Supplement of

Inter-comparison of online and offline methods for measuring ambient heavy and trace elements and water-soluble inorganic ions (NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, and Cl$^-$) in PM$_{2.5}$ over a heavily polluted megacity, Delhi

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Fig. S1. Time series of secondary species ($\text{NO}_3^-$, $\text{SO}_4^{2-}$ and $\text{NH}_4^+$) and $\text{Cl}^-$ during (a) summer campaign at IITD, (b) winter campaign at IITD and (c) winter campaign at IITMD site during 2019.
Table S1. Seasonal average concentration of secondary species (NO$_3^-$, SO$_4^{2-}$ and, NH$_4^+$) and Cl$^-$ at IITD and IITMD.

| Units in μg/m$^3$ | Summer IITD | Winter IITD | Winter IITMD |
|------------------|-------------|-------------|---------------|
|                  | Avg±Stdev   | Min  | Max  | Avg±Stdev | Min  | Max  | Avg±Stdev | Min  | Max  |
| **Online NO$_3^-$** | 4.61±2.40 | 1.19 | 12.61 | 8.53±5.43 | 1.28 | 26.33 | 10.04±6.96 | 0.72 | 30.03 |
| **Offline NO$_3^-$** | 1.15±0.88 | 0.04 | 5.31  | 13.53±9.65 | 2.41 | 45.18 | 9.21±6.5 | 1.17 | 25.79 |
| **Online SO$_4^{2-}$** | 0.97±0.74 | 0.19 | 2.68  | 7.08±4.32 | 1.82 | 19.55 | 9.52±8.2 | 0.81 | 42.46 |
| **Offline SO$_4^{2-}$** | 5.17±4.19 | 0.66 | 16.31 | 12.18±5.75 | 2.61 | 31.68 | 10.84±10.34 | 1.57 | 39.58 |
| **Online NH$_4^+$** | 1.36±0.37 | 0.51 | 3.32  | 6.26±3.63 | 1.74 | 14.73 | 8.24±5.61 | 0.45 | 24.33 |
| **Offline NH$_4^+$** | 2.47±1.32 | 0.96 | 6.43  | 7.55±3.59 | 2.23 | 21.43 | 8.89±6.62 | 1.23 | 27.32 |
| **Online Cl$^-$** | 0.28±0.32 | 0.03 | 1.44  | 1.96±3.59 | 0.14 | 7.04  | 4.48±3.11 | 0.07 | 11.40 |
| **Offline Cl$^-$** | 1.64±0.73 | 0.28 | 3.47  | 3.46±1.86 | 1.14 | 8.57  | 5.18±3.61 | 0.32 | 14.12 |

Fig. S2. Scatter plots between Xact determined Cl$^-$ and offline measured Cl$^-$ concentrations in PM$_{2.5}$ during summer and winter campaign at IITD and during winter campaign at IITMD.
Figure S3. Time series of (a) light group metals, (b) heavy metals and (c) trace metals during summer and winter campaign at IITD and winter campaign at IITMD.

Table S2. Seasonal average concentration of elements at IITD and IITMD with MDLs.

