Supplementary Information

Comparative elemental characterization of atmospheric fine and coarse PM samples by PIXE and ICP-MS/MS: Results from one year measurement campaign in a coal powered thermal power plant city

Abdallah Munır Abdallah Dawood,[ab] Franco Lucarelli,[c] Akif Arı,[da] Emre Can,[a] Pelin Ertürk Arı,[da] Tuncay Döğeroğlu[a] and Eftade O.Gaga*[a]

[a]*Eskişehir Technical University, Engineering Faculty, Department of Environmental Engineering, 26555, Eskişehir, Türkiye.*

[b]*Radiation Protection Institute (RPI) - Ghana Atomic Energy Commission (GAEC), Accra, Ghana.*

[c]*Department of Physics and Astronomy, University of Florence and I.N.F.N., Florence, Via G. Sansone 1, I-50019 Sesto F.no, Florence, Italy.*

[d]*Bolu Abant Izzet Baysal University, Engineering Faculty, Department of Environmental Engineering, Bolu, Türkiye*

* Corresponding author: Eftade O. Gaga, Eskisehir Technical University, Eskisehir-Turkey

E-mail: egaga@eskisehir.edu.tr, Telephone: +90 222 3223662/6648, Fax: +90 222 3239501

Content:

Table S1. Certified elemental areal concentrations for SRM 2783, together with quoted uncertainties

Table S2. Certified and uncertified elemental concentrations in SRM 1648a and average recoveries

Table S3. Descriptive statistics for PIXE and ICP-MS/MS for urban data

Table S4. Descriptive statistics for PIXE and ICP-MS/MS for rural data

Table S5. Calculated MDLs, LOQs and LODs for PIXE method

Table S6. Calculated MDLs, LOQs and LODs, with total uncertainties for ICP-MS/MS

Figure S1-S3. Distribution of datasets

Table S1. Certified elemental areal concentrations for the NIST SRM 2783 standard

Element	Areal concentration (µg cm^{-2})	Uncertainty (µg cm^{-2})
Al	2.33	0.05
Sb	0.0072	0.0003
As	0.0012	0.0001
Ba*	0.034	0.005
Ca*	1.3	0.2
Co	0.0008	0.0001
Cu	0.041	0.004
Cr*	0.014	0.003
Fe	2.7	0.2
Mg	0.87	0.05
Mn	0.032	0.001
Ni	0.007	0.001
K	0.53	0.05
Rb	0.0024	0.0006
Sc	0.00036	0.00003
Si	5.9	0.2
Na	0.19	0.01
S	0.11	0.03
Ti*	0.15	0.02
V	0.0049	0.0006
Zn	0.18	0.01

For the elements marked with the asterisk (*) the concentrations are reference values only

Table S2. Certified and uncertified elemental concentrations in SRM 1648a and average recoveries (n=14)

Elements	Certified Conc. (μg g⁻¹)	Analysis Conc. (μg g⁻¹)	Recovery (%) ± Std. Dev. (n=14)
Al	34300 ± 0.13	32418.9	94.5 ± 15
Sb	45.4 ± 1.4	40.6	89.4 ± 6.1
As	115.5 ± 3.9	120.8	104.5 ± 12.2
Br	502 ± 10	438.3	87.3 ± 6.8
Ca	58400 ± 0.19	41760.27	71.5 ± 3.4
Cd	73.7 ± 2.3	71.1	99.3 ± 8.6
Ce	54.6 ± 2.2	45.9	84.3 ± 4.7
Co	17.93 ± 0.68	16.9	94.5 ± 7.8
Cr	402 ± 13	386.4	96.1 ± 9.7
Cu	610 ± 70	562.8	92.3 ± 11.1
Fe	39200 ± 0.21	38605.8	101.4 ± 11.3
Pb	6550 ± 0.033	6613.8	100.9 ± 9.5
Mg	9130 ± 0.01	8247.1	90.4 ± 13.7
Mn	790 ± 44	808.9	102.3 ± 10.1
Hg	1.323 ± 0.064	1.04	78.3 ± 13.5
Ni	81.1 ± 6.8	74.7	92.3 ± 20.1
K	10560 ± 0.049	9939.3	94.2 ± 17.6
Rb	51 ± 1.5	47	92.2 ± 7.3
Na	4240 ± 60	4336.4	102.7 ± 9.3
Sr	215 ± 17	219.6	102.1 ± 7.4
S	55100 ± 0.36	52889.6	95.9 ± 4.1
Ti	4021 ± 86	3785.9	94.2 ± 11.2
V	127 ± 11	126.8	99.9 ± 11.6
Zn	4800 ± 270	4970.9	103.5 ± 11.6

