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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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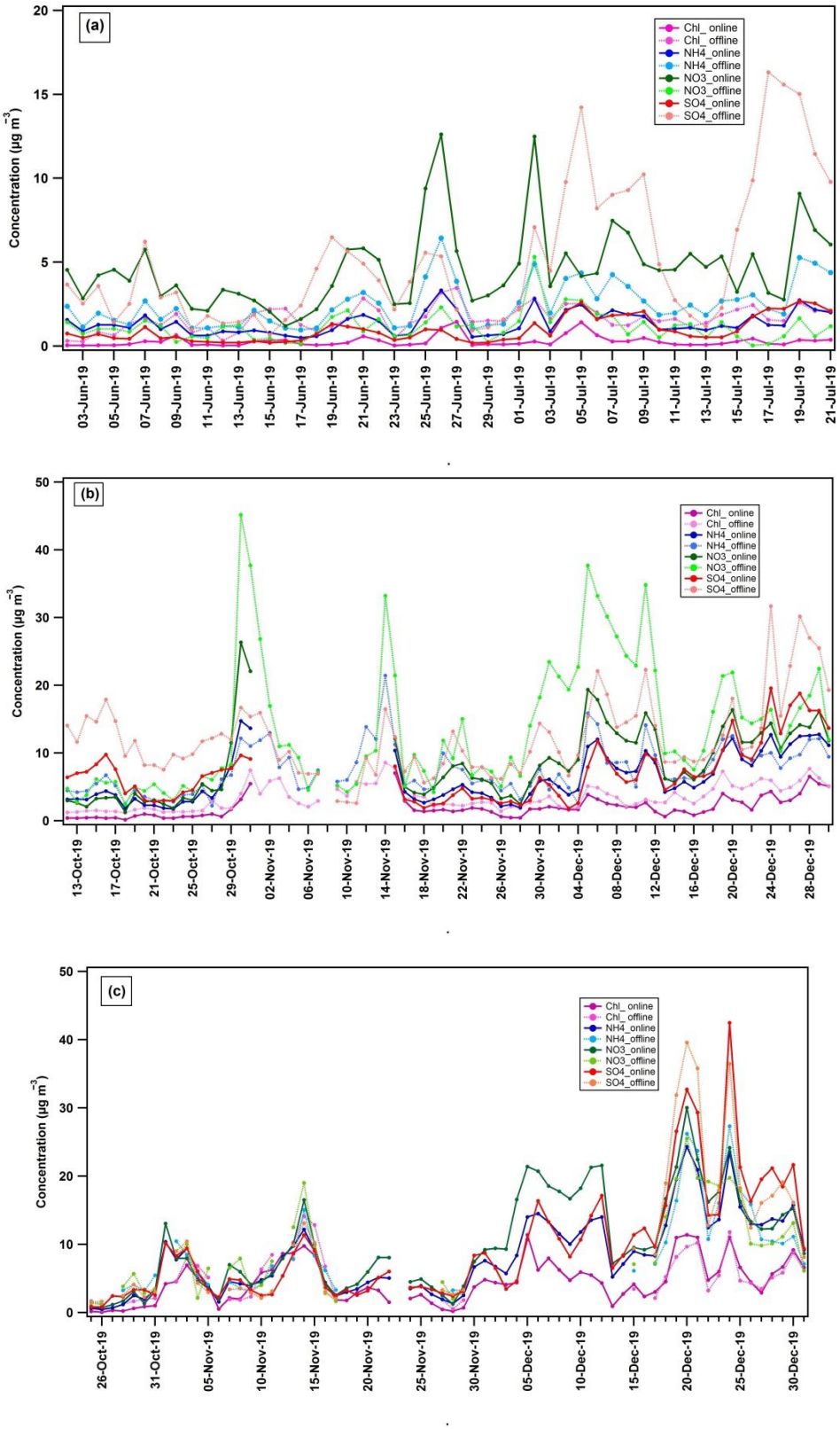


Fig.S1. Time series of secondary species (NO_3^-, SO_4^{2-} and, NH_4^+) and Cl^- during (a) summer campaign at IITD, (b) winter campaign at IITD and (c) winter campaign at IITMD site during 2019.

