Inter-comparison of online and offline methods for measuring ambient heavy and trace elements and water-soluble inorganic ions (NO₃⁻, SO₄²⁻, NH₄⁺ and Cl⁻) in PM_{2.5} over a heavily polluted megacity, Delhi

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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 #1

General Comments: The authors compare online and offline methods for the determination of elements and ions at highly polluted sites in Delhi. The topic is important and online methods would be needed for receptor models as they have better time-resolution. However, online instruments have not been very comparable with the traditional methods, there are problems e.g. with calibration and detection limits.

1. 32 The higher concentrations on the filters were due to the formation of particulate $(NH_4)_2SO_4$. This needs clarification (why?).

Reply: To keep the abstract short and precise we didn't explained the details. Though it has been explained in line 294-299 of the MS as-

"Interestingly during the summer campaign at IITD, though the correlation improves ($R^2=0.91$), the slope decreases to 0.49. This is likely because the vapor concentration of sulfuric acid (H_2SO_4) is higher during summers. As a result of which, the adsorption of sulfuric acid on PM deposited on the filter papers happens during summers which reacts with gaseous ammonia (NH₃) to form a relatively stable particulate (NH₄)₂SO₄ (Zhang et al., 2000), thus increasing ammonium concentration in the offline measurements during the warmer season, especially in the presence of dust (Nicolás et al., 2009)."

And in line 311-318 of the MS as-

"The higher $SO_4^{2^2}$ concentrations on the un-denuded offline filter-based measurements could be due to refractory sulfate (e.g., potassium or calcium sulfate). The higher filter-sulfate could also be possibly because of the positive sampling artifact. The SO_2 is absorbed on the filter by the collected alkaline particles (Nie et al., 2010). The higher concentration could also be due to the formation of ammonium bi-sulfate or ammonium sulfate because of the reaction between gas-phase ammonia with the acidic aerosols (Nicolás et al., 2009). Also, the un-denuded filter measurements could lead to higher filter-sulfate. The interaction of gas phase ammonia with acidic aerosols can be minimized by using denuders while collecting aerosols on the filters (Nault et al., 2020)."

2. 34 Why offline Cl⁻ was higher than that measured by AMS?

Reply: Again we tried to keep the abstract short and precise by avoiding detailed explanations which were discussed in the section 3.1. It has been explained in line 366-368 of the MS as-

"Also, while AMS only measures the NR-Cl⁻ (Manchanda et al., 2021), e.g. NH₄Cl, which can vaporize at 600°C but cannot measure Cl⁻ from refractory-KCl, IC measures chloride from all the water-soluble chloride salts, including NH₄Cl and KCl."

3.82-83... 40 elements, e.g.--- there are more than 40 elements in the list?

Reply: We thank the reviewer for pointing this out. We mistakenly wrote 40. We rectified this in the line 85-87 in the MS as-

"It is capable of measuring 45 elements, e.g., Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pt, Au, Hg, Tl, Pb and Bi with a frequency of every 30 mins to 4 hours."

4. p.5 What were the cut-offs of each instrument? How about inlet lengths and materials?

Reply: The cut-offs of both HR-ToF-AMS and Xact 625 was 2.5µm.

For HR-ToF-AMS, at IITD the inlet length was 2.44 meter and it was made of stainless steel having inner diameter of 0.3 inch and outer diameter of 0.4 inch whereas, at IITMD, a 1.5 m long silicon tubing (TSI Inc) having 0.19 inch inner diameter was used as inlet. It was mentioned in the line no 169-173 in the MS as-

"Ambient fine particulate matters were sampled through $PM_{2.5}$ cyclone (BGI, Mesa Labs. Inc.) inlet at IITD with a flow rate of 5 lpm (l/min) using a 2.44 m long stainless-steel tubing (0.3 inch I.D and 0.4 inch O.D) and through black silicon tubing (0.19 inch I.D) at IITMD, placed 1.5 m above the rooftop. A Nafion dryer (MD-110-144P-4: Perma Pure, Halma, UK) was used to dry the ambient aerosols to maintain the output RH at 20%."

For Xact 625, at both the sites, the inlet length was 2.44 meter and it was made of aluminium having inner diameter of 1.25 inch. It was mentioned in the line no 180-182 in the MS as-

"A separate sampling line of 2.44 meter (1.25 inch I.D) for the Xact which was made of aluminium was installed. A heater was set up at the end of the sampling line to ensure 45% RH set point."

5. 6-7. What was number of samples for each measurement period?

