncertainties given by this instrument (and not by the thermo-optical method) is poorly described in literature and an estimate of 20% for this

C8678

uncertainty was taken here following Peltier et al. (2007). We will state more clearly in the revised MS that measurement uncertainties stand here for the instrument itself and do not refer to positive/negative filter sampling artefacts nor uncertainties associated with the thermo-optical (TOR) method implemented in the Sunset Field Instrument.

Aethalometer – the paper reports excellent agreement between BC measured with Aethalometer and EC measured with the in situ instrument. Better than the comparison of the EC measurements made with the manual and in situ samples, which is somewhat surprising since the EC measurements were made using thermal-optical analysis and the Aethalometer uses a different fundamentally different technique. Previous intercomparison studies have reported larger discrepancies between EC and BC. How were the Aethalometer data analyzed to determined BC? Was there any adjustment made to the absorption coefficient to improve agreement?

Authors: Paris stands for a large and homogeneous source of EC from traffic (mainly of diesel origin). Wood burning EC and/or long range transported EC are expected to poorly contribute to the EC signal in Paris (see previous authors' comments). Consequently, mass absorption efficiency is expected to be quite stable during our study. This could partly explain the reason why a good agreement is observed between EC and BC. Note also that EC is derived from a thermo-optical technique, which comprises an optical correction which is sensitive to absorbing material (like the aethalometer). This may be another reason to explain the close relationship between EC and BC.

Page 16882 – the model derives POA by multiplying EC by a factor? This implies the model is not simulating POA ? What is the basis for this factor?

Authors: As stated previously in response to first reviewer comments, the initial manuscript is misleading. There is no multiplicative factor between POA and EC in the model. A ratio of 1.35 (± 0.15) was derived from the simulated POA / EC concentration

C8679

ratio at the Paris urban site. POA and EC are treated independently in the model, as explained in section 3. However, once emitted there pathways in the atmosphere are similar because POA is considered as non-volatile. The misleading sentence will be removed in the MS and replaced by the arguments given above.

Page 16871 – I am not sure what a semi-volatile VOC is – presumably this is a semivolatile product of a VOC that forms SOA

Authors: This is simply a mistake (should read “semi-volatile OC”). Correction made in the revised MS.

The word “poorly” or “poor” seems to be misused several times in manuscript. E.g. in abstract “poorly contribute” Page 16869 – “poorly affected by water uptake” 18882 “poorly effected by air mass origin” page 16878 “poor temporal variability” My sense is another word would be more appropriate.

Authors: Changes are made in the revised MS. Poorly is replaced by weakly when appropriate.

Fig 3 and elsewhere. The legend in this figure says ion are experimental. This implies they were measured. However, they were not. They are inferred from nephelometer data using a model. Change label to “inferred ions”

Authors: Changes made in the revised MS

REFERENCES cited by the authors

Ansari, A. S., and S. N. Pandis (1999), An analysis of four models predicting the partitioning of semi-volatile inorganic aerosol components, *Aerosol Sci. Technol.*, 31, 129–

C8680

Arhami, M., Thomas Kuhn, Philip M. Fine, Ralph J. Delfino, and Constantinos Sioutas, Effects of Sampling Artifacts and Operating Parameters on the Performance of a Semi-continuous Particulate Elemental Carbon/Organic Carbon Monitor, *Environ. Sci. Technol.*, 2006, 40 (3), pp 945–954, DOI: 10.1021/es0510313

Arnold, S. R., D. V. Spracklen, S. Alvaïn, C. Moulin, J. Williams, N. Yassaa, and J. Sciare, Global estimates of oceanic isoprene emissions from speciated phytoplankton and impacts on marine organic carbon, *Atmos. Chem. Phys.* 9, 1253-1262, 2009

Bae MinSuk, Schauer JJ, DeMinter JT, Turner JR, Smith D, Cary RA. Validation of a semicontinuous instrument for elemental carbon and organic carbon using a thermal-optical method. *Atmos Environ* 2004;38:2885–93.

