ANSWER TO REVIEWERS

Hourly elemental concentrations in $PM_{2.5}$ aerosols sampled simultaneously at urban background and road site in Barcelona - Diurnal variations and PMF receptor modelling

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Reviewer 1: page 2-12

Reviewer 2: page 13-18

Reviewer 1: page 19-23

REVIEW
Manuscript: acp - 2012 - 622
Title: Hourly elemental concentrations in PM2.5 aerosols sampled simultaneously at urban background and road site
Authors: M. Dall'Osto et al.
RECOMMENDATION: Publish after major revision

Comments to the Authors (reviewer 1)

This is an interesting study providing original data for hourly elemental mass concentrations and their receptor modeling by PMF. In general, the study is well conducted and the data presented in the manuscript have been thoroughly analyzed. Nevertheless, there is a major concern depicted below regarding the exact objectives of the PMF source apportionment. A number of technical corrections (conclusions not supported by the data, points of clarity, typographical errors, etc) are also recommended before the manuscript should be published on ACPD.

We thank reviewer 1 for finding this manuscript interesting, we provide extensive reply on comment below (in italic).

Major concern

What is the usefulness of apportioning only 10% of the total PM2.5 mass, about 1.5 μg m ‐ 3, when you can apportion the total PM2.5 fraction? If the authors had available (as they claim in the manuscript and in their response to Reviewer 1) the hourly concentrations of PM2.5 mass and major components (EC, OC, ionic species, etc), it is something of a mystery as to why they did not include them in the PMF analysis. The PMF receptor modeling of the hourly elemental concentrations in the present manuscript failed to identify a significant source "traffic emission", that is inevitable at both sites, particularly the traffic ‐ impacted RS. The authors should, therefore, search this failure since many of the elements determined by PIXE are, at least partly, associated to vehicle exhaust (see several publications reporting chemical source profiles for vehicle exhaust). In my opinion, the introduction of BC (a unique tracer for traffic emissions) in PMF would help so that a "traffic emission" factor be resolved. Therefore, if the objective of PMF was the source apportionment of hourly PM2.5 mass, all available constituents should be used as inputs. If, on the other hand, the objective of hourly elemental concentrations PMF was just to reveal its advantages over the PMF normally applied on daily samples, a comparative demonstration of the two solutions should be presented in the manuscript.

The aim of the work is to use hourly resolution elemental concentrations to identify the main sources and in particular sources whose time trend changes on a time scale of few hours: we clarified it in the text. The high number of samples given by the hourly concentrations ensure a better reliability of the PMF factor profiles.. The hourly resolution allow obtaining a more sound identification and characterisation of the sources; without the supporting information of hourly time trend their identification/interpretation is less certain. Furthermore, it is possible to obtain more accurate source profiles which can be useful, in the future, as reference data or as constraints for PMF analysis of daily data. We address this also in the text.

As correctly said, there are a number of variables that are not included into the current analysis, including for example BC and secondary inorganic species like nitrate. Future studies will use a number of hourly data (including unique ATOFMS particle types and AMS organic factors) as input for PMF receptor modelling. This study aims to test PIXE hourly data as a unique input in the receptor modelling analysis to make aerosol source identification. If we had to include BC, then we should include data from AMS (not yet available at the final stage) too as well as other data (not yet available). We decided to use PIXE data as input only, while future studies will be able to consider other variables. However, in order to accommodate the request of reviewer 1, we run two additional PMF tests, explained in the text. Briefly, the daily resolution data did not allow to identify specific aerosol sources, as the PMF profiles were less defined. As suggested by the reviewer, we now incorporate it in the text.

We would like to remind that we did detect a "traffic component". A non-exhaust traffic component (Dust Fe-Cu) was identified and discussed.

Points of clarification & Technical corrections

- The title of the manuscript is not completely descriptive of the manuscript content. I would suggest the following: "Hourly elemental concentrations in PM2.5 aerosols sampled simultaneously at urban background and road sites - Diurnal variations and PMF receptor modeling "

We changed the title of the paper

- The study area should be reported in Abstract (p.2, l. 2).

Added

- In the Abstract, also, it should be clarified that the percentages given in the parentheses are average source contributions to the total elemental mass measured.

Added

- In the Abstract, conclusions 4 and 5 "(4) PM2.5 traffic brake dust (Fe - Cu) is mainly primarily emitted and not resuspended, whereas PM2.5 urban crustal dust (Ca) is found mainly resuspended by both traffic vortex and sea breeze;" are not obviously supported by data (see a related comment below).

We address this point below

- p.4, l. 14: "WMB" should be explained.

Western Mediterranean Basin (WMB) region

- p.5, l.28: Some information about sampling inlet, sampling flow rate and filter diameter should be briefly provided in Instrumentation section.

In the streaker sampler, particles are separated on different stages by a pre-impactor and an impactor. The pre-impactor removes particulate matter with $D > 10$ µm. The impactor deposits the aerosol coarse fraction (2.5 µm $< D < 10$ µm) on a Kapton® impaction plate, while the fine fraction ($D < 2.5$ µm) is collected on a Nuclepore® filter. The sampler is designed to obtain the nominal cut off diameter at a flux of 1 l/min. The two collecting plates (diameter about 10 cm) are paired on a cartridge, which rotates at constant speed (~ 1.8° per hour) for a week, and this produces a circular continuous deposition of particular matter ("streak") on both stages (see the picture below).

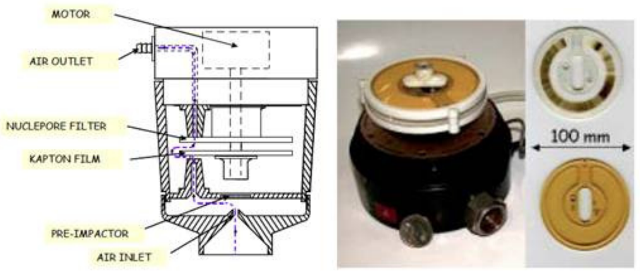


Figure 1.2 – Schematic representation of the Streaker sampler (left); pictures of the sampler (right) together with a nuclepore® filter (above) and kapton foil (below) after sampling.