Table 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

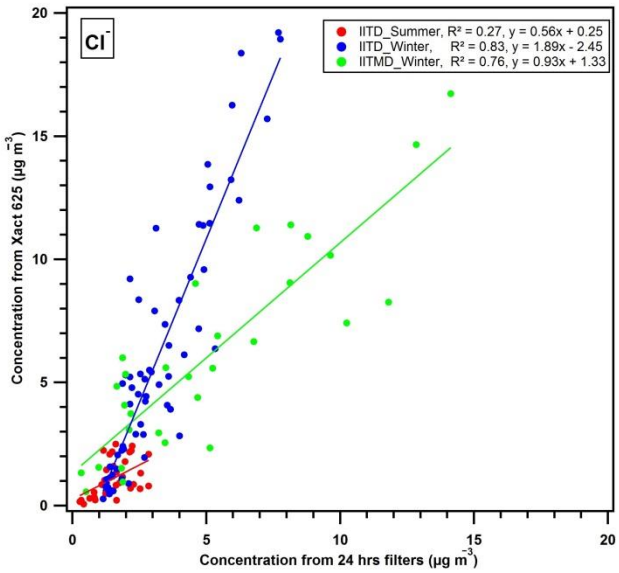
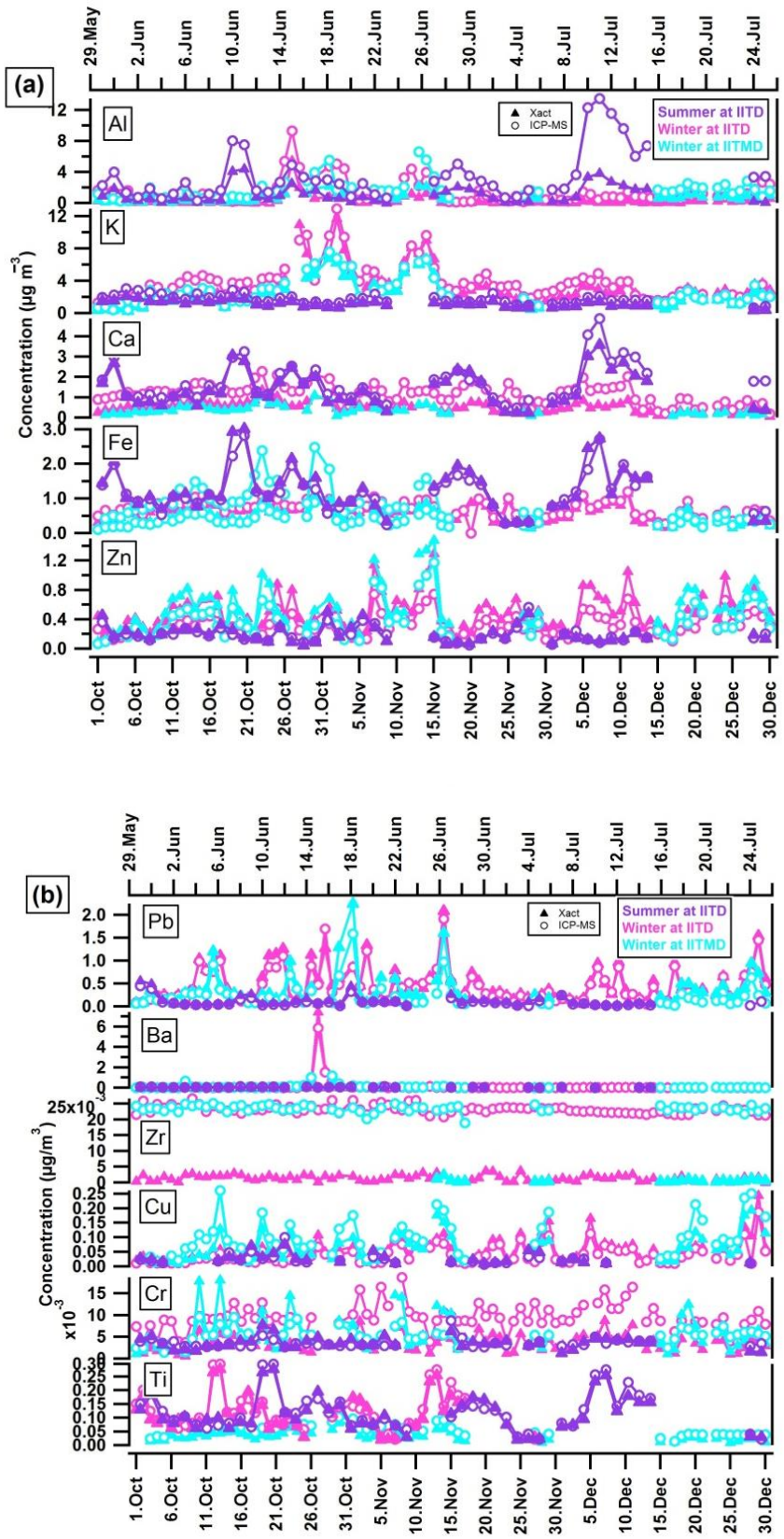


