

**Comments for manuscript:** “Source apportionment and ecotoxicity of particulate pollution events in a Major Southern Hemisphere Megacity: influence of biomass burning and a biofuel impacted fleet” by Guilherme Martins Pereira.

The manuscript investigates the chemical composition of fine particulate matter (PM<sub>2.5</sub>) during a 100-day dry period in 2019 in the Metropolitan Area of São Paulo (MASP), Brazil. Source apportionment using Positive Matrix Factorization highlights vehicular emissions and biomass burning as the dominant PM<sub>2.5</sub> sources. While the main text is well-written and presents compelling results, the data comparisons are primarily limited to previous studies in São Paulo. Expanding comparisons to other major cities or continents could provide broader context and enhance the study’s contribution to global air quality research.

The title should include PM<sub>2.5</sub> and focus firstly on vehicular emissions and afterwards on biomass burning related influence. The figures could benefit from some revisions (see comments below).

### **Major Comments:**

**Line 228:** Could you provide an explanation for why nitrate concentrations surpassed sulfate during this campaign? Are there any measurements of sulfur oxides (e.g., from CETESB) over the last decade that support a reduction in sulfate levels?

**Line 283:** You present back-trajectories for two specific days, describing them as representative of typical air mass influences. Could you include the percentage of air masses arriving from this direction over the entire sampling period? Additionally, please describe the source regions for the remaining air masses during the campaign. Consider including a figure summarizing HYSPLIT-derived air mass sources and their percentages, either in the main text or the Supplementary Information (SI).

**Line 290:** Could you elaborate on xylitol? Why is it of particular interest? How do its concentrations compare to previous campaigns/sites? Are its levels higher during high or low relative humidity? Is there any relationship between xylitol levels and specific air mass orientations?

**Line 318:** Please provide the OC/EC ratio for the entire campaign in the SI. Is the observed increase in the OC/EC ratio during this campaign due to an increase in OC, a decrease in EC, or a combination of both?

**Line 329:** Are ozone (O<sub>3</sub>) measurements from 2019 available to support your observations? If so, please include relevant data.

**Line 369:** Could you clarify what is meant by the “dark” precipitation event? It is clearly not a typical rain event, so this term should be described earlier in the manuscript. Additionally, PM<sub>2.5</sub> concentrations during these days are reported close to 10 µg/m<sup>3</sup>, whereas values below 5 µg/m<sup>3</sup> might be expected. Please explain this discrepancy. PMF may help you here.

**Temperature and RH Time Series:** Could you include the time series for temperature and relative humidity during the measurement period in the SI? The averages are mentioned somewhere in the text but the information is lost.

**Figure 6:** Could you clarify what is meant by "reference runs" and "BS"?

### **PMF Analysis, Section 3.4:**

What is the correlation between the identified factors? For example, does VE1 increase after VE2? To support the resuspension? Providing more details on these relationships would enhance understanding.

**Section 3.7 Placement:** Consider moving Section 3.7 after section 3.4, as this may improve the manuscript's flow.

**Global Comparison of PMF Analysis:** While PMF analysis on PM<sub>2.5</sub> is discussed for MASP, could you expand on comparisons with findings from other global studies? For example, comparisons to Srivastava et al. (2021), Wang et al. (2018), Han et al. (2023), Cheong et al. (2024), Nava et al. (2020), and others could provide broader insights.

**Abstract and Figure 7 Discrepancy:** In the abstract, you state that "sources related to vehicular emissions remain dominant (over 60% of PM<sub>2.5</sub>). However, Figure 7 shows VE1 and VE2 contributing approximately 40%. Could you clarify why secondary formation (SF) factor is included with car-related emissions? Additionally, Line 452 relates this SF factor to industrial emissions rather than vehicular ones. Moreover, in Section 3.7, the SF factor is described as having a weak correlation with NO<sub>3</sub><sup>-</sup>/EC and an opposite trend to the BB, VE1, and VE2 factors. Please reconcile these points.

**Lines 637–644:** Nickel and vanadium are also recognized as tracers for ship exhaust (Zhao et al., 2021). Have you considered this possibility in your analysis?

**VE1 and VE2 vs. Heavy- and Light-Duty Vehicles:** A previous study (Vieira et al., 2023) identified separate factors for heavy- and light-duty vehicles. Could you explain how VE1 and VE2 in your study differ from or align with these factors?

**Marine-Related Factor and 6-Factor Solution:** On August 15 and 29, a sea breeze was observed. Could a marine-related factor be present? Additionally, would a 6-factor solution help better deconvolute the sources? Some factors in Section 3.4 appear to be mixtures of two or more sources, which a 6-factor approach might resolve. Comparison to global studies will shed light on this study's findings.

**Pollution Events and Particle Size Distribution:** This section could benefit from revision to provide greater depth. The first part reads like an introductory paragraph, while the second discusses four specific days without adequately explaining their significance. Additionally, the entire measurement period is only briefly addressed. Including a table summarizing average values (e.g., new particle formation rates, growth rates, nucleation event days) in the main manuscript would enhance clarity and aid the reader.

**Enrichment Factor (EF) Results:** Although the methodology for calculating enrichment factors is described in the data treatment section, no corresponding results, tables, or figures are provided in the main text. Apart from the brief mention in Lines 610–611, could you include these results to strengthen the manuscript?