Table S3. Descriptive statistics of urban station samples measured by PIXE and ICP-MS/MS

Element	Mean µg/m³		Median µg/m³		% BDL		Mean µg/m³		Median µg/m³		% BDL	
	Urban Station PM$_{2.5}$						Urban Station PM$_{2.5-10}$					
	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)
Na	0.0253 ± 0.0259	0.664 ± 0.0505	0.0206	0.0564	21	9	0.0544 ± 0.0544	0.1164 ± 0.1001	0.0406	0.0895	17	1
Mg	0.0459 ± 0.0526	0.1038 ± 0.0869	0.0301	0.0827	17	2	0.1709 ± 0.1709	0.3776 ± 0.2667	0.1319	0.3216	14	0
Al	0.1257 ± 0.1523	0.1931 ± 0.2352	0.0819	0.1319	9	1	0.3802 ± 0.3802	0.5257 ± 0.4178	0.3112	0.422	13	0.3
Si	0.3020 ± 0.3332		0.2023		8		0.9721 ± 0.9721		0.8347		12	
P	0.0077 ± 0.0065		0.0067		25		0.0147 ± 0.0147		0.0132		24	
S	0.5869 ± 0.5395	0.7421 ± 0.6249	0.4543	0.6025	8	1	0.2751 ± 0.2751	0.3896 ± 0.3112	0.2566	0.2929	14	0.3
Cl	0.0190 ± 0.0325		0.0159		12		0.1101 ± 0.1101		0.0814		13	
K	0.0920 ± 0.0915	0.1031 ± 0.0798	0.0727	0.0927	11	8	0.2048 ± 0.2048	0.1433 ± 0.1286	0.1812	0.1065	15	7
Ca	0.3817 ± 0.3429	0.2614 ± 0.3041	0.3426	0.2105	4	2	1.9201 ± 1.9201	1.2765 ± 0.9839	1.7343	1.0392	8	0
Ti	0.0125 ± 0.0134	0.0112 ± 0.0124	0.0102	0.00792	10	9	0.0363 ± 0.0363	0.0303 ± 0.0226	0.0244	0.0314	17	0.3
V	0.0021 ± 0.0021	0.0022 ± 0.0020	0.0014	0.00164	13	0.3	0.0036 ± 0.0036	0.0035 ± 0.0032	0.00269	0.0024	14	0
Cr	0.0021 ± 0.0012	0.0045 ± 0.0045	0.0020	0.00329	41	0.3	0.0039 ± 0.0039	0.0042 ± 0.0020	0.0037	0.0039	43	0
Mn	0.0029 ± 0.0025	0.0031 ± 0.0027	0.0026	0.00237	11	1	0.0078 ± 0.0078	0.0073 ± 0.0055	0.0067	0.00599	13	0
Fe	0.1384 ± 0.1322	0.1564 ± 0.1384	0.1214	0.1192	17	1	0.3884 ± 0.3884	0.3595 ± 0.2567	0.3255	0.3081	16	0

N = number of samples
BDL = below detection limit

Table S3 (Continued). Descriptive statistics of urban station samples measured by PIXE and ICP-MS/MS