The impaction foil is a thin (7.5µm, 1.07 mg/cm2) Kapton® foil ($C_{22}H_{10}N_2O_4$); to avoid particle to bounce or fall off it is spryed with paraffin. The filter is a thin (10µm, 0.92 mg/cm2) Nuclepore® membrane (polycarbonate – $C_{15}H_{14}CO_3$), with a pore size of 0.4 µm.
During these samplings the flux was continuously measured and it remained 1 lpm within 5% uncertainty.
The main limit of this sampler is that the collected matter cannot be weighted gravimetrically. The streaker sampler has been appositely thought for PIXE analyses: the deposit streak can be analysed 'point by point' by an ion beam to reconstruct the elemental concentration time trends, with an overall resolution of one or more hours. We did not insert this part within the text for lack of space and we inserted a reference where the sampler is described.

We included previous references describing this in details.

- p.6, l.23 ‑ 25. The PMF procedure applied needs some clarification at this point. What do the authors mean with "both datasets (UB and RS) were analysed simultaneously"? Was PMF applied on separate data sets, or the datasets (UB and RS) were combined into one? The PMF factor profiles shown in Fig. 4 as averages were different at the two sites?

The two datasets were combined into one, and the result is presented in Figure 4.By doing this, we can compare the two monitoring sites. . The total number of hours for the UB and RS datasets were 318 and 444, respectively. The two datasets were

merged together resulting in a 762 rows (time) by 17 columns (elements). Added in the text.
It is important to remember that we assume that the chemical profiles of the resolved sources do not change between the two sampling sites, given also the short distance between the two sites (2Km).

- p.9, l.10: It is confusing to declare the origin of trace elements before PMF shows their sources (e.g. "Industrial emission related trace elements were found in higher concentrations at 1 the UB site (Pb, Zn and Mn - 42%, 41% and 23%, respectively – Table 1"). For instance Zn that is here declared as originating from industrial emissions has been previously declared as non - exhaust traffic element! I suggest the authors to correct this confuse.

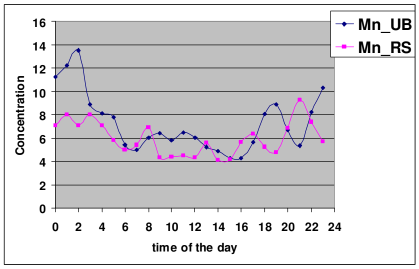
The origin of trace elements is often attributed to specific sources also without the use of PMF receptor modelling. We made this clear and we also corrected the sentence about Zn.

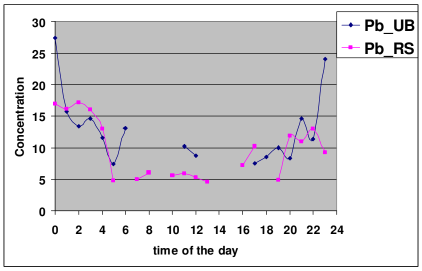
- p.10, l.6: It is a question, why Ni and V were attributed to shipping emissions excluding diesel traffic.

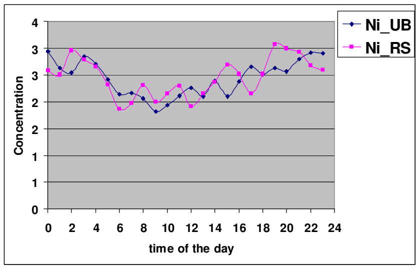
There is extensive literature showing these two elements are more associated with industrial emissions and shipping emissions. Moreover the hourly time trends obtained in this study for V and Ni confirmed it, as they were completely different from the time trend of Cu and Fe and they showed nocturnal peaks that can not be due to traffic.

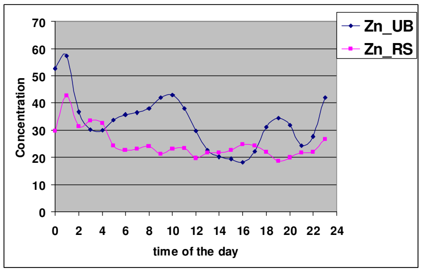
- p.10, l.6: The diurnal profiles of Mn, Zn, and Pb discussed at this point should be shown in Fig. 3. The same also for Ni.

We believe this paper has already a large number of Figures (7, including 2 in the supporting information). We felt it is important to show some diurnal temporal variation of specific metals, but reporting 34 diurnal profiles would be excessive and space consuming. We showed 12 (6 at UB and 6 at RS) in Figure 3 as they represent the major ones and the most interesting ones. We also present later on the 9 diurnal profiles for the nine PMF factor profiles. In summary, we feel it is space consuming to report all the diurnal profiles, especially some of the less interesting ones, which we describe in words. We report for the interest of the reviewer the profiles requested below for information.
Additionally, we expanded the text and commented some of the diurnal profiles of some minor elements not included in the figures.









- p.12: Discussion in Section 3.1.4. "Air mass influence" is poor. It should be clarified what air mass data were examined, air mass back trajectories showing the long range transport of aerosol, the local wind direction? If this analysis has already been included in another publication (maybe in Dall'Osto et al., 2012) overlapping should be avoided.

Indeed we want to avoid overlap and we describe the Air mass back trajectories encountered during the SAPUSS in details in Dall'Osto et al 2012. However, we also include this comment in this current paper by slightly increasing the description of the air masses encountered.

- p.13, l.4 ‐ 7: Use the same "names" for the sources identified by PMF throughout the text.

