Response to Reviewers for the manuscript Amato et al., 2015, under review for ACP. Comments from Referees are numbered as RC1, RC2 .., author's response as AR1, AR2..

RC1. The paper of Amato et al. presents a comparison between 5 cities in the Southern Europe for a full year. This comparison involves PM2.5 and PM10 filter based measurements and source apportionment techniques. The findings are important for the aerosol community and the topic is relevant to the ACP. I recommend publishing of this paper, however after some improvements:

The introduction and especially the conclusion part is too long (almost 2.5 pages), which makes it very difficult for the reader to remember most of the information. I suggest you reduce them highlighting only the most important findings, so that the reader still finds it interesting.

AR1. Both sections have been shortened significantly. We have moved the specific conclusions on PM speciation for each city to the Supplementary Material.

RC2. I recommend adding headlines between the different topics in the section “3.2.8 Source apportionment results” so the reader would be easily guided.

AR2. Headlines for each source category have been added

RC3. The figures 3, 4 and 5 are quite busy and difficult to be read. A lot of information is given in a rather chaotic way. For example in Figure 3 you could make the y axis linear (instead of logarithmic) and ignore values lower than 0.01 (you could give the whole information in the supplement). The size fonts are very small and are difficult to be read. The graphs should be presented in such a way that could be easily read.

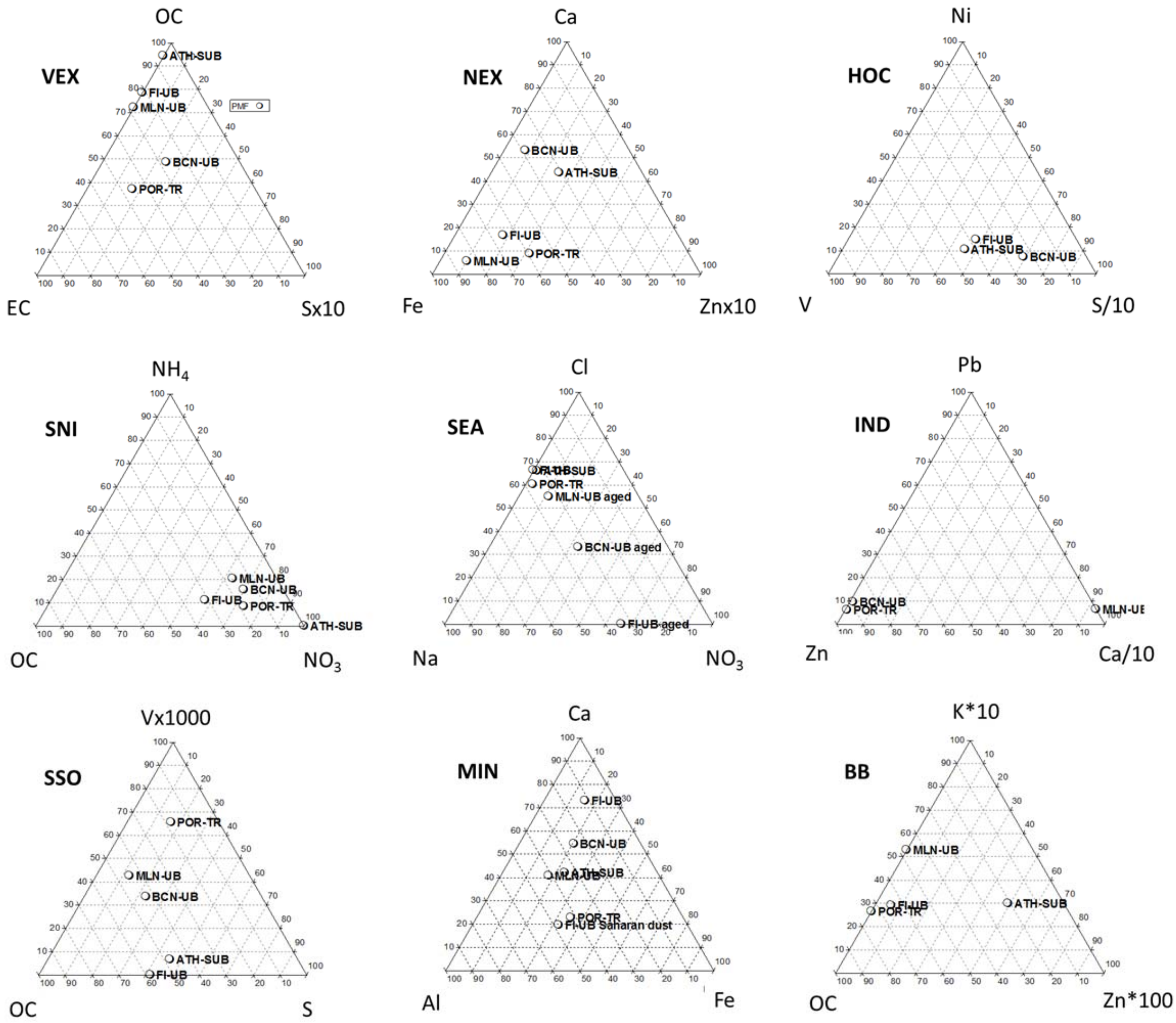
AR3. Figure 3 has been improved ignoring values below 0.001, since 0.01 would not allow showing important tracers (e.g. Sb in the Non-exhaust (NEX) factor and Ni in the Heavy oil combustion (HOC) profile). Font size has been increased. We believe that logarithmic scale is more suitable to identify tracers, since the explained variation is not plotted.