Reply: Daily 24 h PM_{2.5} samples were collected during both the measurement periods. A total of 64 filters (60 from IITD site during June-July 2019 including 4 blanks) were collected in summer whereas, a total of 186 filters (90 from each site during October-December 2019 plus 6 blanks) were collected in winter. It was added in the line no 155-157 in the MS as-

"A total of 64 filters (60 from IITD site during June-July 2019 including 4 blanks) were collected in summer whereas, a total of 186 filters (90 from each site during October-December 2019 plus 6 blanks) were collected in winter."

6. p.9 USEPA written here is as US-EPA and Usepa in the reference list.

Reply: We thank the reviewer for pointing out this mistake. The same has been corrected in the revised manuscript.

7. p.10 D. Zhang should be without D.

Reply: We thank the reviewer for pointing out this mistake. The same has been corrected in the revised manuscript.

8. p.13 NO_3^- Why the filter method gave higher NO_3^- compared to online method in winter? The higher offline NO_3^- concentrations during winter at IITD can be possibly because of the positive artifact due to the absorption of gas-phase nitric acid (HNO₃) on the filter. Why not in summer?

Reply: At IITD, the filter method gave higher NO_3^- compared to online method in winter likely due to the absorption of gas-phase nitric acid (HNO₃) on the filter.

This is not the case in summer. During summer, the evaporation of ammonium nitrate collected on filters can be much higher than the absorption of gas-phase nitric acid. The evaporation increases with the decrease of humidity and the increase of temperature (Chow et al., 2008; Takahama et al., 2004). Also, complete evaporation may occur beyond $25^{\circ}C$ (Schaap et al., 2004). Chow et al., (2008) observed the evaporation loss from quartz filter to be more than 80% during the warm season in central California. The high temperature ($35^{\circ}C-48^{\circ}C$) during the long sampling hours (24 hours) may be a possible reason for the poor correlation between online and offline NO_3^- measurements during the summer campaign at IITD.

9.p.13 This part is not very logically written and difficult to follow: first summer results are compared, then winter and back to summer conditions and evaporation problem.

Reply: We have re-written the part in a logical way which is now easier to follow in line 329-346 in MS as-

"The online and offline NO₃ measurements posed a good correlation during winter ($R^2 = 0.91$ and slope of 1.07 at IITMD, $R^2 = 0.82$ and slope of 0.49 at IITD) whereas the correlation worsens during summer at IITD ($R^2 =$ 0.42 and slope of 1.78) (Fig. 3). The slopes and correlation coefficient for the WSIS are listed in Table 2. The NO_3 concentrations measured by the HR-ToF-AMS were higher than the offline data during summer at IITD and during winter at IITMD whereas, filter-based measurements of NO_3^- were higher during winter at IITD (Fig. 2). The higher offline NO_3^- concentrations during winter at IITD can be possibly because of the positive artifact due to the absorption of gas-phase nitric acid (HNO₃) on the filter (Chow, 1995). Many studies (Chow et al., 2008; Kuokkaet al., 2007; Malaguti et al., 2015) reported higher concentrations of NO_3^- from high time resolution measurements than filter-based measurements due to the evaporation of ammonium nitrate collected on filters over the duration of sample collection (Pakkanen & Hillamo, 2002; Schaap et al., 2004; Kuokkaet al., 2007). Pandolfi et al. (2014) observed NO_3^- HR-AMS/Filter ratios of ~1.7 at Barcelona and Montseny in Europe. This evaporation loss increases with the decrease of humidity and the increase of temperature (Chow et al., 2008; Takahama et al., 2004). Also, complete evaporation may occur beyond 25°C (Schaap et al., 2004). Chow et al., (2008) observed the evaporation loss from quartz filter to be more than 80% during the warm season in central California. The high temperature $(35^{\circ}C-48^{\circ}C)$ during the long sampling hours (24 hours) may be a possible reason for the poor correlation between online and offline NO_3^- measurements during the summer campaign at IITD."

10. 323-327 This part should be rewritten: NO_3^- will not be lost during night, at night filters collect more quantitatively that during warmer daytime...

Reply: We have re-written this part in line 346-352 in MS as-

"Schaap et al. (2004) reported that the NO_3^- volatilization during a 24-h sampling period not only depends on the sampling instruments and ambient conditions, but also on sampling strategy. If the sampling strategy is evening to evening (24 hours), the samples will lose the NO_3^- sampled during night with the increasing temperature during the day. However, during morning-to-morning sampling strategy, the filters will collect the NO_3^- quantitatively at night, and the higher temperature in the afternoon of the previous day may promote the loss of NO_3^- from the filter (Malaguti et al., 2015)."