Charron, A., R. M. Harrison, S. Moorcroft, and J. Booker (2004), Quantitative interpretation of divergence between PM10 and PM2.5 mass measurement by TEOM and gravimetric (Partisol) instruments, *Atmos. Environ.*, 38, 415– 423.

Favez, O., H. Cachier, J. Sciare, Y. Le Moullec, Semi-volatile aerosols in Paris (France): Characterization and contribution to PM2.5, *Atmos. Environ.*, 41, 7969-7976, 2007

Forstner, H. J. L., J. H. Seinfeld, and R. C. Flagan (1997), Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: Molecular composition, *Environ. Sci. Technol.*, 31, 1345–1358.

Gaimoz, C. S. Sauvage, V. Gros, F. Herrmann, J. Williams, N. Locoge, O. Perrussel, B. Bonsang, O. d'Argouges, R. Sarda-Estève, and J. Sciare, Volatile organic compounds sources in Paris in spring 2007. Part II: Source apportionment using positive matrix factorization, *Environ. Chem.*, under revision, 2010

Graham, B., O. L. Mayol-Bracero, P. Guyon, G. C. Roberts, S. Decesari, M. C. Facchini, P. Artaxo, W. Maenhaut, P. KoÅill, and M. O. Andreae (2002), Water-soluble organic compounds in biomass burning aerosols over Amazonia: 1. Characterization by NMR
C8681

and GC-MS, *J. Geophys. Res.*, 107(D20), 8047, doi:10.1029/2001JD000336.

Heald, C. L., et al. (2006), Concentrations and sources of organic carbon aerosols in the free troposphere over North America, *J. Geophys. Res.*, 111, D23S47, doi:10.1029/2006JD007705.

Hennigan, C. J., A. P. Sullivan, C. I. Fountoukis, A. Nenes, A. Hecobian, O. Vargas, A. T. Case Hanks, L. G. Huey, B. L. Lefer, A. G. Russell, and R. J. Weber, On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City, *Atmos. Chem. Phys.*, 2008a

Hennigan, C. J.; Bergin, M. H.; Dibb, J. E.; Weber, R. J. Enhanced secondary organic aerosol formation due to water uptake by fine particles. *Geophys. Res. Lett.* 2008b, 35, L18801, 10.1029/2008GL035046.

Jonson, J. E., J. Bartnicki, K. Olendrzynski, H. A. Jakobsen and E. Berge, EMEP Eulerian model for atmospheric transport and deposition of nitrogen species over Europe, *Environmental Pollution*, 102, 1, Pages 289-298, 1998.

Kondo, Y.; Miyazaki, Y.; Takegawa, N.; Miyakawa, T.; Weber, R. J.; Jimenez, J. L.; Zhang, Q.; Worsnop, D. R. Oxygenated and water-soluble organic aerosols in Tokyo. *J. Geophys. Res.* 2007, 112, D01203, 10.1029/2006JD007056.

Kroll, J. H., N. L. Ng, S. M. Murphy, R. C. Flagan, and J. H. Seinfeld (2005), Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions, *Geophys. Res. Lett.*, 32, L18808, doi:10.1029/2005GL023637.

Mayol-Bracero, O. L., P. Guyon, B. Graham, G. Roberts, M. O. Andreae, S. Decesari, M. C. Facchini, S. Fuzzi, and P. Artaxo (2002), Water-soluble organic compounds in biomass burning aerosols over Amazonia: 2. Apportionment of the chemical composition and importance of the polyacidic fraction, *J. Geophys. Res.*, 107(D20), 8091, doi:10.1029/2001JD000522.

Miyazaki, Y.; Kondo, Y.; Takegawa, N.; Komazaki, Y.; Fukuda, M.; Kawamura,
C8682

K.; Mochida, M.; Okuzawa, K.; Weber, R. J. Time-resolved measurements of water-soluble organic carbon in Tokyo. *J. Geophys. Res.* 2006, 111, D23206, 10.1029/2006JD007125.