Fig. S2. Scatter plots between Xact determined Cl^- and offline measured Cl^- concentrations in $PM_{2.5}$ during summer and winter campaign at IITD and during winter campaign at IIITMD.


(a)
Al
K
Ca
Fe
Zn
Xact
ICP-MS
Summer at IITD
Winter at IITD
Winter at IITMD
Concentration (μg m-3)
29.May
2.Jun
6.Jun
10.Jun
14.Jun
18.Jun
22.Jun
26.Jun
30.Jun
4.Jul
8.Jul
12.Jul
16.Jul
20.Jul
24.Jul
1.Oct
6.Oct
11.Oct
16.Oct
21.Oct
26.Oct
31.Oct
5.Nov
10.Nov
15.Nov
20.Nov
25.Nov
30.Nov
5.Dec
10.Dec
15.Dec
20.Dec
25.Dec
30.Dec
(b)
Pb
Ba
Zr
Cu
Cr
Ti
Xact
ICP-MS
Summer at IITD
Winter at IITD
Winter at IITMD
Concentration (μg/m3)
25x10-3
x10-3

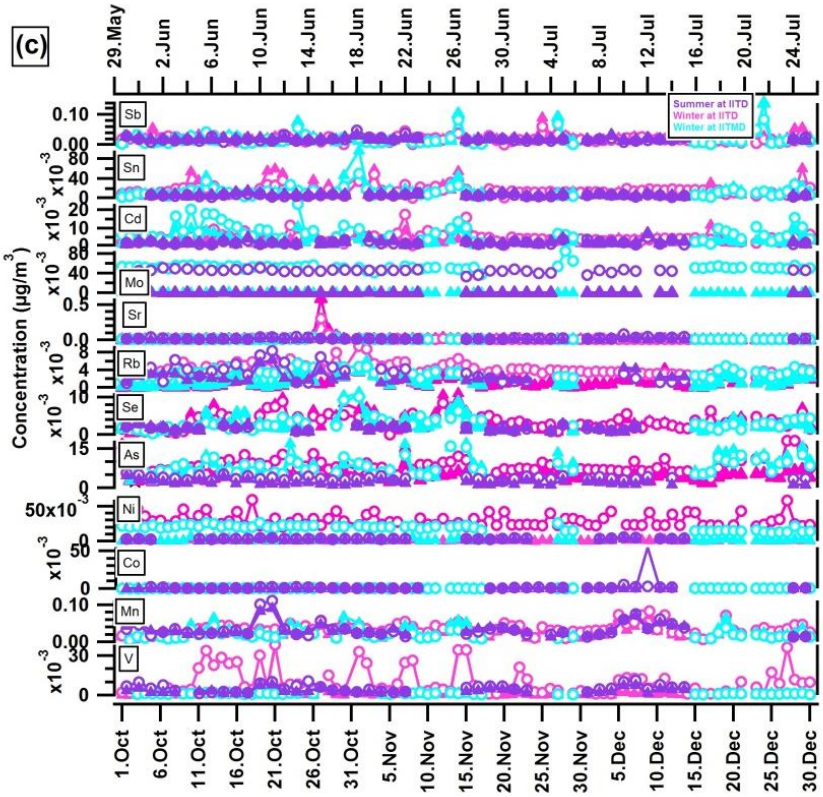


Figure S3. Time series of (a) light group metals, (b) heavy metals and (c) trace metals during summer and winter campaign at IITD and winter campaign at IITMD.

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	
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	11.72	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	12.92	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	0.011	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	0.019	0.21	0.0557	0.0209	0.01	0.10	0.065
Online V	0.0035	0.0027	0.0016	0.008	0.0008	0.0006	0.0001	0.003	0.0006	0.0004	0.0001	0.002	0.60
Offline V	0.0055	0.0018	0.0014	0.011	0.0095	0.0101	0.001	0.038	0.0012	0.0004	0.0005	0.002	0.034
Online Cr	0.0037	0.0010	0.0013	0.008	0.0037	0.0018	0.0006	0.008	0.0059	0.0042	0.001	0.018	0.58

Offline Cr	0.0036	0.0014	0.0027	0.009	0.0095	0.0030	0.003	0.018	0.0053	0.0019	0.001	0.009	0.021
Online Mn	0.0334	0.0211	0.01	0.09	0.0254	0.0137	0.005	0.07	0.0252	0.0166	0.003	0.068	0.71
Offline Mn	0.0341	0.0172	0.01	0.11	0.0343	0.0154	0.007	0.082	0.0198	0.0093	0.004	0.044	0.012
