**Atmospheric
Chemistry
and Physics
Discussions**

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.

Anonymous Referee #2

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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 concerns 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 ug/m3. 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 ug/m3. For their analysis they simply subtracted off this 3 ug/m3 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.

Intercomparison of samplers – In section 2.3 the authors report results from linear re-
gressions 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 particu-
larly 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.

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 ug/m3 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.

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.

Section 4.3 – In this section the authors compare PM2.5 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 is appears that levels in Paris are significantly higher than the Bethune site during 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.

Section 5.2 – In this section they compare model to measurements, concluding "gen-

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eral 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 PM2.5 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 under-predicting 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 comparison s are important.

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.

I did not follow the argument for why local SOA formation was important. Couldn't the SOA in period 2 have been advected into Paris from the marine environment? Is the Primary OC/EC ratio you derive valid for marine air masses? Is WSOC all SOA? 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 ug/m3) would comparisons get better or worse?

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

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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.

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?

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?

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

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.

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"

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