Myriokefalitakis S., Vignati E., Tsigaridis K., Papadimas C., Sciare J., Mihalopoulos N., Facchini M. C., Rinaldi M., Dentener F. J., Ceburnis D., Hatzianastasiou N., O'Dowd C.D., van Weele M., Kanakidou M., Global modelling of the oceanic source of organic aerosols, *Adv. Meteorol.*, in press 2010

Novakov, T., and C. E. Corrigan (1996), Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, 16, 2141–2144.

Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima (1999), Distribution of dicarboxylic acids and carbon isotope compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, 26, 3101–3104.

Offenberg, J.H., Michael Lewandowski, Edward O. Edney, and Tadeusz E. Kleindienst, Investigation of a Systematic Offset in the Measurement of Organic Carbon with a Semicontinuous Analyzer, *Journal of the Air & Waste Management Association*. Vol. 57, no. 5, pp. 596-599, 2007

Polidori A, Turpin BJ, LimHo-Jin, Cabada JC, Subramanian R, Pandis SN, Robinson AL. Local and regional secondary organic aerosol: insights from a year of semi-continuous carbon measurements at Pittsburgh. *Aerosol Sci Technol* 2006;40:861–72.

Robinson, A.L., N.M. Donahue, M.K. Shrivastava, E.A. Weitkamp, A.M. Sage, A.P. Grieshop, T.E. Lane, J.R. Pierce, S.N. Pandis, Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging, *Science*, 315, 1259 – 1262, 2007

Sandradewi, J., Prévôt, A.S.H., Szidat, S., Perron, N., Alfarra, M.R., Lanz, V.A., Weingartner, E., Baltensperger, U., 2008. Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter. *Environ. Sci. Technol.*, 42, 3316-3323.

C8683

Saxena, P., and L. M. Hildemann (1996), Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57– 109.

Sciare, J., H. Cachier, R. Sarda-Estève, T. Yu, and X. Wang (2007), Semi-volatile aerosols in Beijing (R.P. China): Characterization and influence on various PM_{2.5} measurements, *J. Geophys. Res.*, 112, D18202, doi:10.1029/2006JD007448.

Sciare, J., O. Favez, K. Oikonomou, R. Sarda-Estève, H. Cachier, and V. Kazan, Long-term observation of carbonaceous aerosols in the Austral Ocean: Evidence of a marine biogenic origin, *J. Geophys. Res.*, 114, D15302, doi:10.1029/2009JD011998, 2009

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Changes*, John Wiley, Hoboken, N. J.

Sullivan, A. P., R. J. Weber, A. L. Clements, J. R. Turner, M. S. Bae, and J. J. Schauer (2004), A method for on-line measurement of watersoluble organic carbon in ambient aerosol particles: Results from an urban site, *Geophys. Res. Lett.*, 31, L13105, doi:10.1029/2004GL019681.

Sullivan, A. P., R. E. Peltier, C. A. Brock, J. A. de Gouw, J. S. Holloway, C. Warneke, A. G. Wollny, and R. J. Weber (2006), Airborne measurements of carbonaceous aerosol soluble in water over northeastern United States: Method development and an investigation into water-soluble organic carbon sources, *J. Geophys. Res.*, 111, D23S46, doi:10.1029/2006JD007072.

Weber, R. J.; Sullivan, A. P.; Peltier, R. E.; Russell, A.; Yan, B.; Zheng, M.; de Gouw, J.; Warneke, C.; Brock, C.; Holloway, J. S.; Atlas, E. L.; Edgerton, E (2007). A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. *J. Geophys. Res.* 2007, 112, D13302, 10.1029/2007JD008408.

Wexler, A. S. , and S. L. Clegg (2002) Atmospheric aerosol models for systems including the ions H⁺, NH₄⁺, Na⁺, SO₄²⁻, NO₃⁻, Cl⁻, Br⁻ and H₂O. *J. Geophys.*

C8684

Res. 107, No. D14, art. no. 4207, 14 pages.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C8659/2010/acpd-10-C8659-2010-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 16861, 2010.

C8685