We addressed this problem and consistently used the same names throughout the text.

- p.14, l. 28 ‐ 30: It is claimed that "The Brake dust (Fe - Cu) profile was found the only one correlating well (R2 = 0.7) with Black Carbon (BC), likely due to its primary non exhaust vehicles aerosols nature". This is confusing since BC has a primary exhaust vehicles aerosols nature. Please, rephrase.

This profile was found the only one correlating well (R2 = 0.7) with Black Carbon (BC), suggesting that this primary non exhaust traffic brake dust source is co-emitted along with the primary exhaust traffic BC one.

- p.16, l.30: It is misleading to indicate the average with "TOT", please change to "AVER" or "MEAN", here and in Table 3.

modified

- p.17, l.22 ‐ 32: Discussion in this paragraph about the correlations of the PMF profiles between the two sites is rather obscure. As mentioned above, it should be clarified, whether the PMF factor profiles shown in Fig. 4 as averages were different at the two sites. What does R2=0 mean in Table 5 for Brake dust (Al ‐ Ti)? Note that Table 5 is not cited in the text.

The PMF profiles at the RS and at the UB are the same because they are the result of one PMF receptor modelling result as the two datasets (RB and UB) were merged and analysed together. Given the fact that the two monitoring sites were close (only 2 Km apart), we believe this assumption is valid. We modified the R2=0 in the brake dust as the others <0.3 as (---), see new Table 5, which is now cited in the text.

We also clarified across all the wording on "profiles", "sources" and "factors"

Table 5 is cited in the text. "The validity of the PMF solution is also supported by the correlations shown in Table 5 among the two different sites. Whilst elements concentrations among sites (section 3.1, table 2) were not found highly correlated, our receptor modelling study is able to separate local from regional sources quite well. The correlation between Reg. (S) among sites for example is very high (R2=0.88). Other regional sources also show good correlations among the two monitoring sites: Soil dust (Al-Ti) (R2=0.69) and S.S. (Na-Mg) (R2=0.55). By contrast, the Brake dust (Fe-Cu) does not appear correlated with any other factor, due to its local traffic nature. Industrial sources showed weaker correlations among the sites, perhaps due to a number of reasons including RS street canyon characteristics and dimension of aerosol industrial aerosols plumes."

- p.18, l.1 ‐ 20: There are some discrepancies in the interpretation of diurnal variations of PMF factor profiles and elemental concentrations. The diurnal variation of crustal dust (Ca) has been attributed to"re ‐ suspended road dust and soil transported by wind or resuspended by human activities"; nothing is stated about a potential sea breeze effect, in contrast to what is said in the Abstract. As stated in p. 11, the morning Ca peak concentrations are likely due to traffic, while the afternoon peak is likely due to dust resuspension. This interpretation is strongly ambiguous since resuspension in the road side environment is primarily traffic induced and traffic occurs also in the afternoon. On the other hand, if crustal dust (Ca) is attributable mainly to resuspension by traffic vortex, a greater similarity with the Brake dust (Al ‐ Ti) diurnal variation would be expected. Another inconsistency is that, while the peak Ca concentration occurs at 8:00 in the morning, the peak contribution of the crustal dust (Ca) profile appears 1 or 2 hours later. These inconsistencies have to be properly addressed. It should be pointed out that it is very difficult to discriminate emitted particles from those resuspended. Brake dust may be emitted, but it is also deposited on road surfaces and resuspended due to traffic vortex. On the other hand, calcareous urban dust may be resuspended, but it can also be emitted, either primarily, e.g. releases of $CaSO_4$ particles from buildings and other surfaces through weathering and other erosive processes, emissions from coal combustion, metallurgical plants, desulphurization processes using limestone for SO_2 removal, etc., or may be secondarily formed in the atmosphere by heterogeneous reactions of mineral calcite with sulfate.

We first apologise for the different in the time log, we spotted the element concentrations were in local time, but the PMF diurnal profiles were indeed reported shifted by one hour. We now corrected the mistake, and as expected the peak maximums overlap better. The morning peak of the traffic rush hour is at 8am local time for both elemental concentration (figure 3) and PMF results (figure 7).

We included the sea breeze effect in the discussion, and so expanded the discussion.

It is difficult to discriminate emitted particles from resuspended one. However, there are two things to consider: first only the Dust (Fe-Cu) correlates with traffic counts and with BC, whereas the urban dust (Ca) does not. Traffic is reduced in the afternoon, whereas urban dust (Ca) increases. We address this issue pointing out to an additional source of dust (urban dust, from construction, and urban sources) present in the afternoon and concomitant with higher winds from the sea breeze.

- p. 20, l. 11: The authors' statement that "the regional contribution of the B.B. (K) factor is further supported by its correlation with the Reg. (S) profile" is true only for RS, whereas in the case of UB the correlation between B.B. (K) and Reg. (S) is very low (r2 = 0.27). In addition, although in the manuscript, biomass burning is referred to as a regional source, like most frequently in literature, the inter ‐ site correlation of K concentrations in Table 2 is below r2 = 0.30, which leads to question this assumption. Any explanation for these discrepancies?

The correlation is low, but unique among all the other eight factors. We addressed the issues in the text.
Interestingly, the main regional contribution of the B.B. (K) factor is further supported by its correlation with the Reg. (S) profile (Table 5). These two factors were found the only ones to be both inter- and intra- correlated within the two monitoring sites. However, a stronger correlation (R^2=0.52) was found for the RS than for the UB site (R^2=0.27), and the reason may be due to additional local biomass sources impacting the more remote urban background site.

- In Table 1, equations are given such as Y = 0.85. Although it is clarified in the text that linear regressions were obtained by setting intercept to zero (i.e. Y=aX), there is still the question as to which variable is Y, which is X? Therefore, in the Table, equations should be given such as Y = 0.85X with corresponding explanations for Y (PIXE analysis?) and X (off ‐ line technique?). The statistical test used to examine the differences of elemental concentrations between RS and UB and the level of significance should also be provided.