Figure 4 has been improved increasing font size.

Figure 5 has been deleted and replace by 5 tables in the supplementary material.

In order to simplify factor comparison we have produced ternary plots, using specific tracers for each source. These plots allow:

- Identifying “common” chemical signatures among AIRUSE cities (Secondary Nitrate (SNI) and HOC)
- Visualizing clear separation among AIRUSE cities for a single factor (NEX, Sea salt (SEA), Biomass burning (BB) and Mineral (MIN)).



RC4. More specific comments: 1- Please clarify whether or not the filter analysis from these 5 cities was performed by one or more laboratories (i.e. the same or different instrumentation).

AR4. The ICP-MS, PIXE, GC-MS, Infrared, XRF analysis were performed in one laboratory for each technique, while IC and ECOC analysis were performed by each laboratory separately but following the same protocol. This information has been added to the text (Section 2.2)

RC5. 2- Page 8, line 21: Please provide reference.

AR5. We cannot identify exactly what statement the reviewer refers to. If he/she refers to “After sampling, filters were brought back to the laboratory to be weighed two more times every 24 h of conditioning at the same temperature and relative humidity as the first weighing” we do not think a reference is required here, and that maybe reviewer wanted to make ref to another statement.

Anonymous Referee #3

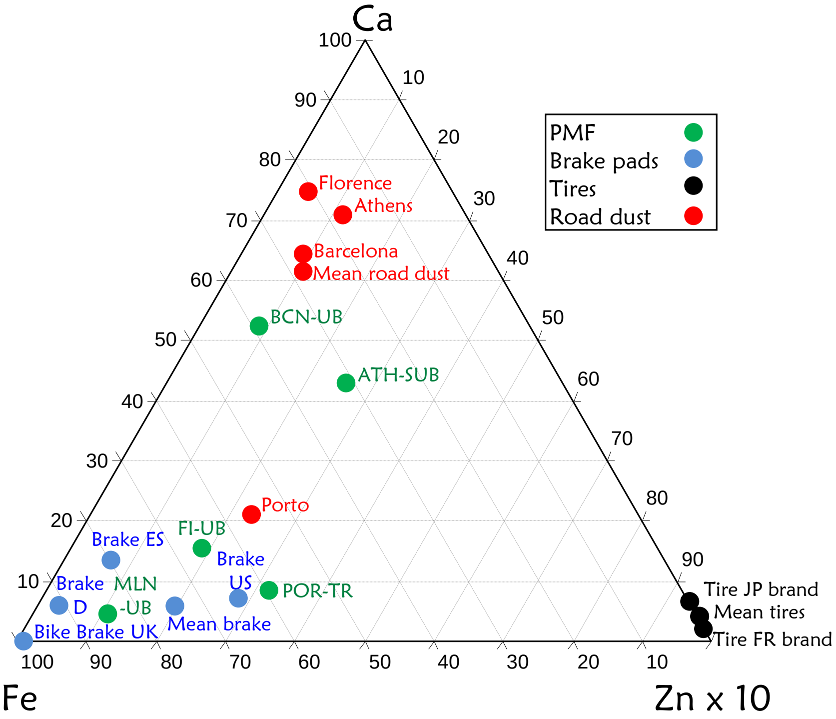
RC6. This paper presents the chemical composition of PM (PM10 and PM2.5) collected simultaneously during one year in five Southern European cities. In addition, the main sources of PM in these cities have been identified by means of receptor modelling (Positive Matrix Factorization, PMF). The article is certainly of high quality and provides a comprehensive picture about PM in southern European cities. However, the article is difficult to read as it is full of abbreviations and acronyms (e.g. site names and types, source categories) as well as percentages (e.g. contributions of species and sources) which make the manuscript hard to read and to memorize the results. This is not untypical for such a paper and only a statement here. I do not know how to avoid this and how to improve readability. Maybe the authors have suggestions?