Element	Urban Station $PM_{2.5}$ Mean µg/m³ PIXE (N = 141)	ICP-MS/MS (N = 300)	Median µg/m³ PIXE (N = 141)	ICP-MS/MS (N = 300)	% BDL PIXE (N = 141)	ICP-MS/MS (N = 300)	Urban Station $PM_{2.5-10}$ Mean µg/m³	PIXE (N = 141)	Median µg/m³ ICP-MS/MS (N = 300)	PIXE (N = 141)	% BDL PIXE (N = 141)	ICP-MS/MS (N = 300)
Ni	0.0021 ± 0.0015	0.0021 ± 0.0023	0.0020	0.0015	6	1	0.0041 ± 0.0041	0.0035 ± 0.0042	0.004	0.0029	12	1
Cu	0.0016 ± 0.0010	0.0016 ± 0.0022	0.0016	0.0011	6	35	0.0028 ± 0.0028	0.0024 ± 0.0046	0.0025	0.0015	8	26
Zn	0.0185 ± 0.0111	0.0175 ± 0.0182	0.0175	0.0131	0	2	0.0226 ± 0.0226	0.0141 ± 0.0129	0.0214	0.0104	0	2
As	0.0007 ± 0.0008	0.0015 ± 0.0016	0.0005	0.0011	29	1	0.0006 ± 0.0006	0.0013 ± 0.0013	0.0004	0.0009	40	1
Se	0.0004 ± 0.0003	0.0003 ± 0.0004	0.0003	0.0003	29	34	0.0002 ± 0.0002	0.0002 ± 0.0002	0.0002	0.0001	58	89
Br	0.0026 ± 0.0017	0.0031 ± 0.0045	0.0025	0.0017	10	59	0.0014 ± 0.0014	0.0057 ± 0.0076	0.001	0.0039	19	60
Rb	0.0004 ± 0.0005	0.0004 ± 0.0004	0.0002	0.0004	46	2	0.0007 ± 0.0007	0.0009 ± 0.0006	0.0005	0.0007	31	0
Sr	0.0006 ± 0.0006	0.0014 ± 0.0016	0.0005	0.0009	24	2	0.0020 ± 0.0020	0.0037 ± 0.0030	0.0017	0.0029	19	0.3
Y	0.0002 ± 0.0002		0.0001		72		0.0004 ± 0.0004		0.0003		61	
Zr	0.0007 ± 0.0008	0.0020 ± 0.0037	0.0005	0.0009	31	33	0.0012 ± 0.0012	0.0022 ± 0.0024	0.001	0.0018	29	1
Mo	0.0002 ± 0.0003	0.0002 ± 0.0002	0.0001	0.0002	83	4	0.0002 ± 0.0002	0.0002 ± 0.0001	0.0002	0.0002	77	7
Pb	0.0060 ± 0.0115	0.0093 ±0.0355	0.0034	0.0039	17	4	0.0060 ± 0.0060	0.0082 ± 0.0210	0.0035	0.0023	23	26

N = number of samples
BDL = below detection limit

Table S4. Descriptive statistics of rural station samples measured by PIXE and ICP-MS/MS