We added corresponding explanations for Y (PIXE analysis) and X (ICP-AES MS technique). We also added significant level across all manuscript (valid at p-value < 0.05, t-test used)

- The effect of rain should be investigated for all 9 source factors, not only for the 3 dust profiles, since rain is expected to wash out aerosol independently from their origin. The authors found a significant reduction for urban dust (Ca) under rainy conditions. The effect of road wetting was not investigated in the present study, hence the conclusion that "wet roads may be a solution for reducing dust concentrations in road sites, far more effective than street sweeping activities", although correct, it is not supported by the results of the study and should be deleted.

The effect was investigated for all 9 sources (and the six non dust ones varied only by a factor of 1-2), but a clear effect was found only for the dust sources. In other words, all were reduced by a factor of 1-2, but the most reduction was found for the dust particles: 3, 4 and 8 was found for the soil dust (Al-Ti), brake dust (Fe-Cu) and urban dust (Ca), respectively

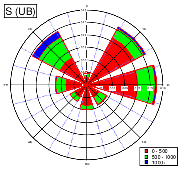
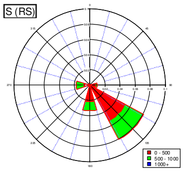
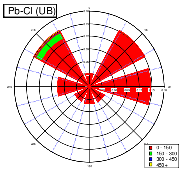
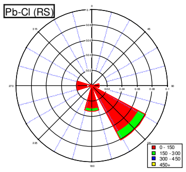
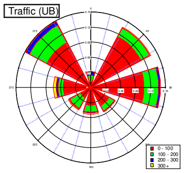
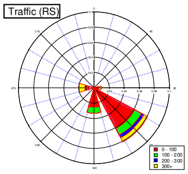
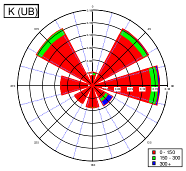
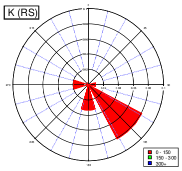
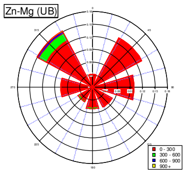
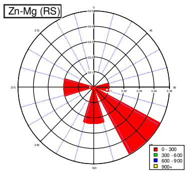
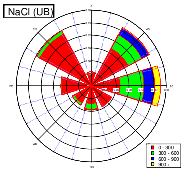
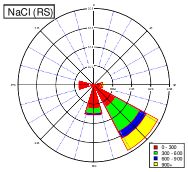
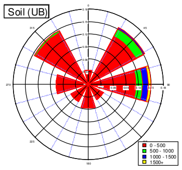
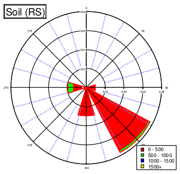
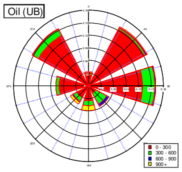
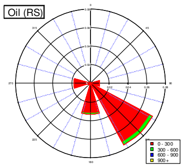
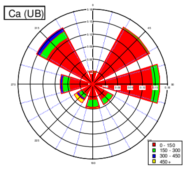
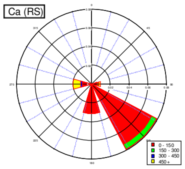
A DD/RD ratio of 1.5±0.5 (1-2) was found for primary aerosols (BC) and the six non dust PIXE PMF factors (Reg. S, B.B. K, S.S. Na-Mg, Ind. Zn-Mn, Ind. Pb-Cl, Oil Ni-V) . By contrast, a ratio of 3, 4 and 8 was found for the soil dust (Al-Ti), brake dust (Fe-Cu) and urban dust (Ca), respectively.

We modified the text and removed part of it as suggested. Therefore, this study suggests that resuspension dust may be reduced (both by rain wash up and/or road wetting hence limiting resuspension) in wetting roads relative to drier ones. We also modified the conclusion part.

"A DD/RD ratio of 1.5±0.5 (1-2) was found for primary aerosols (BC) and the six non dust PIXE PMF factors (Reg. S, B.B. K, S.S. Na-Mg, Ind. Zn-Mn, Ind. Pb-Cl, Oil Ni-V) . By contrast, a ratio of 3, 4 and 8 was found for the soil dust (Al-Ti), brake dust (Fe-Cu) and urban dust (Ca), respectively. In other words - as expected - resuspended urban dust (Ca) is the particle type most affected by the wetness of the land. This effect is likely to be due by both rain wash up and/or road wetting hence limiting resuspension"

- The potential associations of elemental concentrations with wind components (WS, WD) would also be shown.

We tried hard but could not see any clear association, likely to low wind speed encountered (often below 1.5m s-1). For this reason we decided not to include them in the manuscript. Wind roses could not really clearly distinguish anything more than the one reported in the text. As regard of the RS site, the wind tunnel conditions did not allow to obtain any additional information (see table below with the 18 wind roses)..

PIXE PMF profile	Urban Background	Road site
Reg (S)		
Ind (Pb-Cl)		
Dust (Fe-Cu)		
BB (K)		
Ind (Zn-Mn)		
SS (Na-Mg)		
Dust (Al-Si)		
Oil (V-Ni)		
Urban dust (Ca)		

- In Conclusions, p.23, l.15, the "atmospheric pollutants" should change to "elemental components of PM2.5".

Modified

- In Conclusions, p.23, l.24, the "on a mass basis" should be changed to "on a total elemental mass basis" for clarity.

Modified

- Also, in Conclusions, l. 25, the "65%" should be corrected to "27%» according to Table 3!