I got the impression that there is a high degree of subjectivity in the way how the PMF analysis has been done (see Table 2, column "constraints"). The authors are experts in applying this technique and I'm convinced that they know what they were doing. Nevertheless, I feel somewhat uncomfortable with the procedure applied and consequently also with the results: (a) a different team of scientists would likely come to different results, because the applied constraints would not be the same.

AR6. Indeed, subjectivity in PMF analysis does exist, mostly in constrained PMF, where a priori information about the source is added by the user. During the EU intercomparison (led by JRC) for receptor modeling for example, the same dataset (St. Louis, USA) provided different results with the same model, run by different users. There is no solution for this short-coming. This is the reason why we have tried to minimize this subjectivity, by carrying out all PMF analyses (for the five cities) during an intensive 5-days workshop, where all project partners were present (at least 2 members for each partner). In this way, we have discussed altogether each single constraint, in order to ensure that that constraint was necessary and reliable.

RC7. (b) the labels given to the calculated PMF factors imply pure sources. It is, however, unclear if this is true or if factors represent a mixture of different sources and processes. The temporal resolution of the daily PM samples might hamper a perfect decomposition of the source contributions. Consequently, it is unclear what the overall error of the source apportionment results are and how to exactly interpret the results. This point should be stressed in the article. Above objections are not specific for this paper but common to many studies using PMF or other receptor modelling approaches. Therefore and more important because the presented paper is very relevant and informative, it should be published in Atmospheric Chemistry and Physics.

AR7. Factor labeling in PMF is not trivial and we agree with the referee that can significantly affect interpretation and consequent action. Thus, caution is needed. We have labeled PMF factors as conservatively as possible. For example the vehicle non-exhaust label is quite generic, since it include brake wear, tire wear, road wear and road dust resuspension. We have investigated correlation of this factor profile with experimental source profiles at each city, finding that in Barcelona (as expected due to the constraint) and Athens, the factor is more associated to road dust, while in Porto, Milan and Florence to brake wear. Tire wear composition seems less related to this factor. However, for the reasons above we decided not to include such statement and keep a more general definition. We have stressed this concept in the article.



Ternary plot for PMF and experimental source profiles. The composition of PMF profiles and their proximity to road dust profiles, brake pads and tires, indicate chemical similarity.

Other possible mixtures of sources are identified:

- The Secondary Sulphate and Organics (SSO) is enriched in EC (4-5% in BCN-UB and MLN-UB), indicating a mixing of this factor with some primary combustion sources, probably industries.
- The Mineral factor is enriched in NO_3^- at most of sites, but this is attributed to the neutralization of dust cations by nitric acid.
- High OC in the sea salt factor at FI-UB is attributed to the refinery emissions located in the coast of Livorno.

RC8. I have only some additional comments that should be considered for a revised version: Abstract and section 2.1: The exact dates of the sampling period should be given. January 2013 to February 2014 implies that PM samples from more than one year have been analyzed. Are the presented mean values correctly calculated annual means, or are some months (January, February) overrepresented? If the latter is true, this should be corrected.