Element	Rural Station PM$_{2.5}$						Rural Station PM$_{2.5-10}$					
	Mean µg/m³		Median µg/m³		% BDL		Mean µg/m³		Median µg/m³		% BDL	
	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)
Na	0.0223 ± 0.0243	0.0524 ± 0.0624	0.0146	0.0362	22	12	0.0376 ± 0.0643	0.1109 ± 0.1115	0.0406	0.0759	22	5
Mg	0.0383 ± 0.0562	0.075 ± 0.1038	0.0244	0.05	16	6	0.0736 ± 0.0704	0.2174 ± 0.1748	0.1319	0.1828	13	1
Al	0.1462 ± 0.2742	0.1739 ± 0.2642	0.0601	0.0984	9	1	0.2119 ± 0.2410	0.4042 ± 0.4215	0.3112	0.2706	11	1
Si	0.3444 ± 0.5472	0.0658 ± 0.0722	0.1865		6		0.5346 ± 0.5541		0.8347		9	
P	0.0089 ± 0.0061		0.0086		21		0.0086 ± 0.0067		0.0132		20	
S	0.6658 ± 0.5816	0.6824 ± 0.5656	0.5508	0.0477	6	22	0.1284 ± 0.1163	0.1809 ± 0.1367	0.2566	0.1442	9	0.3
Cl	0.0151 ± 0.0096		0.0149		10		0.0674 ± 0.1392		0.0814		10	
K	0.0842 ± 0.0998		0.0565	0.0697	9		0.0976 ± 0.1031	0.1017 ± 0.1114	0.1812	0.0718	9	24
Ca	0.1804 ± 0.2531	0.1208 ± 0.1642	0.1103	0.00694	3	2	0.5886 ± 0.5343	0.3666 ± 0.3456	1.7343	0.2753	5	2
Ti	0.0130 ± 0.0190	0.0118 ± 0.0165	0.0064	0.5586	13	12	0.0242 ± 0.0246	0.0234+0.0220	0.0168	0.0314	11	3
V	0.0011 ± 0.0009	0.0009 ± 0.0007	0.0008	0.00066	19	14	0.0013 ± 0.0012	0.00128 ± 0.0009	0.0024	0.0010	10	0
Cr	0.0024 ± 0.0015	0.0047 ± 0.0069	0.0022	0.00374	61	2	0.0038 ± 0.0028	0.00605 ± 0.0046	0.0037	0.0049	60	15
Mn	0.0044 ± 0.0077	0.0031 ± 0.0045	0.0022	0.00192	11	2	0.0056 ± 0.0066	0.00574 ± 0.0049	0.0067	0.0043	9	1
Fe	0.1514 ± 0.1774	0.1378 ± 0.1592	0.0915	0.0929	20	1	0.2671 ± 0.2318	0.2986 ± 0.2695	0.3255	0.2263	12	1

N = number of samples
BDL = below detection limit

Table S4 (continued). Descriptive statistics of rural station samples measured by PIXE and ICP-MS/MS

Element	Rural Station PM$_{2.5}$ Mean µg/m³		Median µg/m³		% BDL		Rural Station PM$_{2.5-10}$ Mean µg/m³		Median µg/m³		% BDL	
	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)	PIXE (N = 141)	ICP-MS/MS (N = 300)
Ni	0.0027 ± 0.0022	0.0024 ± 0.0022	0.0020	0.00167	4	16	0.0045 ± 0.0048	0.0043 ± 0.0049	0.0040	0.00267	8	14
Cu	0.0011 ± 0.0007	0.0031 ± 0.0163	0.0010	0.00081	5	67	0.0014 ± 0.0043	0.0021 ± 0.0082	0.0025	0.00047	9	81
Zn	0.0187 ± 0.0101	0.0155 ± 0.0494	0.0176	0.00712	0	31	0.0146 ± 0.0088	0.0086 ± 0.0215	0.0214	0.00503	0	14
As	0.0005 ± 0.0005	0.0008 ± 0.0007	0.0003	0.00057	30	2	0.0004 ± 0.0004	0.0007 ± 0.0006	0.0004	0.0005	44	1
Se	0.0002 ± 0.0002	0.0001 ± 0.0001	0.0002	0.00011	49	59	0.0001 ± 0.0001	0.0004 ± 0.0003	0.0002	0.00013	80	98
Br	0.0020 ± 0.0013	0.0048 ± 0.0037	0.0020	0.00388	6	53	0.0005 ± 0.0005	0.0043 ± 0.0136	0.0010	0.00147	47	78
Rb	0.0003 ± 0.0004	0.0003 ± 0.0003	0.0001	0.00017	56	4	0.0006 ± 0.0008	0.0005 ± 0.0005	0.0005	0.00036	35	2
Sr	0.0006 ± 0.0008	0.0010 ± 0.0015	0.0003	0.00059	35	1	0.0010 ± 0.0011	0.0023 ± 0.0026	0.0017	0.00157	21	1
Y	0.0002 ± 0.0001		0.0001		82		0.0002 ± 0.0001		0.0003		75	
Zr	0.0004 ± 0.0004	0.0025 ± 0.0031	0.0003	0.0016	45	55	0.0006 ± 0.0006	0.0017 ± 0.0019	0.0010	0.00106	35	12
Mo	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001	0.000095	88	35	0.0002 ± 0.0001	0.0002 ± 0.0005	0.0002	0.00009	81	14
Pb	0.0023 ± 0.0022	0.0021 ± 0.0038	0.0146	0.00135	30	23	0.0017 ± 0.0020	0.0018 ± 0.0053	0.0035	0.00065	42	78