Modified

- p.24, l. 2 ‑ 4: The statement "Urban areas in south Europe are frequently above legislation limits as a result of road dust and favorable climatic conditions for photochemical conditions and dust resuspension" is irrelevant to the present study and should be removed.

Modified. Given the fact 25% of the mass was attributed to dust, a problem of major concern in South Europe (Putaud et al., 2010). We believe it is important to stress the contribution of dust in the $PM_{2.5}$ *mass.*

- p.24, l.7 ‑ 10: The final sentence about PIXE should be rephrased since PIXE is an analytical technique with high time resolution, capable to detect the diurnal variation of elemental mass concentrations, however, it is not capable to separate different aerosol sources; source separation is the PMF's job.

Correct, modified. Overall, the PMF receptor modelling applied to elemental concentrations at hourly resolution (obtained by PIXE - which detects the diurnal variation of elemental mass concentrations) - has proven useful in separating different regional aerosol sources, different types of dusts, and different types of industrial plume-like events during the SAPUSS campaign.

- Tables 2 & 5 show r2 values lower than 0.3 in contrast to what is stated in their titles. Please, correct. Please remove "Inter - site correlations. Intra - site correlations were generally poor and two additional tables were not found useful and space consuming."

We were asked to add this by the editor and other co-authors

from the title of Table 2, and delete one of the two "Cl". Also, please change "profile" to "profiles" in the Table 5 title.

Title of table 2 has Cl and Cr.
profiles changed in table 5

Typographic Errors

Edited

- p.2., l.2: please change "effective" to "effectively"
- p.9., l.31: please change "level" to "levels"
- p.14, l.12: Please correct "opeations"
- p.18, l.1: Please change “profile sources” to “sources profiles”
- p.19, l.8: please change "techniques" to "technique"
- p.20, l. 12: Table 4 should rather be Table 5

References

The number of references listed in the manuscript is very large. I would suggest the authors to reduce it by keeping only the references that are really relevant

OK - we reduced the number of references (remove 18 references)

Anonymous Referee #2
Received and published: 29 October 2012

The subject manuscript addresses the characterization of fine particulate matter at a roadside site and an urban site in Barcelona and a comparison of the metals and sources of metals at the two sites. The sampling was conducted over a one month periods, which included impacts from a dust storm originating in the Sahara Desert. Although the subject matter is of interest to the readership of Atmospheric Chemistry and Physics, there are a number of issues that need to be addressed before the manuscript is suitable for publication.

We thank reviewer 2 for the time spent in reviewing this paper, we address all comment below in italic.

General Comments

1) The authors need to more clearly define the goals of the study and the rethink the conclusion in the context of the fact that the data presented is only a short snapshot of one month that is impacted by a dust storm. Do the authors believe that the results are representative of other seasons and the annual average? This issue needs to be clarified in the abstract and the conclusions.

Well this is a problem of intensive field studies, which are difficult to compare with long term seasonally and annually studies. It is important to note that the Saharan dust event was moderate, and did not affect the PM concentrations dramatically. Indeed, as reported by Dall'Osto et al (2012, overview) the PM values never exceeded thee EU daily limits. We clarify this in the abstract and conclusion.

A key question is how representative the SAPUSS field study is in general, and whether a one month snapshot well represent the longer-term position. Comparative data for particulate matter are available from several previous long term measurements (Pey et al., 2010, Perez et al., 2010) and agreed well (see Dall'Osto et al., 2012 for more information).

2) More information about the quality of the PIXE analysis needs to be provided. Table 1 suggests that very few of the elements measured by PIXE show good agreement with the off-line optical IPC and IPC-MS measurements. Likewise, what can be said about the uncertainties of these measurements that provide the basis for PMF and statistical analyses?

The experimental uncertainties on the areal elemental concentrations (ng/cm2) measured by PIXE are given by the sum of independent uncertainties on certified standard sample concentrations (5%) and peak areas. We used mono- o bi-elemental thin standards of known surface density by Micromatter (http://www.micromatter.com/xrf.php).
The uncertainty on peak areas includes the x-rays counting statistics and all the fitting uncertainties (background subtraction, peak overlaps, etc.). Although the experimental set-up has been optimized to balance for the different yields of the

various elements, due to the wide range of concentration values of the different elements, and also of the same element in different samples, the counting statistics uncertainty may vary from few percents up to 20-30% or more when concentrations approach minimum detection limits (MDLs). We always make some reproducibility checks measuring the same spot many times. We have found a good reproducibility, always within the experimental uncertainties. We have also analyzed the SRM2783 (Standard Reference Material) by NIST (National Institute of Standard and Technology) to check the accuracy of our PIXE measurements, with an accordance between the experimental results and the certified quantities within the experimental uncertainty (see figure reported in the answer to specific comment 3 and 4 below). To obtain uncertainties on elemental concentrations in air (ng/m3), the uncertainties on sampling parameters should of course be taken into account. The uncertainty on the flux measurement is about 2-3% for both samplers. However, as in all sampling devices with size segregation by inertial impaction with many stages, the collection efficiency curves are not step functions: as a consequence the collecting bins partially overlap. Moreover, particle bouncing may introduce further uncertainty. It is not easy to estimate these uncertainties, which depend on the sampler design and assembling, on the collection substrates mounting, on particle bouncing, etc. We compare data collected by completely different aerosol samplers, so the upper collecting cut could not be same. Another important reason for the observed discrepancies may be the fact that for many hours the concentrations of the elements (for example Mg, Cl, Ti, V, Mn, Ni, Zn, Pb) collected on a hourly basis are below or close to the MDL, what it is not true for the daily samples (so in the daily averages were included many hours with values below or close to the MDL where, as explained, the experimental uncertainties are higher).

