Supplementary Materials:

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Table S1.1. Limits of detection (LODs) of the concentrations (µg/L) detected in river water samples of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations.

	UoM	LODs
Ba	µg/L	1.6
Cd	µg/L	0.0088
Cr	µg/L	0.24
Cs	µg/L	0.0095
Cu	µg/L	0.15
Fe	µg/L	1.8
Li	µg/L	0.011
Mn	µg/L	0.11
Mo	µg/L	0.99
Ni	µg/L	0.14
Pb	µg/L	0.02
Rb	µg/L	0.026
Sb	µg/L	0.0094
Sn	µg/L	0.043
Sr	µg/L	0.7
Ti	µg/L	0.079

Table S1.2. Limits of detection (LODs) of the concentrations (µg/L) detected in PM_{10} samples, of the water-soluble and insoluble fraction of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations.

	UoM	LODs Water-soluble Fraction	LODs Insoluble Fraction
Ba	µg/L	3.7	0.44
Cd	µg/L	0.0038	0.0031
Cr	µg/L	0.081	0.86
Cs	µg/L	0.0033	0.0017
Cu	µg/L	0.2	0.24
Fe	µg/L	3	9.6
Li	µg/L	0.0063	0.004
Mn	µg/L	0.17	0.17
Mo	µg/L	0.049	0.012
Ni	µg/L	0.35	0.17
Pb	µg/L	0.1	0.15
Rb	µg/L	0.031	0.023
Sb	µg/L	0.0094	0.0094
Sn	µg/L	0.013	0.027
Sr	µg/L	0.2	0.57
Ti	µg/L	0.15	0.4

Table S1.3. Limits of detection (LODs) of the concentrations (µg/L) detected in washed and unwashed *A. donax* leaves of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations.

	UoM	LODs *A. donax* leaves
Ba	µg/L	6.7
Cd	µg/L	0.33
Cr	µg/L	0.22
Cs	µg/L	0.0021
Cu	µg/L	0.12
Fe	µg/L	30

Li	µg/L	0.014
Mn	µg/L	1.1
Mo	µg/L	0.13
Ni	µg/L	0.18
Pb	µg/L	0.059
Rb	µg/L	0.028
Sb	µg/L	0.011
Sn	µg/L	0.019
Sr	µg/L	0.63
Ti	µg/L	0.47

Table S2.1. Average mean (AM) values and standard deviations of element concentrations detected in unwashed *A. donax* leaves at the six monitoring sites.

***A. donax* unwashed leaves element concentrations**													
		TE1		**TE2**		**TE3**		**TE4**		**TE5**		**TE6**	
	UoM	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**
Ba	ng/mg	13	3.3	5	1.9	16	4.2	16	4.3	32	8.6	47	15
Cd	ng/mg	0.26	0.1	1.6	0.53	3.4	0.94	1.6	0.47	3.9	1.4	0.26	0.069
Cr	ng/mg	1.2	0.38	1.6	0.42	1.6	0.4	2.2	0.47	6.2	2.1	6.6	1.8
Cs	ng/mg	0.18	0.061	0.23	0.074	0.2	0.063	0.078	0.028	0.071	0.023	0.031	0.011
Cu	ng/mg	5.7	1.3	6.6	1.4	5.2	1.2	5.1	1.3	8.9	2.2	11	2.5
Fe	ng/mg	125	20	117	11	133	15	110	11	271	28	269	15
Li	ng/mg	0.037	0.011	0.047	0.018	0.053	0.018	0.036	0.0084	0.055	0.014	0.086	0.02
Mn	ng/mg	36	10	26	6.0	15	5.6	51	16	31	11	128	43
Mo	ng/mg	1.2	0.29	0.87	0.14	1.3	0.28	0.94	0.18	3.9	0.41	5.7	0.64
Ni	ng/mg	1.1	0.43	1.8	0.42	1.9	0.63	1.3	0.23	3.4	0.37	4.1	0.81
Pb	ng/mg	0.2	0.063	0.15	0.048	0.18	0.052	0.35	0.12	0.3	0.072	0.33	0.14
Rb	ng/mg	30	8.6	36	11	33	9.2	31	8.8	25	7.2	26	9.5
Sb	ng/mg	0.021	0.0069	0.009	0.003	0.039	0.017	0.01	0.0025	0.009	0.0023	0.024	0.009
Sn	ng/mg	0.053	0.015	0.055	0.018	0.051	0.015	0.06	0.019	0.055	0.015	0.058	0.021
Sr	ng/mg	17	3.5	22	5.0	23	5.0	32	7.4	28	6.7	53	13
Ti	ng/mg	1.8	0.44	1.6	0.34	1.5	0.4	1.7	0.75	2.7	0.58	3.8	0.4

Table S2.2. Average mean (AM) values and standard deviations (SD) of element concentrations detected in washed *A. donax* leaves at the 6 monitoring sites.