N = number of samples
BDL = below detection limit

Table S5. Calculated MDLs, LODs and total uncertainties for PIXE method

ELEMENT	MDL (μg m^{-3})	LOD (μg m^{-3})	Total uncertainty (%)
Na	5.0×10^{-3}	6.9×10^{-1}	5-20
Mg	4.0×10^{-3}	5.5×10^{-1}	5-20
Al	3.0×10^{-3}	4.2×10^{-1}	5-20
S	1.3×10^{-3}	6.2×10^{-1}	5-20
K	4.0×10^{-5}	5.5×10^{-1}	5-20
Ca	4.0×10^{-4}	5.5×10^{-1}	5-20
Ti	9.0×10^{-6}	1.3×10^{-1}	5-20
V	8.0×10^{-6}	1.1×10^{-1}	5-20
Cr	5.0×10^{-6}	6.9×10^{-2}	5-20
Mn	4.0×10^{-6}	5.5×10^{-2}	5-20
Fe	3.0×10^{-4}	4.2×10^{-2}	5-20
Ni	1.0×10^{-4}	1.4×10^{-2}	5-20
Cu	9.0×10^{-5}	1.3×10^{-2}	5-20
Zn	8.0×10^{-5}	1.1×10^{-2}	5-20
As	2.0×10^{-6}	2.8×10^{-2}	5-20
Se	9.0×10^{-6}	1.3×10^{-2}	5-20
Br	8.0×10^{-5}	1.1×10^{-2}	5-20
Rb	4.0×10^{-4}	5.5×10^{-2}	5-20
Sr	2.0×10^{-5}	2.8×10^{-2}	5-20
Mo	1.5×10^{-4}	2.1×10^{-1}	5-20
Pb	2.0×10^{-3}	6.9×10^{-1}	5-20

MDL: Method detection limit
LOD: Limit of determination
Average sampling volume = 825 m³

Table S6. Calculated MDLs, LODs and total uncertainties for ICP-MS/MS

Elements	MDL ($\mu g\ m^{-3}$)	LOD ($ng\ mL^{-1}$)	Total uncertainty (%)
Na	4.8×10^{-5}	40	9%
Mg	1.3×10^{-5}	11	9.2%
Al	7.6×10^{-6}	6.25	6.6%
S	8.5×10^{-5}	70.25	6.7%
K	6.9×10^{-5}	57.25	6%
Ca	1.3×10^{-5}	11	2%
Ti	5.1×10^{-6}	4.25	1.2%
V	4.2×10^{-7}	0.35	9.6%
Cr	5.5×10^{-7}	0.45	3.6%
Mn	6.7×10^{-7}	0.55	1.2%
Fe	2.1×10^{-5}	0.69	9%
Ni	4.8×10^{-7}	17.25	7%
Cu	7.0×10^{-6}	0.40	0.2%
Zn	2.9×10^{-6}	5.75	5%
As	6.0×10^{-8}	2.38	8%
Se	1.2×10^{-6}	0.05	8.8%
Br	2.5×10^{-5}	1.03	8%
Rb	3.9×10^{-7}	20.25	2%
Sr	2.4×10^{-7}	0.20	5%
Mo	2.0×10^{-6}	1.73	6%
Pb	5.8×10^{-6}	4.75	9%