AR8. A few samples were overrepresented for BCN (4), MLN (9), FI (4) and ATH (9). We have corrected the average concentrations, although changes are minimal, and reported exact dates in Table S1. The text of the manuscript has been revised accordingly.

RC9. Abstract, line 10: SSO and SNI have not been defined so far, similarly later VEX + NEX. Abbreviations should be defined before they are used.

AR9. The text has been revised.

RC10. Page 23995, lines 22/23: The full information about the used filter material should be given (brand and product name).

AR10. The brand and product name of filters have been added to the text

RC11. Page 24000, line 17: What exactly is the "daily PM10 WHO threshold"? The 50ug/m3 as a 24h mean (99 percentile)? Should be exceeded at more sites than POR-TR, e.g. MLN-UB (see page 23999).

AR11. The referee is right. The text has been revised, including also the PM2.5 threshold.

RC12. Sections 3.2.2 and 3.2.3: Where do all the numbers/factors used for the calculation of sea salt and mineral dust come from? Please provide references. Mineral dust calculation is based on Si. How has this been done for PM collected on quartz fibre filters?

AR12. The references for the formulae used are the following, and have been added:

- S. Nava, S. Becagli, G. Calzolai, M. Chiari, F. Lucarelli, P. Prati, R. Traversi, R. Udisti, G. Valli, R. Vecchi, "Saharan dust impact in central Italy: An overview on three years elemental data records", Atm. Env. 60 (2012), 444-452

- G. Calzolai, S. Nava, F. Lucarelli, M. Chiari, M. Giannoni, S. Becagli, R. Traversi, M. Marconi, D. Frosini, M. Severi, R. Udisti, A. di Sarra, G. Pace, D. Meloni, C. Bommarito, F. Monteleone, F. Anello, D. M. Sferlazzo, "Characterization of PM10 sources in the central Mediterranean", Atmos. Chem. Phys. 15 (2015), 13939-13955

Concerning Si determination, this was performed at most of the sites on Teflon filters by PIXE, except, in the case of quartz filters for BCN-UB, where Si was estimated based on Al, using a ratio SiO_2/Al_2O_3=3.

RC13. Page 24004, line 11. It is argued that high NH4NO3 in MLN is due to high NOx and NH3 emissions. What is the role of temperature here? From the considered sites, MLN is probably the one with the coldest temperatures in winter, favouring particulate ammonium nitrate.

AR13. We agree with the referee and added this statement in the discussion.

RC14. Section 3.2.8: 1st para, it should be explained in a few words what dQ is and what this means.

AR14. dQ is the increase of the object function due to the auxiliary equations. It has been added to the text.

RC15. 2nd para, "The distribution of residuals, G-space plots, Fpeak . . .". This sentence is only understandable for PMF experts. This should be rephrased.

AR15. The text has been simplified, although for more general description we need to address to the references used (USEPA, 2014)

RC16. Page 24009, line26: What does "(EC)" mean here? EC is not a tracer for brake wear!

AR16. EC is indeed not a tracer of brake wear, but it can be a main component of brake particles. Here we refer to the chemical abundance in the profile, not to the explained variation. We have clarified this in the text.

RC17. Page 24009, line27: Should be "Ca".

AR17. The typo has been corrected.

RC18. Page 24011, lines 9 and 10: It is found that "At the TR site (POR-TR) the VEX contribution is significantly higher (by a factor > 2)." This is counter-intuitive. NEX should increase with the proximity to traffic sources. Could this point to a decomposition problem (VEX and NEX should temporally be highly correlated)? Please comment and/or revise.

AR18. We don't have a clear interpretation of the higher VEX/NEX ratio at POR-TR. The correlation between VEX and NEX contributions (to PM10) at the traffic site of Porto, is higher than those at other AIRUSE stations; on the one hand may suggest a weaker separation between the two sources, as suggested by the referee, but on the other hand the lack of OC in the NEX factor indicates a quite good separation. Another reason could be the rather low braking frequency at the specific location of the monitoring site.