| Units in μg/m³ | Summer IITD | Winter IITD | Winter IITMD | MDL_xact (ng/m³) or MDL_ICP-MS (µg/m³) |
|---------------|-------------|-------------|--------------|----------------------------------------|
|               | Avg        | Stdev       | Min          | Max          | Avg        | Stdev       | Min          | Max          | Avg        | Stdev       | Min          | Max          | Avg        | Stdev       | Min          | Max          | Avg        | Stdev       | Min          | Max          | Avg        | Stdev       | Min          | Max          | Avg        | Stdev       | Min          | Max          | Avg        | Stdev       |
| Online Al     | 1.1442     | 3.2011      | 0.02         | 4.37         | 0.3438     | 0.6512      | 0.01         | 5.43         | 0.6820     | 0.5001     | 0.13         | 2.24         | 500         |
| Offline Al    | 3.5220     | 1.1293      | 0.31         | 13.46        | 1.3343     | 1.4870      | 0.15         | 9.3          | 1.6646     | 1.2526     | 0.29         | 6.61         | 1.121       |
| Online K      | 1.1930     | 0.5567      | 0.38         | 2.13         | 3.0451     | 2.2140      | 0.55         | 11.7         | 2.2780     | 1.6029     | 0.29         | 6.85         | 5.8         |
| Offline K     | 1.7743     | 0.3936      | 0.67         | 3.05         | 3.8032     | 2.1616      | 1.11         | 12.9         | 2.6374     | 1.7313     | 0.39         | 5.58         | 0.366       |
| Online Ca     | 1.4247     | 0.9429      | 0.24         | 3.58         | 0.5145     | 0.2398      | 0.06         | 1.35         | 0.3856     | 0.2265     | 0.11         | 1.11         | 1.5         |
| Offline Ca    | 1.7680     | 0.8708      | 0.48         | 4.87         | 1.1780     | 0.4636      | 0.19         | 2.28         | 0.8686     | 0.4918     | 0.17         | 2.48         | 0.987       |
| Online Ti     | 0.1144     | 0.0686      | 0.02         | 0.29         | 0.0424     | 0.0191      | 0.01         | 0.12         | 0.0340     | 0.0160     | 0.01         | 0.08         | 0.79        |
| Offline Ti    | 0.1216     | 0.0643      | 0.02         | 0.27         | 0.0834     | 0.0292      | 0.01         | 0.21         | 0.0557     | 0.0209     | 0.01         | 0.10         | 0.065       |
| Online V      | 0.0035     | 0.0027      | 0.00         | 0.00         | 0.0008     | 0.0006      | 0.00         | 0.00         | 0.0006     | 0.0004     | 0.0001       | 0.002        | 0.60        |
| Offline V     | 0.0055     | 0.0018      | 0.00         | 0.01         | 0.0095     | 0.0101      | 0.00         | 0.03         | 0.0012     | 0.0004     | 0.0005       | 0.002        | 0.034       |
| Online Cr     | 0.0037     | 0.0010      | 0.00         | 0.00         | 0.0008     | 0.0037      | 0.0001       | 0.00         | 0.0059     | 0.0042     | 0.001        | 0.018        | 0.58        |
| Element | Offline Cr | 0.0036 | 0.0014 | 0.00 | 0.009 | 0.0095 | 0.0030 | 0.00 | 0.0053 | 0.0019 | 0.001 | 0.009 | 0.021 |
|---------|------------|--------|--------|-------|-------|--------|--------|-------|--------|--------|-------|-------|-------|
| Online Mn | 0.0334 | 0.0211 | 0.01 | 0.09 | 0.0254 | 0.0137 | 0.00 | 0.0252 | 0.0166 | 0.003 | 0.068 | 0.71 |
| Offline Mn | 0.0341 | 0.0172 | 0.01 | 0.11 | 0.0343 | 0.0154 | 0.00 | 0.0198 | 0.0093 | 0.004 | 0.044 | 0.012 |
| Online Fe | 1.2613 | 0.5812 | 0.29 | 3.01 | 0.6049 | 0.2300 | 0.16 | 0.4358 | 0.2191 | 0.11 | 1.08 | 0.85 |
| Offline Fe | 1.1948 | 0.6788 | 0.24 | 2.8 | 0.7044 | 0.2193 | 0.27 | 0.3742 | 0.1613 | 0.10 | 0.89 | 0.042 |
| Online Co | 0.0013 | 0.0009 | 0 | 0.05 | NA | NA | NA | NA | 0.0003 | 0.0001 | 0.0001 | 0.0007 | 0.68 |