LOD: Limit of determination
MDL: Method detection limit
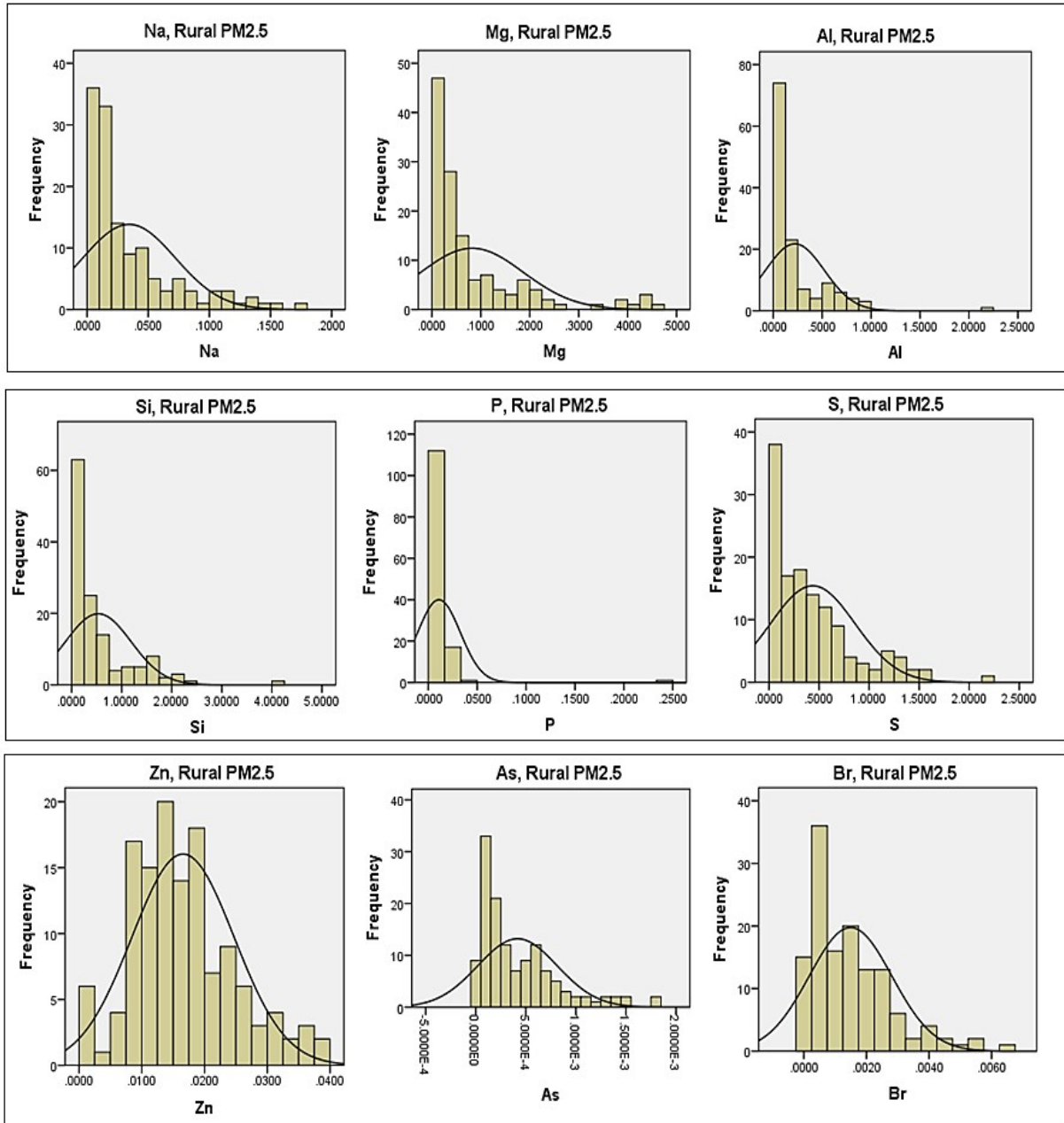*Average sampling volume = 825 m³*