Online Fe	1.2613	0.5812	0.29	3.01	0.6049	0.2300	0.164	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	0.275	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	0.0003	0.005	NA	NA	NA	NA	0.0003	0.0001	0.0001	0.0005	0.035
Online Ni	0.0019	0.0008	0.001	0.004	0.0010	0.0005	0.0002	0.002	0.0021	0.0015	0.0004	0.0066	0.47
Offline Ni	0.0037	0.0007	0.0024	0.006	0.0297	0.0087	0.021	0.059	0.0193	0.0037	0.012	0.026	0.102
Online Cu	0.0283	0.0180	0.01	0.08	0.0536	0.0394	0.011	0.24	0.0607	0.0466	0.009	0.19	0.39
Offline Cu	0.0251	0.0179	0.007	0.1	0.0401	0.0308	0.009	0.186	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	0.001	0.005	0.0044	0.0021	0.001	0.016	0.0082	0.0040	0.002	0.017	0.31
Offline As	0.0038	0.0009	0.002	0.006	0.0082	0.0028	0.003	0.018	0.0082	0.0028	0.002	0.016	0.036
Online Se	0.0017	0.0006	0.0008	0.003	0.0036	0.0024	0.0002	0.011	0.0030	0.0022	0.0005	0.011	0.40
Offline Se	0.0018	0.0006	0.0009	0.003	0.0035	0.0019	0.0005	0.009	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	0.001	0.008	0.0042	0.0013	0.001	0.009	0.0034	0.0009	0.002	0.005	0.057
Online Sr	0.0088	0.0133	0.001	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	0.009	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	0.001	0.007	0.0032	0.0017	0.001	0.011	0.0035	0.0025	0.0008	0.01	12
Offline Cd	0.0021	0.0011	0.001	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	0.004	0.014	0.0157	0.0140	0.004	0.06	0.0165	0.0133	0.007	0.096	20
Offline Sn	0.0064	0.0020	0.003	0.011	0.0156	0.0079	0.001	0.05	0.0129	0.0082	0.003	0.051	0.041
Online Sb	0.0201	0.0073	0.014	0.033	0.0237	0.0108	0.015	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	0.002	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	0.003	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