11. 341-342 Why Xact online instrument gave 1.9 times higher than IC?

Reply: Interestingly, IC measurements of Cl⁻ were found to be higher than Xact 625i measurements during summer at IITD and winter at IITMD. The Cl measurements from Xact 625i were ~1.9 times higher than the measurements from IC during winter at IITD. It could be due to the differences in water-soluble fraction of chloride in the samples, as ionic concentration (IC) represents water-soluble fraction whereas elemental concentration (Xact 625i) represents total concentration. Also, a lot particulate bound chloride in the atmosphere is in the form of ammonium chloride (Manchanda et al., 2021). Part of the ammonium chloride collected during the day long offline sampling would have vaporized, giving lower concentration from IC measurements. Further investigation is needed to draw a firm conclusion. We added this in line no 370-381 in MS as-

"We also compared Cl⁻ measurements from Xact 625i with the measurements from IC. Interestingly, IC measurements of Cl⁻ were found to be higher than Xact 625i measurements during summer at IITD and winter at IITMD. The Cl measurements from Xact 625i were ~1.9 times higher than the measurements from IC during winter at IITD (see fig. SM2 in supplementary material). The correlations were found to be good during winter $(R^2 = 0.83 \text{ and } 0.76 \text{ at IITD} \text{ and IITMD} \text{ respectively})$ and worsen during summer $(R^2 = 0.27 \text{ at IITD})$, similar to what we observed for AMS_Cl⁻ and IC_Cl⁻. It could be due to the differences in water-soluble fraction of chloride in the samples, as ionic concentration (IC) represents water-soluble fraction whereas elemental concentration (Xact 625i) represents total concentration. Also, a lot particulate bound chloride in the atmosphere is in the form of ammonium chloride (Manchanda et al., 2021). Part of the ammonium chloride collected during the day long offline sampling would have vaporized, giving lower concentration from IC measurements. Further investigation is needed to draw a firm conclusion."

12. 346 What were the cut-offs of online instruments?

Reply: The cut-offs of both HR-ToF-AMS and Xact 625 was 2.5µm.

13. Fig 4. Online and offline instrument results could be better marked to separate them. You can't see well the smallest concentration.

Reply: We divided the elements in the plots, based on their concentration ranges. We agree that the smallest concentration can't be separated well compared to its adjacent concentration. We reorganised some elements but that could not work out as well. For example the difference in concentration of online V vs offline V and online Ni vs offline Ni will still be present if we make a separate plot for them (see Fig. SM4 (d)). In Fig. 4, we only kept some major elements and the box plots for rest of the elements were placed in the supplementary material as suggested by referee #3. We modified Fig. 4. In the MS as-



Fig.4. Box plots of some major elements measured offline and online during (a) summer campaign at IITD, (b) winter campaign at IITD, and (c) winter campaign at IITMD site. The box plots for rest of the heavy and trace elements are shown in fig. SM4 of the supplementary material.

14. Fig 5. The highest shares are easy to separate, but the smallest cannot be seen.

Reply: We agree with the reviewer that the smallest shares cannot be seen in the pies. In the modified plots the lowest shares are grouped and named as 'others' beside the highest shares. The elements, that consisted 'others' and their shares are also annotated.



Fig.5. Fractions (%) of elements in total element concentration in $PM_{2.5}$ presented in pie format for online (a,c,e) and offline (b,d,f) measurements during winter and summer at IITD and during winter at IITMD.

15. Fig 6. There are far too many slopes in one picture, and they cannot be separated. Why there was so big "inside element" difference between the different measurement period e. g. for Al?

Reply: We thank the reviewer for the comment. We agree with the reviewer that there are far too many slopes in one picture, and they cannot be separated. We have categorised the elements in three groups according to their comparable characteristics (A, B, and C) and compared them at three locations in three sub plots. We modified the plots in Fig 6 in the MS in such a way that the slopes could be easily separated.



Fig. 6. Scatter plots and regression lines of Xact 625i vs. ICP-MS data for groups A, B, and C during (a) summer at IITD, (b) winter at IITD, (c) winter at IITMD, and (d) comparison of slopes (online/offline) & R^2 of the measured heavy and trace metals in PM_{2.5} during the summer and winter campaign at IITD and winter campaign at IIITMD.

The different range of concentrations during different measurement periods and, the solubility of the element in acid-matrix used for digestion for offline analysis can cause "inside element" difference between the different measurement periods.

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