### **Minor Comments:**

**Line 89.** Replace the word "extended"

**Line 118.** Rewrite the phrase “the first...derivatives”. The second step looks like is missing something.

**Lines 157-159.** Replace “BaPTEQ” to “BaP<sub>TEQ</sub>”, “BaPMEQ” to “BaP<sub>MEQ</sub>”, “BaPEq” to “BaP<sub>Eq</sub>”. Fix/increase the “(2)” to be the same as the others. Explain in what units the BaA, BkF etc. are referring to.

**Line 177.** Add reference after “depleted”. Replace “It” with “EF”. Add “with” before EF.

**Lines 179-180.** Either use parentheses for all CXp etc., or for none of the four. I recommend you use parentheses for none. Also, from which study do you take the concentration in the Earth’s crustal material? Please add references.

**Line 251.** Please present Figure 2 in order, for example not first the Fig. 2e and then Fig. 2c-d. Change the order of chart pies in Figure 2 to be consistent with the manuscript.

**Lines 252-256.** What are EC1, EC2, OC1, OC2 etc. are referring to? Please explain.

**Figure 2.** Increase the fonts for Lev, Lev/Man, PM2.5, EC and OM. Add to the caption that the time series in a and b refer to daily data. What do you mean by “dark” rain event?

**Line 276.** Add reference of previous campaign (2014).

**Figure 4.** Increase fonts. Increase the graph to be clearer to the reader. It would be nice to add the annual limit recommended by the European Environment Agency with different color.

**Figure 5:** Could you provide additional details in the main text on how these polar plots were generated?

**Line 362.** The number “10” and “9” it is not very clear to what they are referring to.

**Line 364.** Same for number “19”

**Line 367.** Maybe wanted to write “Figure 2” instead of “Figure 1”?

**Line 434.** Mention the factors by the order you present those in Figure 6. It’s easier for the reader.

**Figure 6.** Increase all fonts (axis, species, Factors). Especially, the “y-axis” cannot be read. Also, you could use a common x-axis in the bottom of the figure and increase the bars (maybe use different colors for each factor).

**Line 457.** Move “Factor 3” to another paragraph.

**Figure 7.** Better use  $\mu\text{g m}^{-3}$  instead of  $\text{ng m}^{-3}$ . Increase fonts. Add dark rain event purple bar.

**Figure 8.** In the caption there is a “b)” in the end of the sentence without anything following. Maybe move a) the b) before “trajectory” and “participation”, respectively.

**Line 541.** Remove the double dot.

**Figure 9.** Increase all fonts. At the caption, move (a)-(d) before the dates.

**Line 561.** Units for number concentration?

**Lines 562-563.** “The distribution, which had a geometric mean diameter of  $94.7 \pm 2.0$  nm at 8 AM, shifted to particles with a mean size of  $43.8 \pm 2.2$  nm.” And? What is the explanation for this? The key point?

**Line 570.** A dot is missing after “...83%)”

**Section 3.6:** A Table with the polluted/ clean concentration values for all species would be an interesting addition.

### References:

Cheong, Y., Kim, T., Ryu, J. *et al.* Source apportionment of PM<sub>2.5</sub> using DN-PMF in three megacities in South Korea. *Air Qual Atmos Health* (2024). <https://doi.org/10.1007/s11869-024-01584-5>.

Yun-Sung Han, Da-Mee Eun, Greem Lee, Sung Yong Gong, Jong-Sang Youn, Enhancement of PM<sub>2.5</sub> source appointment in a large industrial city of Korea by applying the elemental carbon tracer method for positive matrix factorization (PMF) model, *Atmospheric Pollution Research*, Volume 14, Issue 11, 2023, 101910, ISSN 1309-1042, <https://doi.org/10.1016/j.apr.2023.101910>.

Nava, S.; Calzolari, G.; Chiari, M.; Giannoni, M.; Giardi, F.; Becagli, S.; Severi, M.; Traversi, R.; Lucarelli, F. Source Apportionment of PM<sub>2.5</sub> in Florence (Italy) by PMF Analysis of Aerosol Composition Records. *Atmosphere* **2020**, *11*, 484. <https://doi.org/10.3390/atmos11050484>.

Srivastava, D., Xu, J., Vu, T. V., Liu, D., Li, L., Fu, P., Hou, S., Moreno Palmerola, N., Shi, Z., and Harrison, R. M.: Insight into PM<sub>2.5</sub> sources by applying positive matrix factorization (PMF) at urban and rural sites of Beijing, *Atmos. Chem. Phys.*, *21*, 14703–14724, <https://doi.org/10.5194/acp-21-14703-2021>, 2021.

Vieira, E. V. R., do Rosario, N. E., Yamasoe, M. A., Morais, F. G., Martinez, P. J. P., Landulfo, E. and Maura de Miranda, R.: Chemical characterization and optical properties of the aerosol in São Paulo, Brazil, *Atmosphere*, *14*(9), 1460, <https://doi.org/10.3390/atmos14091460>, 2023.

Wang Q.Q., L.P. Qiao, M. Zhou, S.H. Zhu, S. Griffith, L. Li, J.Z. Yu Source Apportionment of PM<sub>2.5</sub> Using Hourly Measurements of Elemental Tracers and Major Constituents in an Urban Environment: investigation of Time-Resolution Influence *J. Geophys. Res.-Atmos.*, *123* (2018), pp. 5284-5300.

Zhao, J., Zhang, Y., Xu, H., Tao, S., Wang, R., Yu, Q., Chen, Y., Zou, Z., Ma, W., 2021. Trace elements from ocean-going vessels in east Asia: vanadium and nickel emissions and their impacts on air quality. *J. Geophys. Res. Atmos.* *126*, 1–16. <https://doi.org/10.1029/2020JD033984>.