Supplementary Material

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 $\text{PM}_{2.5}$ over a heavily polluted megacity, Delhi

Himadri Sekhar Bhowmik¹, Ashutosh Shukla¹, Vipul Lalchandani¹, Jay Dave², Neeraj Rastogi², Mayank Kumar³, Vikram Singh⁴, and Sachchida Nand Tripathi^{1*}

¹ Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur, India

^{1*} Department of Civil Engineering and Centre for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, India

² Geosciences Division, Physical Research Laboratory, Ahmedabad, India

³ Department of Mechanical Engineering, Indian Institute of Technology Delhi, New Delhi, India

⁴ Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, India

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

Keywords: Aerosol mass spectrometer (AMS), Xact 625 ambient metal mass monitor, Ion Chromatography (IC), ICP-MS, elemental composition.

Fig.SM1. Time series of secondary species (NO_3^- , SO_4^{2-} and, NH_4^+) and Cl^- during (a) summer campaign at IITD, (b) winter campaign at IITD and (c) winter campaign at IITMD site during 2019.

Table SM1. Seasonal average concentration of secondary species (NO_3^- , SO_4^{2-} and, NH_4^+) and Cl^- at IITD and IITMD.

Units in $\mu\text{g}/\text{m}^3$	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. SM2. Scatter plots between Xact determined Cl^- and offline measured Cl^- concentrations in $\text{PM}_{2.5}$ during summer and winter campaign at IITD and during winter campaign at IITMD.

Figure SM 3. 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 SM2. Seasonal average concentration of elements at IITD and IITMD with MDLs.

Units in $\mu\text{g}/\text{m}^3$	Summer _{IITD}				Winter _{IITD}				Winter _{IITMD}				MDL _{Xact} or MDL _{ICP-MS}
	Avg	Stdev	Min	Max	Avg	Stdev	Min	Max	Avg	Stdev	Min	Max	ng/m^3
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	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	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 1	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 9	0.21	0.0557	0.0209	0.01	0.10	0.065
Online V	0.0035	0.0027	0.00 16	0.008	0.0008	0.0006	0.00 01	0.00 3	0.0006	0.0004	0.0001	0.002	0.60
Offline V	0.0055	0.0018	0.00 14	0.011	0.0095	0.0101	0.00 1	0.03 8	0.0012	0.0004	0.0005	0.002	0.034
Online Cr	0.0037	0.0010	0.00 13	0.008	0.0037	0.0018	0.00 06	0.00 8	0.0059	0.0042	0.001	0.018	0.58
Offline Cr	0.0036	0.0014	0.00 27	0.009	0.0095	0.0030	0.00 3	0.01 8	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 5	0.07	0.0252	0.0166	0.003	0.068	0.71
OfflineMn	0.0341	0.0172	0.01	0.11	0.0343	0.0154	0.00 7	0.08 2	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 4	1.14	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 5	1.19	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	0.00 03	0.005	NA	NA	NA	NA	0.0003	0.0001	0.0001	0.0005	0.035
Online Ni	0.0019	0.0008	0.00 1	0.004	0.0010	0.0005	0.00 02	0.00 2	0.0021	0.0015	0.0004	0.0066	0.47
Offline Ni	0.0037	0.0007	0.00 24	0.006	0.0297	0.0087	0.02 1	0.05 9	0.0193	0.0037	0.012	0.026	0.102
Online Cu	0.0283	0.0180	0.01	0.08	0.0536	0.0394	0.01 1	0.24	0.0607	0.0466	0.009	0.19	0.39
Offline Cu	0.0251	0.0179	0.00 7	0.1	0.0401	0.0308	0.00 9	0.18 6	0.0980	0.0621	0.019	0.26	0.074
Online Zn	0.1989	0.1001	0.04	0.51	0.5006	0.2351	0.14	1.29	0.5431	0.3063	0.09	1.47	0.33
Offline Zn	0.1950	0.1146	0.05	0.56	0.3103	0.1515	0.07	0.74	0.3781	0.2372	0.07	1.17	0.098
Online As	0.0020	0.0007	0.00 1	0.005	0.0044	0.0021	0.00 1	0.01 6	0.0082	0.0040	0.002	0.017	0.31
Offline As	0.0038	0.0009	0.00 2	0.006	0.0082	0.0028	0.00 3	0.01 8	0.0082	0.0028	0.002	0.016	0.036
Online Se	0.0017	0.0006	0.00 08	0.003	0.0036	0.0024	0.00 02	0.01 1	0.0030	0.0022	0.0005	0.011	0.40
Offline Se	0.0018	0.0006	0.00 09	0.003	0.0035	0.0019	0.00 05	0.00 9	0.0031	0.0017	0.0003	0.010	0.067

Online Rb	0.0025	0.0020	0.0011	0.006	0.0012	0.0010	0.0001	0.006	0.0014	0.0012	0.0002	0.006	0.95
Offline Rb	0.0034	0.0012	0.0001	0.008	0.0042	0.0013	0.0001	0.009	0.0034	0.0009	0.002	0.005	0.057
Online Sr	0.0088	0.0133	0.0001	0.023	0.0124	0.0636	0.0007	0.58	0.0043	0.0064	0.0006	0.037	1.1
Offline Sr	0.0248	0.0062	0.01	0.08	0.0184	0.0322	0.0009	0.31	0.0126	0.0040	0.009	0.034	0.063
Online Zr	NA	NA	NA	NA	0.0014	0.0009	0.0001	0.004	0.0006	0.0005	0.0003	0.002	1.6
Offline Zr	NA	NA	NA	NA	0.0232	0.0012	0.02	0.026	0.0235	0.0011	0.018	0.025	0.121
Online Mo	0.0003	0.0037	0.0001	0.0005	NA	NA	NA	NA	0.0002	0.0003	0.0001	0.0014	2.4
Offline Mo	0.0450	0.0001	0.03	0.05	NA	NA	NA	NA	0.0520	0.0056	0.04	0.09	0.097
Online Cd	0.0023	0.0009	0.0001	0.007	0.0032	0.0017	0.0001	0.011	0.0035	0.0025	0.0008	0.01	12
Offline Cd	0.0021	0.0011	0.0001	0.005	0.0049	0.0027	0.0006	0.017	0.0077	0.0049	0.001	0.023	0.101
Online Sn	0.0073	0.0020	0.0004	0.014	0.0157	0.0140	0.0004	0.06	0.0165	0.0133	0.007	0.096	20
Offline Sn	0.0064	0.0020	0.0003	0.011	0.0156	0.0079	0.0001	0.05	0.0129	0.0082	0.003	0.051	0.041
Online Sb	0.0201	0.0073	0.0104	0.033	0.0237	0.0108	0.0105	0.089	0.0209	0.0247	0.006	0.14	26
Offline Sb	0.0196	0.0038	0.010	0.049	0.0191	0.0092	0.0002	0.06	0.0205	0.0181	0.003	0.084	0.048
Online Ba	0.0049	0.0358	0.0002	0.013	0.1373	0.8084	0.0007	7.42	0.0319	0.0770	0.001	0.41	1.9
Offline Ba	0.0597	0.0038	0.01	0.13	0.1183	0.6416	0.0003	5.85	0.1011	0.2092	0.005	1.17	0.097
Online Pb	0.1226	0.0947	0.019	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	0.013	0.45	0.4349	0.3643	0.05	1.91	0.2349	0.2619	0.02	1.58	0.035

Figure SM4. 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.