Atmospheric
Chemistry
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Discussions

ACPD

Interactive
comment

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.**

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The authors thank the comments. The author's comments are presented below:

1- Revise the numeration of chapters and subchapters.

AC. Corrected in the reviewed version.

2- Abstract: Please explain in short the location of the sampling site in the abstract, and that there is only one site where the samples were collected. As Sao Paulo is a

megacity with plenty of possible sites with potentially different sources of pollutants, it should be clear for the reader, that this study is different from several other papers publishing e.g. measurements in tunnels in Sao Paulo. The word airborne in the title and abstract is a bit misleading, as it is mostly associated with measurements on airplanes. It is very important to give the sampling height in the abstract and chapter 1.1.

AC. Modifications in the text:

The title is changed to: "Particulate pollutants in the Brazilian city of São Paulo: One-year investigation for the chemical composition and source apportionment"

Part of the Abstract was modified to: "In order to evaluate the sources of particulate air pollution and related health risks, a year-round sampling was done at the University of São Paulo campus (20 m above ground level), a green area near an important expressway. The sampling was performed for PM2.5 ($\leq$ 2.5 μm) and PM10 ($\leq$ 10 μm) in 2014 through intensive (every day sampling in wintertime) and extensive campaigns (once a week for the whole year) with 24 h of sampling".

In the item 2 "Methodology", section 2.1. Sampling campaigns: "Aerosol samples were collected at a São Paulo site (SPA, 23°33âĂš34"S and 46°44âĂš01"W) located on the rooftop of the Atmospheric Sciences Department (about 20 m above ground level), at Institute of Astronomy and Atmospheric Sciences (IAG-USP) building, within the campus of University of São Paulo."

3- Page 2, line 67: please write which primary sources PAHs have.

AC. Modifications in the text:

"Particulate organic carbon includes key species including polycyclic aromatic hydro-carbons (PAHs) and monosaccharides. The last are considered as biomass burning tracers (such as levoglucosan, mannosan, and galactosan) (Simoneit et al., 1999). PAHs have natural sources (synthesis by plants and bacteria, degradation of plants, forest fires and volcanic emissions), but are mostly emitted by anthropogenic sources

in urban sites (such as domestic, mobile, industrial and agricultural sources) (Abdel-shafy and Mansour, 2016; Ravindra et al., 2008)."

4- Table 2: As some species measured from the same instrument have apparently huge DL-differences, it is not helpful to just give the range of DLs. Additionally, add horizontal lines between the different instruments for a better separation.

AC. More than 80 species were determined and it would be difficult to present all detection limits. That is why the authors presented in such way. Lines were added between the different instruments.

5- Table 2: For the IC, do all ions really have exactly the same DL (6.4)? If so, the authors should write (in short) the reason for equal DLs and/or refer to a publication for this measurement technique.

AC. I noticed there was a typo in this table, in fact the DL value is 1.27 ng m-3 for all ions (corrected in the reviewed version), and this was calculated with basis on detection limit of 1 ng ml-1 (per volume of analyte solution on the IC). These values were provided by the FMI research group and are based on the signal to noise ratio of the IC baseline. Similar DLs were observed for the ions Na+, NH4+, K+, Cl-, NO3-, SO42- and MSA.

6- Page 3, line 135: I guess, all carbon should be 'oxidized' to CO2, not 'volatilized'?

AC. Corrected in the reviewed version.

7- Page 5, line 188: At that point, it is not clear for me how "missing data" occur. Do you mean missing filter samples for certain days, or missing data from specific species of a filter sample? If it is the last, how can that happen? Were there some species from a filter measured, but others not?

AC. The group decided to determine elements after few samples (n=8) were collected in fiber glass filters. In these filters it is not possible to determine trace elements (the blank filters presented high levels of elements). To avoid discarding these samples (other species) we decided to do the statistical treatment as suggested by Brown et al.

(Science of Total Environment 518–519, 2015, pp. 626-635). This paper suggests that the missing values are replaced by the median values of the valid samples.

8- Table S1: Please explain "Therm. Ampl." and the possible reason for its correlation to PM2.5 and PM10. I am asking as these values are highlighted and not mentioned anywhere in the manuscript.

AC. This is the thermal amplitude on the sampling days (maximum temperature minus minimum temperature) and will be removed from the supplementary information.

9- Page 6, line 229: Here the authors should make clear, that their data set does not have the data coverage over the year to be fully representative and comparable with the mentioned guidelines. To my knowledge, for both the EU and WHO guidelines, a coverage of 75% for one day and 90% for one calendar year, respectively, is mandatory for a proper risk assessment. Regarding the annual mean limits, the presented data is quite far away from that, considering there is only one day of sampling per week during the extensive campaign.

AC. The comparisons were removed from the paragraph, but the WHO guidelines were kept cited as a reference. The text:

"In the extensive campaign, the PM mass concentrations exhibited a wide range of concentrations. The concentrations in the Ext2.5 ranged from 8 to 78 μg m-3 (average 30 μg m-3), whereas Ext10 values varied between 12 and 113 μg m-3 (average 44 μg m-3) (Fig. 3). The World Health Organization (WHO) recommends a daily limit for PM10 of 50 μg m-3 and of 25 μg m-3 for PM2.5, (WHO, 2006) while the Brazilian Environmental Agency (CONAMA) recommends a threshold of 150 μg m-3 for PM10 (CONAMA, 1990; Pacheco et al., 2017). When considering the CONAMA standards, only one day in the extensive campaign was near the target limit. The Ext10 campaign was divided into two periods: dry (April to September) and rainy (October to March). It was observed that the average PM10 was 52 μg m-3 in the dry period and of 35 μg m-3 in the rainy period."