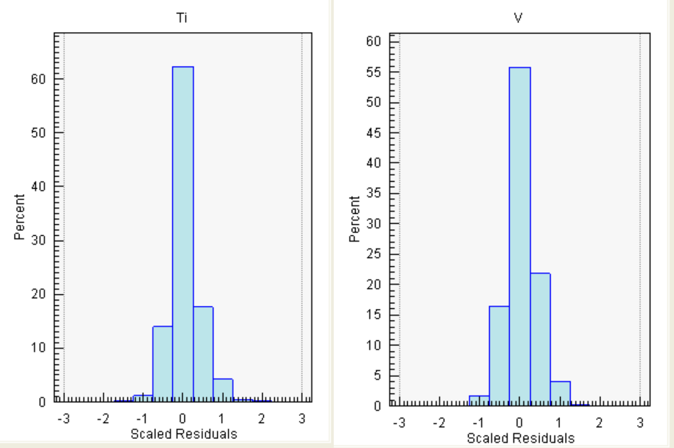
Nevertheless, the observed accordance is in line with what was observed in the study of Amato et al. showing an accordance in the range of 10-35%, also when a completely different system was used (DRUM impactor with hourly resolution followed by X-Ray Fluorescence Analysis of the samples) - see references included.

3) The set-up of the PMF model needs to be better explained. It appears that the PMF model only uses the elements measure by PIXE but the manuscript seems to imply that the results are the source apportionment of PM2.5 mass. Was mass data used to obtain a mass apportionment or is the apportionment just the sum of the measured species. If the apportionment is just the sum of the measured species that this needs to be clearly presented as the absence of OC, EC, nitrate, ammonium and the oxygen component of sulfate is very significant and are not in this sum.

We now state very well it is only the mass of the measured species, also in the abstract.

4) The basis of the uncertainties of the measurements used in the PMF model as well as the PMF model sensitivity to the uncertainties needs to be presented or an explanation of why such a sensitivity analysis is not important to the results. Likewise, it would be good to present the sensitivity of the model to the selection of species, factors and extreme events (i.e. dust storm). The robustness of the results depends on the sensitivity of the results to these assumptions and input data.

Input data were treated following the method reported in Polissar et al. (J. Geo. Res. 103, 1998, pp. 19045-19057). Total and realistic experimental data uncertainties (sampling included), plus 1/3 of the MDL, were used for PMF. Values below MDL were replaced by half of the MDL; the uncertainty was calculated as 1/2 of the average MDL plus 1/3 of the specific case MDL. We have discussed this point in the text (Methods).Further information can also be found in key references reported (for example Lucarelli et al 2011). These uncertainties were then revaluated on the basis of the obtained residuals and on this basis they resulted not overestimated nor underestimated (residuals were regularly distributed within 3 sigma). Species with a signal to noise ratio lower than 0.2 were excluded. Ti, V, Pb, and Cr resulted week variables (signal to noise ratio between 0.2 and 2). We decided to keep Ti, V and Pb as they are important tracers and their time trends showed interesting peaks, while Cr time trends were very noisy and, after some PMF tests we decided to remove these elements. We did not increase the uncertainty of V and Ti as they were already conservative and the residuals turned out well within 3 sigma (see figure below).



For what concerns the number of factors, solutions from 5 to 10 factors were systematically explored (also changing the FPEAK value). We found very stable results. The increase in the number of factors produced the detection of finer structures but did not resulted in instable situations. Finally. also the source profiles of the already identified sources did not change while increasing the number of factors.

We also tried to run PMF without the dust storm event i.e. we removed days 8-9-10th of October 2010. As expected, since the PMF analysis is sensitive to the input data (reducing the information available we can obtain less factors or mixed sources, mainly when some important episodes are removed) we obtained only one soil source since we removed the most relevant episode. We decided to keep the days 8-9-10 in the dataset as the provide a distinct mineral source.

Specific Comments

1) Page 20136, lines 6-8 – I imagine that most European aerosol researchers will be family with the FP7-EU terminology but given that ACP is an international journal, I think this will be confusing to readers from the Americas and Asia.

OK - removed

2) Page 20136, lines 19-21 – The correlation of the PMF results with the ATOFMS measurements provide some support for the metals measurements but do not really validate the PMF analysis. There could be good agreement with the PIXE and ATOFMS measurements and there could still be major issues with the PMF analysis. This statement should be re-written or removed.

We believe this is a key part of the paper. PMF receptor modelling results compared with external correlations are stronger, as they are supported by data taken with different measurements. On this regard, for example Ulbrich et al. (2009), state that "It is critical to use correlations between PMF factor time series and external measurement time series to support factor interpretations." and again " There is generally not a mathematical basis for choosing a particular PMF solution, though correlation with external tracers and reference mass spectra may be used to narrow the set of plausible rotations." (Ulbrich et al. 2009, Atmos. Chem. Phys., 9, 2891–2918, 2009).

The fact that ATOFMS shows single particles with a composition similar to one PMF profile and with a time trend similar to the PMF factor time trend strengthen the source identification.

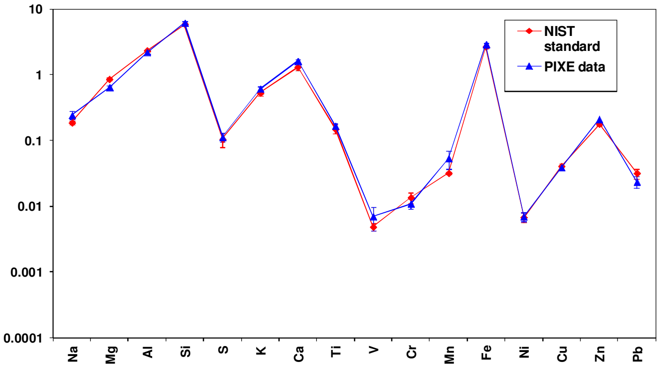
3) Page 20140, lines 15-19 – It appears that the uncertainties of the PIXE analysis are based on reference samples. Were any duplicated or Reference materials analyzed to address interferences and uncertainties at low concentrations?