| Offline Co | 0.0013 | 0.0084 | 0 | 0.00 | NA | NA | NA | NA | 0.0003 | 0.0001 | 0.0001 | 0.0005 | 0.035 |
| Online Ni | 0.0019 | 0.0008 | 0 | 0.00 | 0.0010 | 0.0005 | 0 | 0.0021 | 0.0015 | 0.0004 | 0.0066 | 0.47 |
| Offline Ni | 0.0037 | 0.0007 | 0 | 0.00 | 0.0297 | 0.0087 | 0 | 0.0193 | 0.0037 | 0.012 | 0.026 | 0.102 |
| Online Cu | 0.0283 | 0.0180 | 0 | 0.08 | 0.0536 | 0.0394 | 0 | 0.0607 | 0.0466 | 0.009 | 0.19 | 0.39 |
| Offline Cu | 0.0251 | 0.0179 | 0 | 0.1 | 0.0401 | 0.0308 | 0 | 0.0980 | 0.0621 | 0.019 | 0.26 | 0.074 |
| Online Zn | 0.1989 | 0.1001 | 0 | 0.51 | 0.5006 | 0.2351 | 0.14 | 1.5431 | 0.3063 | 0.09 | 1.47 | 0.33 |
| Offline Zn | 0.1950 | 0.1146 | 0 | 0.56 | 0.3103 | 0.1515 | 0.07 | 0.3781 | 0.2372 | 0.07 | 1.17 | 0.98 |
| Online As | 0.0020 | 0.0007 | 0 | 0.005 | 0.0044 | 0.0021 | 0 | 0.0082 | 0.0040 | 0.002 | 0.017 | 0.31 |
| Offline As | 0.0038 | 0.0009 | 0 | 0.006 | 0.0082 | 0.0028 | 0 | 0.0082 | 0.0028 | 0.002 | 0.016 | 0.036 |
| Online Se | 0.0017 | 0.0006 | 0 | 0.003 | 0.0036 | 0.0024 | 0 | 0.0030 | 0.0022 | 0.0005 | 0.011 | 0.40 |
| Offline Se | 0.0018 | 0.0006 | 0 | 0.003 | 0.0035 | 0.0019 | 0 | 0.0031 | 0.0017 | 0.0003 | 0.010 | 0.067 |
| Online Rb | 0.0025 | 0.0020 | 0 | 0.006 | 0.0012 | 0.0010 | 0 | 0.0014 | 0.0012 | 0.002 | 0.006 | 0.95 |
| Offline Rb | 0.0034 | 0.0012 | 0 | 0.008 | 0.0042 | 0.0013 | 0 | 0.0034 | 0.0009 | 0.002 | 0.005 | 0.057 |
| Online Sr | 0.0088 | 0.0133 | 0 | 0.023 | 0.0124 | 0.0636 | 0 | 0.0043 | 0.0064 | 0.0006 | 0.037 | 1.1 |
| Offline Sr | 0.0248 | 0.0062 | 0 | 0.08 | 0.0184 | 0.0322 | 0 | 0.0126 | 0.0040 | 0.009 | 0.034 | 0.063 |
| Online Zr | NA | NA | NA | NA | 0.0014 | 0.0009 | 0 | 0.0006 | 0.0005 | 0.0003 | 0.002 | 1.6 |
| Offline Zr | NA | NA | NA | NA | 0.0232 | 0.0012 | 0 | 0.0235 | 0.0011 | 0.018 | 0.025 | 0.121 |
| Online Mo | 0.0003 | 0.0037 | 0 | 0.005 | NA | NA | NA | NA | 0.0002 | 0.0003 | 0.0001 | 0.0014 | 2.4 |
| Offline Mo | 0.0450 | 0.0001 | 0 | 0.05 | NA | NA | NA | NA | 0.0520 | 0.0056 | 0.04 | 0.09 | 0.097 |
| Online Cd | 0.0023 | 0.0009 | 0 | 0.007 | 0.0032 | 0.0017 | 0 | 0.0035 | 0.0025 | 0.0008 | 0.01 | 12 |
| Offline Cd | 0.0021 | 0.0011 | 0 | 0.005 | 0.0049 | 0.0027 | 0 | 0.0077 | 0.0049 | 0.001 | 0.023 | 0.101 |
| Online Sn | 0.0073 | 0.0020 | 0 | 0.014 | 0.0157 | 0.0140 | 0 | 0.0165 | 0.0133 | 0.007 | 0.096 | 20 |
| Offline Sn | 0.0064 | 0.0020 | 0 | 0.011 | 0.0156 | 0.0079 | 0 | 0.0129 | 0.0082 | 0.003 | 0.051 | 0.041 |
| Online Sb | 0.0201 | 0.0073 | 0 | 0.033 | 0.0237 | 0.0108 | 0 | 0.0209 | 0.0247 | 0.006 | 0.14 | 26 |
| Offline Sb | 0.0196 | 0.0038 | 0 | 0.049 | 0.0191 | 0.0092 | 0 | 0.0205 | 0.0181 | 0.003 | 0.084 | 0.048 |
| Online Ba | 0.0049 | 0.0358 | 0 | 0.013 | 0.1373 | 0.8084 | 0 | 0.0319 | 0.0770 | 0.001 | 0.41 | 1.9 |
|          | 0.0597 | 0.0038 | 0.01  | 0.13  | 0.1183 | 0.6416 | 0.00 | 5.85 | 0.1011 | 0.2092 | 0.005 | 1.17 | 0.097 |
|----------|--------|--------|-------|-------|--------|--------|------|------|--------|--------|-------|------|-------|
| Offline Ba | 0.1226 | 0.0947 | 0.01  | 0.55  | 0.4751 | 0.3879 | 0.08 | 2.09 | 0.3836 | 0.3867 | 0.07  | 2.24 | 0.63  |
| Offline Pb | 0.0941 | 0.1221 | 0.01  | 0.45  | 0.4349 | 0.3643 | 0.05 | 1.91 | 0.2349 | 0.2619 | 0.02  | 1.58 | 0.035 |

Figure S4. Box plots of rest of the elements measured offline and online during (a & b) summer campaign at IITD, (c & d) winter campaign at IITD, and (e & f) winter campaign at IITMD site.
Figure S5. Trends of element’s concentration in decreasing order for ICP-MS (a,c,e) and Xact 625i measurements (b,d,f) during winter and summer at IITD and during winter at IITMD.