***A. donax* washed leaves element concentrations**													
		TE1		**TE2**		**TE3**		**TE4**		**TE5**		**TE6**	
	UoM	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**
Ba	ng/mg	5.3	1.4	5.4	1.8	5.3	1.4	16	4.2	31	8.3	46	15
Cd	ng/mg	0.26	0.1	1.1	0.39	3.3	0.92	1.6	0.46	3.8	1.4	0.26	0.068
Cr	ng/mg	0.75	0.23	0.92	0.24	0.84	0.21	1.4	0.31	2.3	0.59	1.7	0.49
Cs	ng/mg	0.16	0.055	0.21	0.069	0.16	0.051	0.078	0.027	0.069	0.023	0.022	0.0075
Cu	ng/mg	5.2	1.2	6.5	1.4	5.1	1.2	4.5	1.2	7.4	1.8	8.7	1.9
Fe	ng/mg	109	27	100	18	74	8	103	20	199	20	188	20
Li	ng/mg	0.026	0.0079	0.029	0.011	0.03	0.01	0.033	0.0077	0.045	0.012	0.062	0.014
Mn	ng/mg	35	10	24	5.6	14	5	48	15	27	9.1	121	40
Mo	ng/mg	1.2	0.27	0.74	0.12	1.2	0.27	0.88	0.17	3.1	0.67	5.6	0.59
Ni	ng/mg	1.1	0.4	1.6	0.38	1.8	0.58	1.2	0.22	2.5	0.27	2.1	0.33
Pb	ng/mg	0.14	0.043	0.047	0.015	0.18	0.051	0.13	0.048	0.29	0.071	0.25	0.1
Rb	ng/mg	29	8.4	36	11	34	9	30	8.6	25	7.1	25	9.3
Sb	ng/mg	0.02	0.0067	0.009	0.003	0.0089	0.0039	0.0093	0.0024	0.0092	0.0023	0.0089	0.0034

Sn	ng/mg	0.016	0.0043	0.015	0.0048	0.017	0.0044	0.048	0.015	0.017	0.0043	0.016	0.0055
Sr	ng/mg	16	3.2	18	4.2	15	3.3	31	7.2	27	6.5	52	13
Ti	ng/mg	1	0.25	1.2	0.26	0.87	0.23	1.5	0.67	1.2	0.17	1.6	0.18

Table S2.3. Average mean (AM) values and standard deviations of element concentrations detected in river water samples at the six monitoring sites.

		River water element concentrations											
		TE1		**TE2**		**TE3**		**TE4**		**TE5**		**TE6**	
	UoM	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**
Ba	µg/l	96	11,2	66	5,3	71	6,0	60	4,3	95	11	86	9,0
Cd	µg/l	0,012	0,00057	0,013	0,00065	0,019	0,0014	0,033	0,0042	0,036	0,0050	0,034	0,0044
Cr	µg/l	0,84	0,022	1,56	0,077	1,61	0,082	0,53	0,0089	28	5,4	0,30	0,0028
Cs	µg/l	0,15	0,016	0,14	0,014	0,20	0,028	0,10	0,0068	0,24	0,038	0,11	0,0077
Cu	µg/l	1,4	0,19	0,84	0,065	1,4	0,18	0,93	0,079	2,15	0,42	1,28	0,15
Fe	µg/l	1,2	0,068	1,9	0,16	1,9	0,16	1,9	0,17	16	2,8	1,9	0,17
Li	µg/l	6,3	1,1	4,9	0,65	7,2	1,4	5,4	0,79	7,9	0,87	4,7	0,6
Mn	µg/l	0,12	0,014	0,13	0,014	0,13	0,014	0,057	0,0028	0,14	0,016	0,12	0,013
Mo	µg/l	5,2	0,59	5,2	0,59	7,8	1,3	3,6	0,28	39	4,6	2,0	0,087
Ni	µg/l	7,1	0,83	5,2	0,45	9,4	1,5	4,2	0,29	23	4,2	4,9	0,39
Pb	µg/l	0,14	0,017	0,035	0,0029	0,053	0,0066	0,037	0,0032	0,029	0,0019	0,037	0,0032
Rb	µg/l	3,3	0,56	1,7	0,15	2,3	0,27	1,8	0,16	2,6	0,35	2,0	0,20
Sb	µg/l	0,094	0,016	0,055	0,0054	0,091	0,015	0,051	0,0047	0,19	0,026	0,055	0,0055
Sn	µg/l	0,20	0,028	0,23	0,030	0,0094	0,00020	0,012	0,00035	0,024	0,0013	0,053	0,0064
Sr	µg/l	978	172	859	133	1084	211	904	147	986	175	900	146
Ti	µg/l	1,8	0,22	1,6	0,15	1,9	0,22	1,5	0,15	3,2	0,32	1,5	0,15

Table S2.4. OK (ordinary kriging) interpolated concentrations of water-soluble fraction of atmospheric elements at the six monitoring sites.