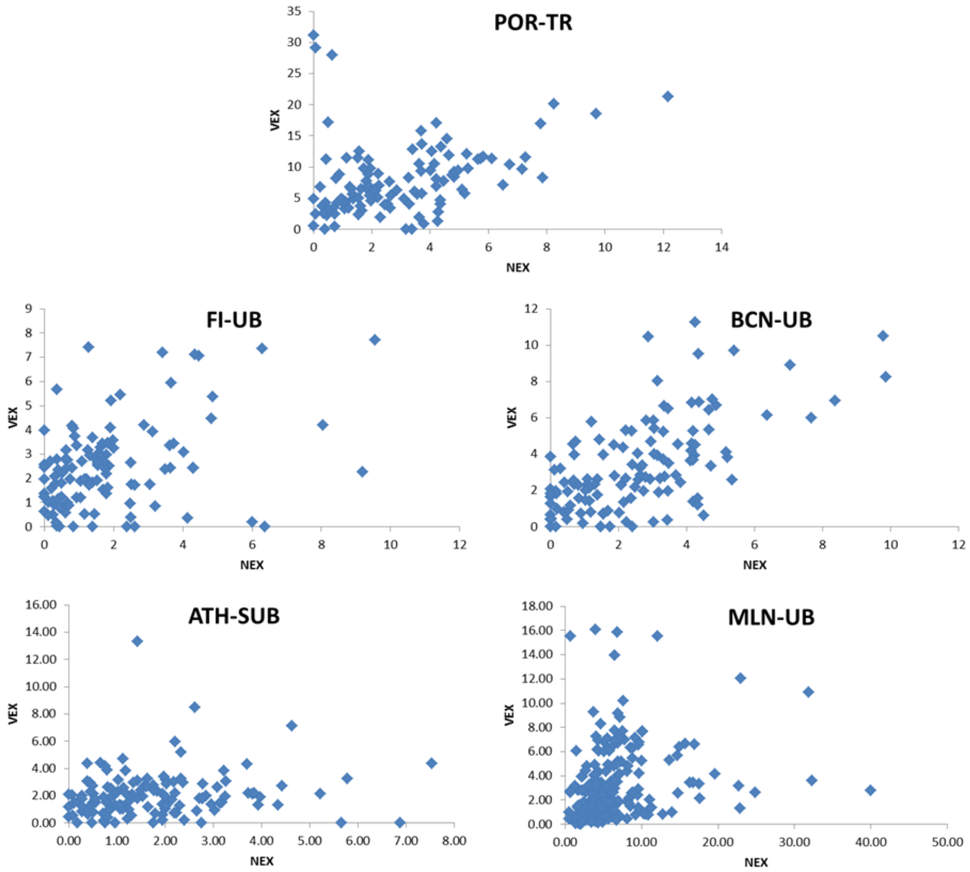
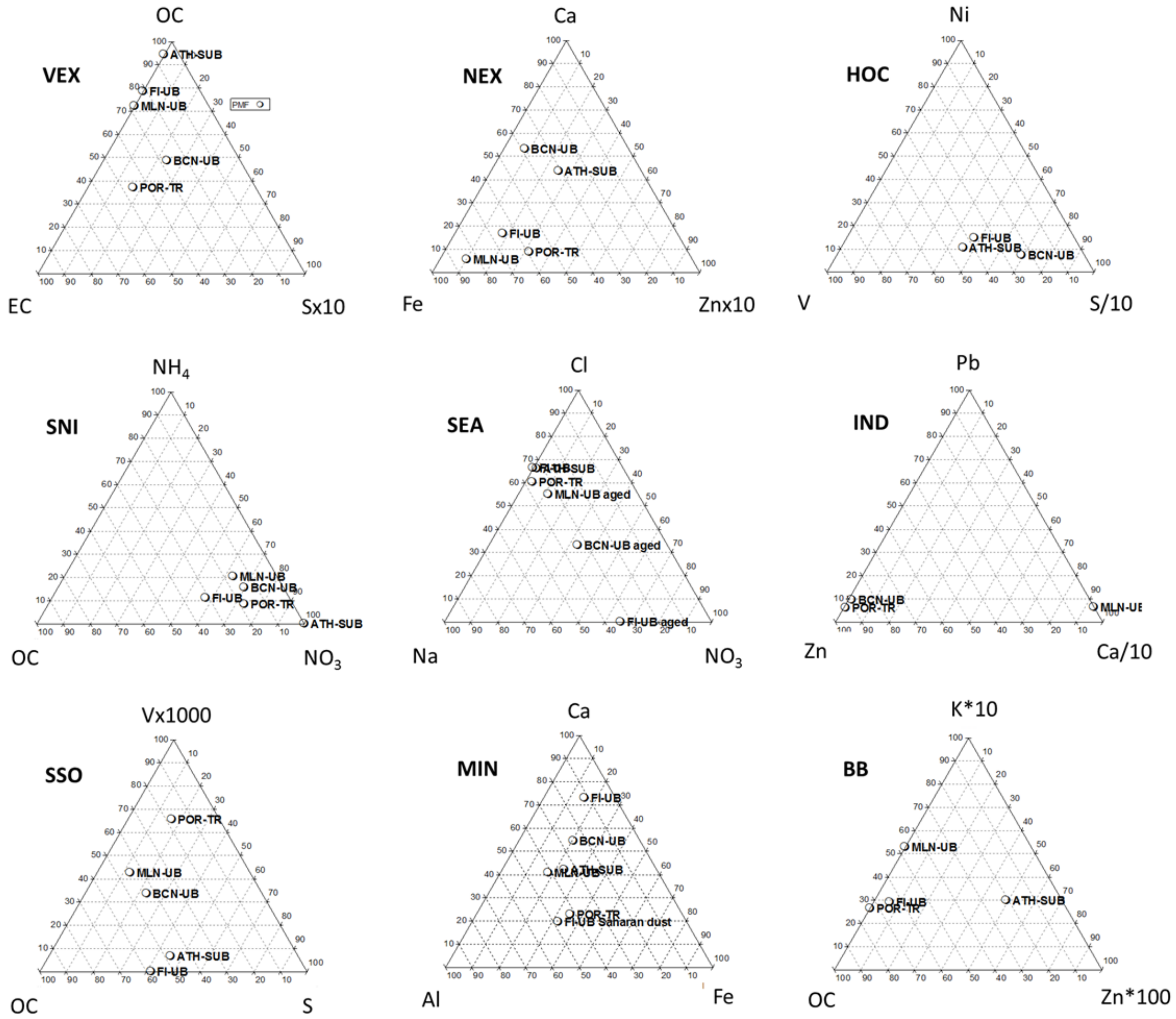


