

## Comment on amt-2021-191

Anonymous Referee #3

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Referee comment on "Inter-comparison of online and offline methods for measuring ambient heavy and trace elements and water-soluble inorganic ions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{Cl}^-$ ) in  $\text{PM}_{2.5}$  over a heavily polluted megacity, Delhi" by Himadri Sekhar Bhowmik et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-191-RC2>, 2022

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Bhowmik et al. presents an intercomparison for on- and off-line measurements of water-soluble inorganic ions and heavy and trace metals during two different periods in the Delhi-NCR region of India. The on-line measurements included an Aerodyne High-Resolution Aerosol Mass Spectrometer (herein AMS) for water soluble inorganic ions and the Xact 625i Ambient Metals Monitor for heavy and trace metals. The off-line measurements involved collecting aerosols on quartz filters, prepared (depending on what was being extracted), and analyzed by ion chromatography (IC) for water soluble inorganic ions or inductively coupled plasma mass spectroscopy (ICP-MS) for heavy and trace metals. Though of potential interest to the AMT community, especially as the study covers different seasons and a polluted megacity, there are many concerns that need to be addressed prior to publication, as discussed below and outlined by the other reviewer.

1) As this is a techniques paper and is comparing different methods to measure aerosol, more information needs to be added concerning the instruments. For example, the authors say that more details about the AMS can be found in Lalchandani et al. (2021, under review). As it is under review, it is difficult to understand how the AMS was ran and analyzed and would be beneficial for this manuscript to be included, at minimum briefly. This includes:

- 1a) How frequently was IE conducted? How stable was it?
- 1b) What  $\text{NH}_4$  RIE was used?
- 1c) What  $\text{SO}_4$  RIE was used?
- 1d) Was the vaporizer a capture or standard vaporizer? What CE was used?

2) Another important aspect in better understanding the comparisons includes how the aerosols were sampled. This includes:

- 2a) How long was the sampling line for each instrument? What was the residence time for each sampling line? What material is used throughout? E.g., line 162-163, it appears that a combination of black silicon tubing and stainless-steel was used.
- 2b) How close were the inlets for the instruments (same line and split, inlets co-located, etc.)?
- 2c) Were the instruments located in a temperature controlled area? What was the temperature difference between inside and outside, as this could potentially lead to biases

in the aerosol (e.g., evaporation or high water content)?

2d) Was a denuder used for the offline sampling?

2e) Line 161, the authors mentioned they operated a PM<sub>2.5</sub> cyclone in front of the PM<sub>2.5</sub> lens AMS. Did they operate the PM<sub>2.5</sub> cyclone at different flow rates to ensure the cyclone had a  $d_{50} > PM_{2.5}$  or did they operate the cyclone normally? If the latter (normally), the aerosol being measured by the AMS will be much less than PM<sub>2.5</sub> as the combination of the PM<sub>2.5</sub> cyclone (operated normally) and PM<sub>2.5</sub> lens would significantly cut-off the large particles.

2f) Was a cyclone or impactor used to collect the aerosol on the filters? Was there a dryer in front of the filters?

3) There is some potential concern in the AMS interpretation. Within the AMS community, it is well established that the NH<sub>4</sub>, SO<sub>4</sub>, and NO<sub>3</sub> signal is a combination of organic and inorganic aerosol (e.g., Farmer et al., 2010, Almeida et al., 2013, Fry et al., 2013, Ge et al., 2014, Kiendler-Scharr et al., 2016, Chen et al., 2019, Schueneman et al., 2021, Nault et al., 2021, Day et al., 2022). Thus, there could be some nuances that are not considered in the direct comparison of the inorganic aerosol observed by IC vs the NH<sub>4</sub>, SO<sub>4</sub>, and NO<sub>3</sub> observed by AMS, especially during biomass burning events (e.g., nitrocatechol, Finewax et al., 2018). Further, as the AMS has difficulty observing refractory chloride (e.g., Tobler et al., 2020), is there a way to filter the observations of chloride to better compare? However, as a different on-line measurement showed even higher chloride measurements, it is currently unclear all the sources of chloride here (e.g., line 341).

4) Though it is important to document the biases in the aerosol collected on filters, it is not clear what is novel in this analysis concerning the water soluble inorganic ions. Artifacts from filter measurements have been well documented for decades (Klockow et al., 1979, Hayes et al., 1980, Koutrakis et al., 1988, Hering and Cass, 1999, Chow et al., 2005, Nie et al., 2010, Liu et al., 2014, 2015, Heim et al., 2020, Nault et al., 2020). Please be more intentional in explaining the novelty of this analysis.

5) The discussion about filter sulfate being higher than AMS sulfate is confusing in regards to the reaction of NH<sub>3</sub> with H<sub>2</sub>SO<sub>4</sub> to form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Various studies have shown that sulfate can be measured as sulfuric acid from filters and compare well with on-line measurements (Klockow et al., 1979, Hayes et al., 1980, Koutrakis et al., 1988, Nault et al., 2020). Instead, this reaction leads to the off-line measurement being biased high in NH<sub>4</sub> compared to on-line measurements (Nault et al., 2020). Rather, could it mainly be due to refractory sulfate (e.g., potassium or calcium sulfate) or as the authors pointed out chemistry occurring on the filters (line 295, SO<sub>2</sub> reacting with alkaline particles)?

6) The overall general concern about the paper is that the authors present the comparisons; however, they do not really present either steps forward to improve the comparisons or which method may be improved.

7) Another concern is that the authors discarded data that was below 3xMDL. This can artificially raise the average value of the observations (potentially leading to the on-line measurement 24 hr avg being higher than the filter measurement). There is inherent

noise in measurements that can be above and below MDL and should not be discarded for that. At minimum, the authors should investigate whether removing this data leads to differences in the comparisons or not.

8) I agree with Reviewer #1 that the discussion about when the filter is sampled/collected, as written, is very confusing and makes it unclear what is the best method. Also, did the authors try both methods to verify this?

9) Many of the figures are too busy and difficult to interpret. E.g., Fig. 6a-c could go into the SI and keep Fig. 6d in the main document, as this best summarizes the results. Further, for Fig. 3 and 6d, the authors may consider adding on the right axis what the R<sup>2</sup> is for each slope. Further, it is unclear what Fig. 5 adds to the discussions in the paper. Finally, for Fig. 4, the authors may consider only showing one or two of the important subplot and placing the rest into the SI.

10) A table that summarizes the measurements, their LOD and uncertainty, and their size cut off would be beneficial.

11) Please read through the manuscript again. There are some grammatical concerns and things that need to be defined to improve readability. Some examples are included below:

11a) Line 27-28, IITD and IITMD are not known and need to be defined.

11b) Line 133, cum?

11c) Line 163, capitalize r in Research

11d) Line 228, 6N?

11e) Fig. 2, symbols, box not defined as in Fig. 4

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