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
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.

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.

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

- 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.
- 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).
- p.4, l. 14: "WMB" should be explained.
- p.5, l.28: Some information about sampling inlet, sampling flow rate and filter diameter should be briefly provided in Instrumentation section.
- 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?
- 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.
- p.10, l.6: It is a question, why Ni and V were attributed to shipping emissions excluding diesel 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.
- 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.
- p.13, l.4-7: Use the same "names" for the sources identified by PMF 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 (R^2 = 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.
- p.16, l.30: It is misleading to indicate the average with "TOT", please change to "AVER" or "MEAN", here and in Table 3.
- 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 R^2=0 mean in Table 5 for Brake dust (Al-Ti)? Note that Table 5 is not cited in the text.
- 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.

- 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 (r^2 = 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 r^2 = 0.30, which leads to question this assumption. Any explanation for these discrepancies?
- 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.
- 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 potential associations of elemental concentrations with wind components (WS, WD) would also be shown.
- The industrial source types
- In Conclusions, p.23, l.15, the "atmospheric pollutants" should change to "elemental components of PM2.5".

- In Conclusions, p.23, l.24, the "on a mass basis" should be changed to "on a total elemental mass basis" for clarity.
- Also, in Conclusions, l. 25, the "65%" should be corrected to "27%» according to Table 3!
- 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.
- 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.
- Tables 2 & 5 show r^2 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*." from the title of Table 2, and delete one of the two "Cl". Also, please change "profile" to "profiles" in the Table 5 title.

Typographic Errors

- 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 he references that are really relevant.