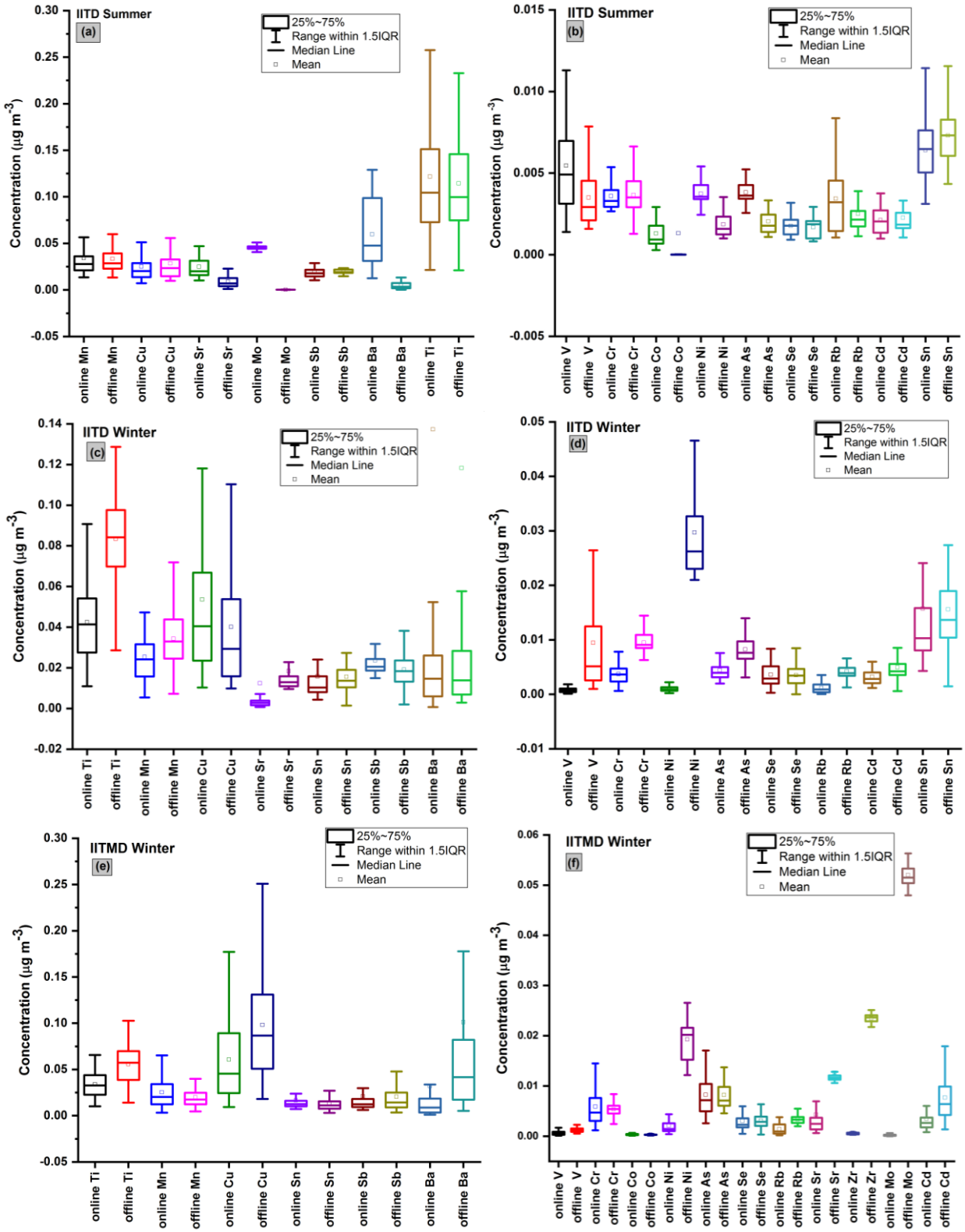


Figure S4. Box plots of rest of the elements measured offline and online during (a & b) summer campaign at IITD, (c & d) winter campaign at IITD, and (e & f) winter campaign at IITMD site.

