Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-317-AC1, 2017

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Airborne particles in the Brazilian city of São Paulo: One-year investigation for the chemical composition and source apportionment" *by* Guilherme Martins Pereira et al.

Guilherme Martins Pereira et al.

martinspereira2@hotmail.com

Received and published: 9 June 2017

The authors thank the referee for the comments. The issues raised on the comments are answered bellow:

1) Number of chapters and subchapters are inconsistent.

AC: This was corrected for the reviewed version.

2) It would be better to mention that also metals are analyzed in the abstract otherwise the reader should wait several pages before to understand that also some metals are investigated.

AC: Metals are mentioned on the reviewed abstract: "…thermal-optical analysis. Trace elements were determined by inductively coupled plasma mass spectrometry. The associated risks…"

3) Section 1.2. The height of the back-trajectories used start at 500 m that are not exactly near the ground. Why a lower starting point has not been chosen?

AC: Using a lower starting point can be challenging, the height of trajectories was selected to avoid the characteristics of the urban surface (with high rugosity height inducing mechanical turbulence).

4) Section 1.4 (line 180). It is reported that PMF was applied to PM10 but I understand that all data including PM2.5 were used together. Please correct this incongruence.

AC: The PMF was applied considering all data (PM2.5 and PM10), this incongruence was corrected in the reviewed text: "The widely used source apportionment model, positive matrix factorization (PMF), was applied to all samples dataset (Paatero and Tapper, 1994)."

5) Equation (3). The symbol EC was already used for elemental carbon, another symbol should be used in this equation otherwise it is confusing.

AC: This symbol for Element Concentration was be changed from EC to C in the reviewed equation: "Unc= ([EF×C]ˆ2+[0.5×DL]ˆ2)ˆ(1/2) Where EF is the error fractions and C is the element concentration."

6) Section 3.1 line 210. Why correlation with minimum relative humidity and not with the average relative humidity measured during the collection of samples?

AC: Correlations with average and minimum relative humidities will be included on the reviewed text: "There were moderate negative correlations between PM10 and average wind speed, minimum and average relative humidities; and between PM2.5 and average wind speed and minimum relative humidity (Table S1).

7) Section 3.1 lines 226-227. It is not clear why a comparison with London and Madrid? If a comparison with other urban areas is needed it would be better to expand it or explain why choosing specific towns.

AC: The authors tried to compare particulate matter concentrations with those found in metropolis in different continents, such as Europe and Asia. It will be rewritten in order to explain the choice over those cities: “The average values for PM2.5 were higher than those obtained in a year study done in traffic sites in two European metropolis: London and Madrid in 2005 (warm period: 19.40 and 20.63 μg m-3 for PM2.5, respectively) (Kassomenos et al., 2014). The European Union has a more restrictive control of pollutant emissions compared to Latin American countries, since an annual mean of 40 μg m-3 is established for PM10 and a limit value of 25 μg m-3 is imposed for PM2.5 (Kassomenos et al., 2014). However, these averages in São Paulo are lower than the observed in year-round studies performed in Chinese megacities. . ...”.

8) Section 3.3 lines 275-279. This aspect should be discussed in more detail, are authors suggesting that the missing negative charges could be associated to carbonates, like calcium and/or magnesium carbonates? This could be put in evidence looking at the correlation between anion deficit and nss-Ca2+ concentrations as done, for example, in Contini et al. (Science of the Total Environment 472, 2014, pp. 248–261).

AC: Authors suggested that the missing charges are associated to calcium and magnesium carbonates. Unfortunately we were unable to determine ionic Ca2+ and Mg2+. The authors decided to withdraw this balance.

9) Section 3.3. line 312. What are IC2.5 and EC2.5?

AC: They were the previous terms for extensive and intensive campaigns, and were changed to Int2.5, Ext2.5 and Ext10 for the final text. This was corrected for the reviewed version: “As observed for nss-K+, elemental K average concentration was more than twice higher in Int2.5 than Ext2.5 ($p < 0.05$).”

10) Section 3.3. Line 298-299. This sentence is strange. It is not clear if authors speaks about PM2.5 or PM10.

AC: This paragraph refers to Ext2.5 (extensive fine, PM2.5) and Ext2.5-10 (extensive coarse, PM2.5-10), and will be rewritten in order to make it clearer: “Na+ was strongly correlated with Cl- in Ext2.5 (R = 0.78) and had relatively higher correlations with this species (R = 0.35) in Ext2.5-10.”

11) Section 3.3. Line 323. I do not believe that there are anomalous enrichments, there are only enriched or not enriched elements if a single threshold approach is used.

AC: This terminology was done similarly as in Pereira et al. (Atmospheric Environment 41, 2007, pp. 7837–7850) and is also found in Odabasi et al. (Atmospheric Environment 36, 2002, pp. 5841–5851).

12) Section 3.4. Lines 342-343. The ratio OC/EC is also strongly depending on the measurement protocol used. This aspect should be discussed.

