

## 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

Himadri Sekhar Bhowmik<sup>1</sup>, Ashutosh Shukla<sup>1</sup>, Vipul Lalchandani<sup>1</sup>, Jay Dave<sup>2</sup>, Neeraj Rastogi<sup>2</sup>, Mayank Kumar<sup>3</sup>, Vikram Singh<sup>4</sup>, and Sachchida Nand Tripathi<sup>1\*</sup>

<sup>1</sup> Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur, India

<sup>1\*</sup> Department of Civil Engineering and Centre for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, India

<sup>2</sup> Geosciences Division, Physical Research Laboratory, Ahmedabad, India

<sup>3</sup> Department of Mechanical Engineering, Indian Institute of Technology Delhi, New Delhi, India

<sup>4</sup> Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, India

Correspondence to: S. N. Tripathi (snt@iitk.ac.in)

### Responses (text in blue) to comments by the reviewer (text in black)

We thank the referee for his/her valuable comments which have greatly helped us to improve the manuscript. Please find below our point-by-point responses (in blue) after the referee comments (in black). The changes or existing lines in the revised manuscript are written in *italic (red)*.

#### Referee #3

**General Comments:** Bhowmik et al. present comparisons between on- and off-line measurements of both refractory and non-refractory aerosol. They show differences between the measurements, related to either the limitations of the instrument (e.g., AMS only observing non-refractory aerosol) or known interferences with the technique (e.g., volatilization / reactions).

The authors have taken great care in addressing the majority of the comments from the reviewers. This in turn has generally improved the manuscript and the figures. However, there are still a few details that need to be improved upon for the paper to be accepted to AMT.

**Comment 1:** Page 13, lines 322 - 325: Sorry for miscommunicating this point. The concern is not for the inorganic ions having interference with organic ions (though that is a concern for m/z 30). The concern is in regards that the organic sulfate / nitrate / reduced nitrogen will thermally decompose and / or under electron ionization, produce that inorganic ion (e.g., for organic nitrate, a large fraction of the signal is  $\text{NO}^+$  and  $\text{NO}_2^+$  (Day et al., 2022) and for organic sulfates, a large fraction of the signal is  $\text{SO}^+$ ,  $\text{SO}_2^+$ , and  $\text{SO}_3^+$  (Chen et al., 2019)). At minimum, please rephrase those lines to reflect this aspect of the AMS.

**Response:** We thank the reviewer for communicating this point. The lines has been rephrased in the MS in lines 318-323 as-

*“Some studies suggested that the organic sulfate, nitrate, and reduced nitrogen thermally decompose and/or under electron ionization in AMS, producing inorganic ions.  $\text{NO}^+$  and  $\text{NO}_2^+$  contribute a significant fraction in organic nitrate (Day et al., 2022) whereas, for organic sulfates, a large fraction of the signal is contributed by  $\text{SO}^+$ ,  $\text{SO}_2^+$ , and  $\text{SO}_3^+$  (Chen et al., 2019). Though the additional inorganics are minimum, this could lead to possible marginal biases between the online and offline measurement of the inorganics.”*

**Comment 2:** Page 16, line 365 - 367: It is still unclear if the filters are so warm from the afternoon that they cause lost of ammonium nitrate collecting during the night.

**Response:** In the morning-to-morning sampling strategy, the filters changed in the morning will sample nitrate quantitatively throughout the night as evaporation will be less at a relatively lesser temperature during the night. The nitrate collected during the afternoon of the previous day will be lost at the higher temperatures during noon-afternoon ( $20^\circ\text{C}$ - $25^\circ\text{C}$  during the winter campaign and  $38^\circ\text{C}$ - $45^\circ\text{C}$  during the summer campaign). While the filters changed in the afternoon or evening may lose the nitrate sampled during the night since the evaporation increases with the increase of temperatures during the day. For better understanding, we rephrased the lines in the MS in lines 349-353 as-

*“If the sampling strategy is evening-to-evening (24 hours), the samples will lose the night  $\text{NO}_3^-$  sampled during the night with the increasing temperature during the day. However, during morning-to-morning sampling strategy, the filters will collect the night  $\text{NO}_3^-$  quantitatively throughout the night, but the higher temperature in the afternoon of the previous day may promote the loss of afternoon  $\text{NO}_3^-$  from the filters (Malaguti et al., 2015).”*

**Comment 3:** Minor but of use: I understand the meteorology for the location of the measurement was not working; however, were there other meteorological stations in the city that could be used? It is not critical for the paper or for it to be accepted; instead, it would just improve it.

Response: We understand that the meteorology would have improved the manuscript. We looked through data from the nearby meteorological stations managed by Central Pollution Control Board (CPCB), India but, the quality of the data was poor. Hence we did not add the data to our manuscript.