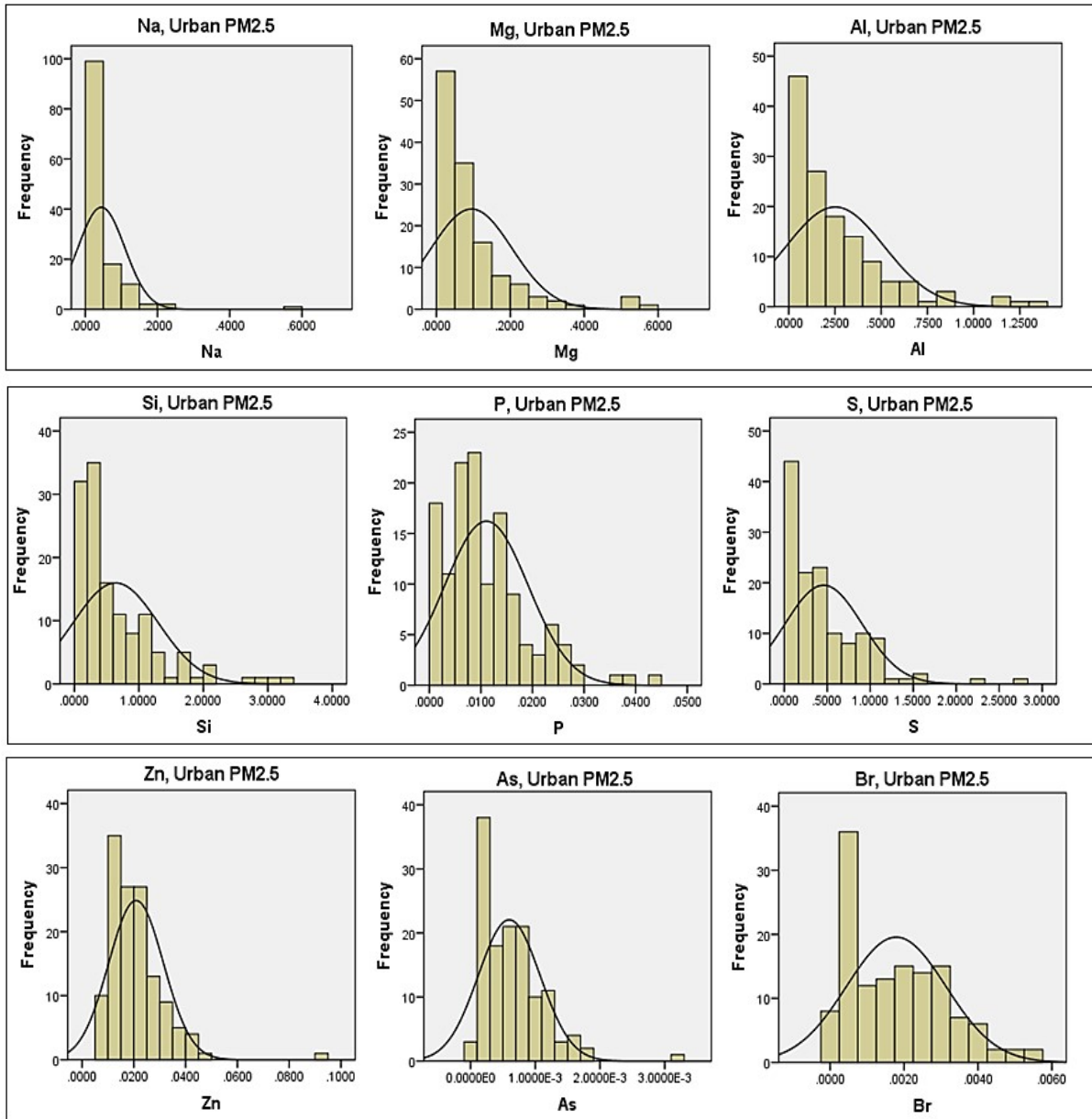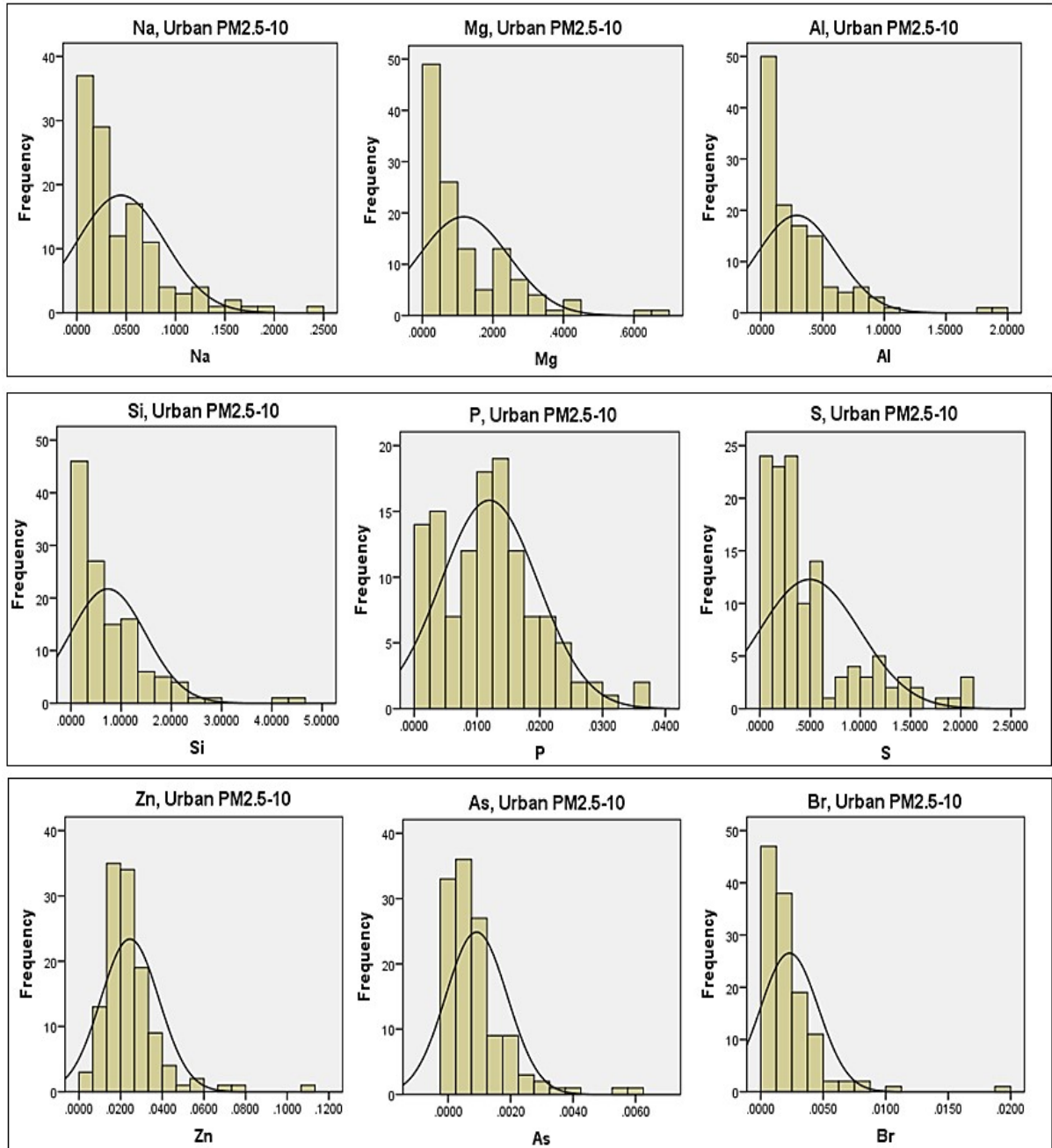**Figure S1.** Distribution of selected crustal and anthropogenic source elements in rural-fine PM

Figure S2. Distribution of selected crustal and anthropogenic source elements in urban-fine PM

Figure S3. Distribution of selected crustal and anthropogenic source elements in urban-coarse PM