AC: The OC/EC ratios were determined with equivalent measurement protocols in Pio et al. (Atmospheric Environment 45, 2011, pp. 6121–6132). We emphasize this in the reviewed version. Some improvements were done; the references Querol et al., 2013 and Viana et al. 2007 were replaced by Amato et al., 2016 (Atmospheric Chemistry and Physics 16, 2016, pp. 3289–3309), which is a work where equivalent techniques were used: “Ratios lower than 1 are constantly observed in roadway tunnels and are assumed to describe the composition of fresh traffic emissions (Pio et al., 2011). Amato et al. 2016 found values ranging from 1.8 and 3.7 at the urban background sites using equivalent measurement protocols. It was attributed to the distance from main roads, which can increase the influence of secondary OC (Pio, 2011). In this way, the values for OC/EC found in the present study may be due to vehicle emissions with contribution of secondary organic aerosols.”

13) Section 3.3. Lines 345-349. The mass closure analysis has been done considering metal oxides and possible contribution of carbonates like done, for example, in Cesari et al. (Environmental Science and Pollution Research 23, 15, pp 15133–15148, 2016)? The Si concentrations could be evaluated starting from Al concentrations. I believe that some more details are necessary to actually interpret the unaccounted mass.

AC: Only the oxides were considered for the mass closure analysis, as in Alves et al. (Atmospheric Research 153, 2015, pp. 134–144). The concentrations of Si were evaluated from Al considering a ratio of 3.4 as in Clements et al. (Atmospheric Environment 89, 2014, pp. 373–381), but it may have been overestimated this way; the total accounted mass exceeds in 20% the PM2.5 concentration for the intensive campaign.

14) Section 3.4.3 regarding the PAHs risks. It could be useful if the calculated values are compared with typical values found in other areas, see for example, Gregoris et al (Science of the Total Environment 476–477 (2014) 393–405) and references therein.

AC: The authors improved the paragraph considering more references: “DBA had the largest contribution to carcinogenic potential and BaP the highest to mutagenic potential. In studies performed in Italian urban areas, BaP was the compound that most contributed to total carcinogenicity in PM, although the TEF used for DBA was lower in those cases (Cincinelli et al., 2007; Gregoris et al., 2014). LCR from exposure to atmospheric PAH was estimated by multiplying BaP-TEQ and BaP-MEQ by the unit risk (87×10-6 (ng m-3)-1) for exposure to BaP established by WHO (de Oliveira Alves et al., 2015; WHO, 2000) (Fig. 5) and was possible to observe an increase during the intensive campaign. In all campaigns, the values observed were higher than the observed in studies done in the Amazon during dry season with events of biomass burning (de Oliveira Alves et al., 2015); also in studies in urban areas like New York and Madrid (Jung et al 2010 and Mirante et al., 2013). “

15) Section 3.6 Lines 471-475. It is not clear why only a few species are included in this

analysis and not all measured components. This is a little confusing, I can understand that some species were eliminated in PMF for one reason or the other but it is not clear why the other Figures and Tables reports different groups of species.

AC: More than 80 species were determined in this study, so they had to be selected in order to be included in this graph because of the lack of space for it. The ratios were calculated for all species, but only the species more important were discussed on the text: for being source tracers, having higher concentrations and/or health effects.

16) Section 3.7 line 503. Why it is necessary to add such a large uncertainty? Could this be due to an underestimation of the uncertainties of chemical determination of the different species?

AC: The uncertainties were increased in order to avoid discarding measurements that have poor data quality, due to some measurements below detection limits, this procedure was done according to reference of Paatero and Hopke (Analytica Chimica Acta 490, 2003, pp. 277-289).

17) Section 3.7 lines 515-516. Mention what is the relative change in Q due to the application of constraints.

AC: The relative change in Q (dQ = 0.4 %) due to application of constraints is mentioned in the reviewed version: “Lev and Man were pulled up maximally in the biomass burning factor in order to have a better separation between both factors, relative change in Q was of 0.4 %”.

18) Section 4 line 567. Better high than higher.

AC: Corrected in the reviewed text.

19) Table 2 is not very useful because the detection limits vary for several order of magnitudes and it is not clear which species have low detection limits and which species have high detection limits. I believe that a more descriptive table could be constructed.

AC: The authors suggest keeping this table, showing the range of those detection limits. More than 80 species were determined.

20) Table 4. It is not clear the difference between under detection limit and not detected. Essentially not detected for what reason? Because it is under detection limit?

AC: The term “under detection limit” was adopted for all tables in the reviewed version.

21) The correlation table in supplementary materials is not readable too many small numbers.

AC: The table file in excel will be uploaded as supplementary material, so it can be better understood.

22) In table S7. I do not understand the last line with the percentages.

AC: These are the percentages over the reduction on the ratio Qrobust/Qexpected as the number of factor increases, in the Q value analysis. These percentages could be removed for the reviewed final version of supplementary information file.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-317, 2017.