See point 2 on page 12

" The experimental uncertainties on the areal elemental concentrations (ng/cm2) measured by PIXE are given by the sum of independent uncertainties on certified standard sample concentrations (5%) and peak areas. We used mono- o bi-elemental thin standards of known surface density by Micromatter (http://www.micromatter.com/xrf.php).
The uncertainty on peak areas includes the x-rays counting statistics and all the fitting uncertainties (background subtraction, peak overlaps, etc.). Although the experimental set-up has been optimized to balance for the different yields of the various elements, due to the wide range of concentration values of the different elements, and also of the same element in different samples, the counting statistics uncertainty may vary from few percents up to 20-30% or more when concentrations approach minimum detection limits (MDLs). We always make some reproducibility checks measuring the same spot many times. We have found a good reproducibility, always within the experimental uncertainties. We have also analyzed the SRM2783

(Standard Reference Material) by NIST (National Institute of Standard and Technology) to check the accuracy of our PIXE measurements, with an accordance between the experimental results and the certified quantities within the experimental uncertainty"

Additionally to general point 2 on page 13, we have also analyzed the SRM2783 (Standard Reference Material) by NIST (National Institute of Standard and Technology) to check the accuracy of our PIXE measurements. In the figure below we report the results.



4) Page 20141, line 7 – The use of the "inorganic species" is confusing here. I would recommend inorganic carbon or elemental carbon.

OK modified

5) Table 1 – Some discussion of the poor agreement of the PIXE and off-line measurements is needed and a justification that the quality of the data is suitable for the analysis and conclusion of the study.

This agreement is in line with previous studies. We would like to stress that this is also due to the fact that some elements were at times below the detection limit, hence limiting the comparison.

6) Page 20147, line 16 – Are the PMF results really mass apportionment or just the sum of the measured species?

sum of mass measured, addressed in abstract and text

7) Page 20148-20149 – Did the authors conduct a sensitivity analysis to understand if the apportionment results are stable in the context of the dust event, species used in the model. The number of factors, or the measurement uncertainties?

The dust event was a smaller one. The temporal trends seen in Figure 6 shows the concentrations were in the same order of magnitude of other sources. If removed days 8-9-10, only one general type of dust was found.

8) Page 20150 – The discussion of the ATOFMS data and Figures 5ab really

add very little to the manuscript or the conclusions of the study. I would recommend removing these results unless a more robust and quantitative use of the ATOFMS data can be provided. This is true for section 4.1 as well.

We partially answer to this question (specific comment 2, reviewer 2, page 16). This is a new source never reported before in the study area, and add important information on other studies also showing a source of Pb internally mixed with Cl in an large urban agglomerate. Several studies (Moffet el al., 2008a, b; Salcedo et al., 2010, Hodzic et al., 2012, Li et al., 2012, as well as Christian et al. (2010) and relative ACPD discussions (http://www.atmos-chem-phys-discuss.net/9/10101/2009/acpd-9-10101-2009-discussion.html) shows it is important to correctly characterised this source. In order to support our results, we use data from both PMF analysis of the PIXE data as well as single particle mass spectrometry information to validate and describe as better as we can this source. We believe the correlation of this source detected with the PIXE technique with the ATOFMS Pb-Cl particle type strongly supports its validity.

We also added an additional part in the text with additional inter-comparison between the results presented in this study and the ATOFMS results (section 4.1 of the manuscript).

9) Pages 20155-20157 – I find the discussion in section 4.2 to add very little to the manuscript. This seems to restate concepts that have already been discussed and given the short duration of the study, I am not sure that these are higher level conclusion that can be more broadly applied.

Section 4.2 addresses several points not discussed elsewhere in the manuscript, including the correlation of regional sources, the discussion of the abrasion of road pavement, the wind effect on dust concentrations, the rain effect on the aerosol sources detected, the source attribution of Cl in the urban area and the lunch maximum peak. However, we reduce this section in order to make the conclusions clearer.

10) Figure 1 – There appears to be some missing data from the time series. How was missing data addressed when comparisons of concentrations and PMF results from the two sites were compared?

We selected only the overlapping temporal trends, addressed in the text.

11) Figure 2 – Were the dust events includes in all of the statistical comparison and the OMF results? Does removing the dust days greatly change the results and conclusions?

Results and conclusion do not change. A new better figure 2 is now incorporated.

LATE REVIEWER number 3,

15th November 2012

The MS deals with the PM2.5-fraction aerosol samples collected by a streaker in a roadside site and urban background site in Barcelona for 528 h. The samples were measured by PIXE analysis for concentrations of 17 elements with a time resolution of 1 h. Evaluation and statistical treatment of the analytical data were performed by descriptive statistics and positive matrix factorization (PMF).

The topic and objectives of the MS are definitely timely and are of interest for the international research community. The MS represents a useful contribution to the growing literature on the emission sources in large cities. The experimental and evaluation methods utilized were selected well for the purpose of the study. The work is part of a more comprehensive research program.

We thank reviewer 3 for the time spent in reviewing this paper, we address all comment below in italic. We also appreciate the fact these results are timely and of interest for the international community.

Unfortunately, the MS is written and elaborated in a sloppy way which is not at all acceptable for a high quality journal. It should be improved substantially in many ways before it is considered for publication in the ACP. The present reviewer will focus less attention to the PMF results and their conclusions because 1) I am not a real expert in the field, and 2) it seems to me that they are presented in a loose and incomplete way which detracts from a deeper understanding.

We tried to present the results in a better way.