Figure 3: It is very difficult to judge the similarity of the obtained source profiles from these logarithmic bar charts. It is unclear, if the same labelled source factor corresponds to the same chemical fraction of PM10/PM2.5, i.e. if the degree of decomposing sources is the same at all sites. There are some obvious peculiarities: E.g. High contribution of OC in sea salt at one of the sites, high contributions of OC in secondary nitrate in all sites, ... Please comment. Ideally also provide a better way for comparison of the calculated PMF factor profiles. In the legend the unit of the factor profiles should be changed to microgram per microgram of PM10 or PM2.5, respectively. Figure 6: The error bars are misleading. They have been calculated from regression of PM versus estimated source activities but do not include the modelling error which is unknown. This should be clearly stated in the legend.

We have changed the minimum value of the y axis, in order to better identify main components and tracers of the factor profiles. Removing the log scale would imply adding the "% of species" which in our opinion would complicate the reading of the plots, which are already dense of information.

In order to simplify factor comparison we have produced ternary plots (new figure 4), using specific tracers for each source. These plots allow:

- Identifying "common" chemical signatures among AIRUSE cities (SNI and HOC)
- Visualizing clear separation among AIRUSE cities for a single factor (NEX, SEA, BB, MIN).



The labelled source profiles correspond to both PM fractions, given that the PMF analysis was performed in the combined matrix (PM10 and PM2.5 together), therefore we did not change the unit of y axis. The factors labels changes from site to another only in the case of SSO at MLN-UB and POR-TR where it includes heavy oil combustion, and the aged/fresh sea salt factors. This information is added to Figure 3.

High OC in the aged sea salt factor at FI-UB is attributed to the refinery emissions located in the coast of Livorno. We added this info to the manuscript. High OC in the secondary nitrate factor is interpreted as the condensation of semi volatile organic compounds to the high specific surface area of ammonium nitrate particles (Amato et al., 2009).

Information on the error estimates have been added to the caption of the Figure.