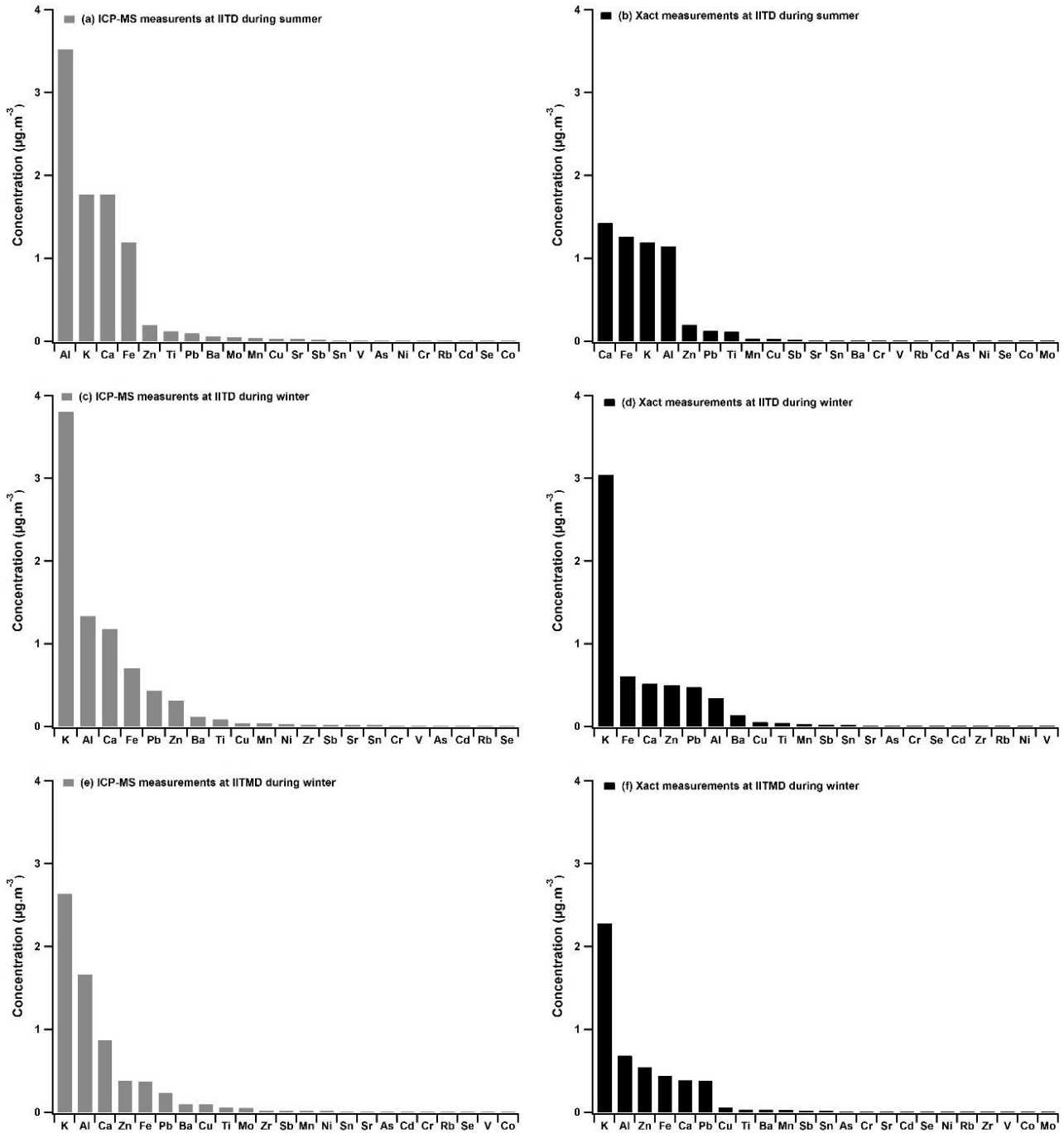


Figure S5. Trends of element's concentration in decreasing order for ICP-MS (a,c,e) and Xact 625i measurements (b,d,f) during winter and summer at IITD and during winter at IITMD.