Page 20137, line 11, and analogously lines 12 and 19

Abbreviation PM stands for particulate matter, which is a set of aerosol particles. Expression “PM_2.5 (PM<2.5 microm, fine)” has no sense, and it should be replaced by e.g. PM_2.5 (d<2.5 microm, fine particles).

Edited

Page 20137, lines 21 and 22 Expressions PM_0-1 and PM_0-2.5 are not acceptable because the diameter of the particles does not start at 0 microm but at 1-2 nm. They should be replaced by e.g. PM_1 and PM_2.5, respectively.

Edited

Page 20137, line 18 The formulation “the size cut at PM_2.5” should be replaced by “the size cut at 2.5 microm”.

Edited

Page 20137, line 25 – page 20138, line 3 The authors may want to discuss briefly that the time resolution selected is also limited by the amount of aerosol particles to be obtained during the collection and which is necessary for the subsequent chemical analysis, so with the air flow rate of the sampler and the determination/detection limit of the analytical method to be applied.

This is due to a number of reasons, including the air flow rate of the sampler and the detection limit of the analytical method to be applied on the collected aerosol mass.

Page 20138, lines 13, 16, 19 and 21 Abbreviations SAPUSS, RS, UB, PMF, WMB are not at all explained or are not explained when they are used at first.

They are all explained in the abstract. We however repeat them once again in pg 20138.

Page 20140, line 4 There is no "fine mode of an aerosol", and the authors can use "fine size fraction of aerosol particles" instead.

Edited

Page 20140, section 2.2 Instrumentation No mention was made on the off-line sampling and analytical methods although data from them are later included in the evaluations. Sentences from page 20142, lines 10-16 belong to section Instrumentation and should be shifted there.

Corrected, edited and moved

Page 20141, line 2 There were 18 elements listed on page 20140 line 20 but 17 elements were used in the PMF calculations. Explain the difference.

Sr was not used in the PMF analysis as often below detection limit, edited.

Page 20142, lines 6-7 Give the standard deviation of the mean PM mass values. The authors show later that the distribution of the atmospheric concentrations is a lognormal function (page 20145, lines 10- 16), and, therefore, the medians would represent the data sets better. Adopt the values in this sense.

Edited

Page 20143, section 3.1.2 One can only wonder how the diff RS-UB (%) was determined to be a number or a comment "not sign." More information is required to evaluate its relevance.

Edited - we now call it sum. The difference was found significant via t-test of different averages. addressed in the text.). Diff RS-UB (%) represents the difference between the RS and UB values (in %), whenever not significant (Not. Sign.) via t-test (assessing whether the means of two groups were statistically different from each other).

Page 20143, line 10 Replace organic carbon with organic matter.

We measure organic carbon and elemental carbon

Page 20143, line 12 and 18 Adjective “fine” is redundant because the authors only measured fine size fraction. The concentration ratio Mg/Al probably concerns the mean ratio.

Edited, correct

Page 20143, line 21 It is not clear which episode the authors refer to.

Edited, removed

Page 20143, line 26 It is wondered if the authors really meant soil urban dust. More explanation is needed.

We separate soil coming from the outskirt of the city (for example regional dust and Saharan dust) from soil originated more within the city, and often composed by Calcium (construction activities). Expanded in the text.

Page 20144-20145 (section 3.1.2) and/or 20158 (section 4.2.3) The present reviewer misses a clear discussion that the non-exhaust vehicle emissions also include Sb (from break wear) and Zn (from tire wear) which are associated with the coarse mode (together with Cu, Ba and Fe). Major amounts of this mode do not belong to the PM2.5 size fraction investigated in the present MS but are linked to PM_2.5-10 (coarse) size fraction.

We included a sentence on this matter. Although some of these traffic related metals can be distributed mainly in the $PM_{2.5\text{-}10}$ *(coarse) size fraction, it is also important to study them in the finer (*$PM_{2.5}$*) fraction.*

Page 20146, lines 8-9 Effects of the planetary boundary layer mixing height are missing from the discussion. They should be adopted.

Edited

Page 20148, lines 11-16 Explain briefly why Cu and Pb are associated with the biomass burning profile.

We have references about it, we included a line about it. This profile does not show presence of S, but presents an enhancement of Cu and Pb as reported in previous studies, likely to be due to anthropogenic contaminants burned along with open log-wood fires (Nriagu and Pacyna, 1988; Schauer et al., 2001; Karanasiou et al., 2009; Richard et al., 2011).

Page 20154, line 8 Change “inorganic elements” to “elements”.

Removed

Page 20156, line 9 There is no Fig. 8; correct the number.

Edited, figure 7

Page 20156, line 29 It is unusual to write “rain concentration”. Replace with an appropriate expression.

Rain amount

Page 20157, line 12 and some other places in the text Chloride is ion, while PIXE measures chlorine. Correct the expression.

Correct

Page 20158, line 23 The authors may want to replace “atmospheric pollutants” with “aerosol particles” because the former expression has too broad meaning here.

Edited

Page 20159, line 14 Replace South Europe with Southern Europe.

Edited

Page 20173, Fig. 1 The workdays and holidays should be indicated in the Figure, and this difference should be part of the interpretation as well.

Edited

Page 20174, Fig. 2 and page 20177 Fig. 5a Square layout for correlation-type figures is strongly suggested.

Edited

Page 20175, Fig. 3 It is thought that the figures represent mean diurnal variations. Change the figure caption accordingly.

Edited

The MS is very difficult to read in detail. It should be shortened and clarified.
Examples are: page 20139 lines 10-11, lines 19-23, page 20145, lines 10-16, and pages 20155 and 20156 which contain many redundant repetitions.

Edited

There are many grammatical and typing errors which should also be corrected.

Some examples are:
page 20138, line 29: is given in describing,
page 20142, line 25- page 20143, line 1: filters based technique,
page 20144, lines 27-28: power plant generators in the Barcelona province are natural gas base.

Edited