10- Page 7, line 279: Which other cationic species are you suggesting?

AC. The authors decided to remove the cation/anion ratio discussion from the manuscript. Important species are missing for a complete analysis.

11- Page 8, line 291: Where and at which height were of gaseous species from CETESB measured? Collocated to the filter sampling?

AC. The gaseous species data were taken from two monitoring stations (CETESB). The first one (NOx) is located inside the university campus (800 m far from the sampling site, at ground level) and another station is 3.2 km far (for CO, at 2m height). The sources that affect these stations are similar to those that affect the sampling site (Marginal Pinheiros expressway and local traffic). Other studies identified high correlations of pollutants concentrations between IPEN station and IAG sampling site; Oyama et al, (Atmospheric Chemistry and Physics, 16, 2016, 14397-14408) and Vara-Vela et al. (Atmospheric Chemistry and Physics, 16, 2016, 777-797).

12- Page 8, line 298: A R=0.35 is not relatively higher than R=0.78. Which correlation(s) are you comparing with R=0.35?

AC. It was not properly written, leading to the misunderstanding that these correlations were compared, but they were not. This part was rewritten:

"Na+ was strongly correlated with Cl- in Ext2.5 (R = 0.78) and in Ext2.5-10 presented a relatively moderate correlation (R = 0.35)".

13- Table 4: What is the difference between "below detection limit" and "not detected?" Beside that "DL" is not used in table 4, but solely in Table 5, and there, "DL" is not explained.

AC. Corrected in the reviewed version.

14- Page 9, line 347: If the unaccounted part may be attributed to absorbed water, can you see a correlation between this part and ambient humidity?

AC. This correlation was determined and it was very low (R=0.2).

15- Page 10, line 447: I do not think it is necessary to mention the location of a chamber (Florida), but rather the institute.

AC. Modifications in the text:

"The Lev/Man ratios are characteristic of each type of biomass. The ratios were similar to that obtained in a chamber study with sugarcane burning (Lev/Man = 10, Hall et al., 2012), and also to that reported for the 2013 intensive campaign (Lev/Man = 12, Pereira et al., 2017)."

16- Page 13, line 500: The authors mention the strong and weak variables. Do all species, which are not mentioned, belong to the bad variables or are they simple not taken into account? Why and how did you define the 25% additional uncertainty? You combine species from different instruments, which have different uncertainties, as you pointed out in Table 2. Inserting these uncertainties into the error matrix usually cause that PMF strongly under- and overestimated the importance of variables within the solutions. Did you scale in some way the uncertainties to each other? Please explain also, why the organic character of Lev and Man justify to set them as weak variables.

AC. Some species were rejected due to low S/N ratio and other could not be included due to the relative high number of species compared to the number of samples. Some variables were not considered in the analysis and considered as bad variables, because they are highly correlated with other variables (high co-linearity and redundancies) and don't give us more information related to the sources. PAHs could also not be included because of the great effect of gas-particulate partitioning that is influenced by meteorological conditions. Maybe it was not well understood, but the organic character of Lev and Man mean they are a little partitioned between gas and particle and also can be decomposed in the atmosphere, as discussed in Pio et al. (Atmospheric Environment 42, 2008, pp. 7530-7543) that's why they were considered as weak species. 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). The additional uncertainty was applied to all the variables increasing proportionally the uncertainties. Besides the increase of the uncertainty, the physical solution does not change, presenting the same factors and results. We concluded that the solution is stable, because the same sources could be identified in most of the solutions generated, with different additional uncertainties.

17- Table S7: What do the percentages mean in the last row?

AC. Percentage of reduction over Qrobust/Qexpected with the increase in the number of factors. It was withdraw in the new version (Supplementary information).

18- General aspects to PMF: I understood that the source of both the RD and VE factor is the traffic. It is not clearly seen in the polar plots (maybe because of the very high RD concentration point coming from NW) how well both factors are correlated to each other. The authors should add a comment on a possible correlation. I also do not understand why all factors were not compared to the gaseous CO and NOx time series, as these gases are commonly used to be correlated with primarily emitted factors, especially traffic sources. This would also justify additionally the author's choice of the 5-factor-solution.

AC. There was a weak correlation between RD and VE and maybe it should not be expected to have such correlation, since the aerosol emitted by RD has a larger aerodynamic diameter than the aerosol related to VE. RD sources are primary and VE can be primary but they also can be secondarily formed from vehicular primarily emitted precursors. RD can be influenced by traffic but also by high wind speed. High correlations were observed between CO and NOx with primary sources factors as VE and BB. It may be due to the difficulty in separating these factors from each other, since their contributions increase with meteorological conditions (wind direction). Correlations were moderate between the gases and IN and RD and no correlation was

observed between these gases and the SP (secondary processes). These findings will be included in the PMF discussions (section 3.7):

"...Vehicular source seemed to increase with winds coming from the North and North-west, passing by the expressway, but decreased with SE winds, as observed previously (Sánchez-Ccoyllo and Andrade, 2002). The polar plots profiles of VE and RD factors presented a different pattern, since the aerosol from road dust suspension has a larger aerodynamic diameter (Karanasiou et al., 2009) and tends to increase with wind speed".

"High correlations (R > 0.8) were observed between the gases CO and NOx and the primary sources factors VE and BB. These gases are related to vehicular emissions (Alonso et al., 2010) and the correlations with the biomass burning factors may be due to the fact that it increases with the same wind direction as the vehicular factor. No correlations were found between these gases and SP factor."

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