Water-soluble interpolated atmospheric element concentrations							
	UoM	**TE1**	**TE2**	**TE3**	**TE4**	**TE5**	**TE6**
Ba	ng/m^3	6.1	4.7	4.1	4.7	5.3	4.8
Cd	ng/m^3	0.03	0.047	0.052	0.032	0.039	0.05
Cr	ng/m^3	0.88	1.3	2	1.1	1.9	1.9
Cs	ng/m^3	0.012	0.017	0.017	0.015	0.015	0.016
Cu	ng/m^3	2.5	2.6	2.7	1.5	2.5	1.9
Fe	ng/m^3	9.8	11	10	7.5	9.9	12
Li	ng/m^3	0.059	0.088	0.12	0.085	0.11	0.12
Mn	ng/m^3	4.2	4.3	2.6	3.8	4.8	5.6
Mo	ng/m^3	2.3	3.0	2.4	4.8	14	11
Ni	ng/m^3	0.92	0.81	1.2	0.68	1.1	1.7
Pb	ng/m^3	0.32	0.41	0.42	0.4	0.29	0.36
Rb	ng/m^3	0.34	0.43	0.4	0.3	0.36	0.37
Sb	ng/m^3	0.45	0.35	0.26	0.51	0.31	0.29
Sn	ng/m^3	0.25	0.16	0.18	0.15	0.16	0.17
Sr	ng/m^3	1.7	2.1	1.4	1.7	1.9	1.8
Ti	ng/m^3	0.08	0.091	0.12	0.089	0.1	0.13

Table S2.5. OK (ordinary kriging) interpolated concentrations of insoluble fraction of atmospheric elements at the six monitoring sites.

Insoluble interpolated atmospheric element concentrations							
	UoM	**TE1**	**TE2**	**TE3**	**TE4**	**TE5**	**TE6**
Ba	ng/m^3	7.3	6.9	4.9	6.2	6.5	4
Cd	ng/m^3	0.006	0.022	0.016	0.021	0.025	0.026
Cr	ng/m^3	13	14	30	12	45	48
Cs	ng/m^3	0.021	0.03	0.035	0.025	0.031	0.032
Cu	ng/m^3	8.9	7.3	9.3	4.7	11	6.6
Fe	ng/m^3	351	344	577	218	332	504
Li	ng/m^3	0.12	0.1	0.15	0.087	0.15	0.1
Mn	ng/m^3	6.3	7.1	3.5	5.3	11	14
Mo	ng/m^3	0.8	1.3	1.4	0.96	2.1	4.1
Ni	ng/m^3	4.8	6.3	4.3	3.4	19	23
Pb	ng/m^3	3	3.3	4.6	3	4.5	3.4
Rb	ng/m^3	0.45	0.32	0.43	0.16	0.44	0.3
Sb	ng/m^3	0.66	0.4	0.3	0.64	0.73	0.25
Sn	ng/m^3	2	1.7	2.1	0.85	2.3	1
Sr	ng/m^3	1.2	1.4	1	2.4	2.3	1.3
Ti	ng/m^3	4.5	4.3	7.1	3.6	7.1	8

Table S2.6. Mean values and standard deviations calculated between monthly values of interpolated concentrations of the total fraction of PM_{10} elements at the six monitoring sites.

Total interpolated PM_{10} element concentrations													
		TE1		**TE2**		**TE3**		**TE4**		**TE5**		**TE6**	
	UoM	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**
Ba	ng/m^3	13	0.87	12	1.2	9.0	1.3	11	0.90	12	0.82	8.8	1.1
Cd	ng/m^3	0.036	0.0029	0.069	0.0073	0.068	0.0041	0.054	0.0021	0.063	0.0055	0.076	0.0065
Cr	ng/m^3	14	0.45	15	1.1	32	0.98	13	2.1	47	4.0	49	4.4
Cs	ng/m^3	0.033	0.0065	0.047	0.010	0.052	0.0090	0.041	0.011	0.046	0.0093	0.048	0.011
Cu	ng/m^3	11	0.74	9.9	0.18	12	0.093002	6.1	0.25	13	0.39	8.5	0.41
Fe	ng/m^3	361	14	355	24	588	19	226	31	343	47	514	62
Li	ng/m^3	0.18	0.0099	0.19	0.022	0.27	0.015001	0.17	0.036	0.26	0.034	0.23	0.047
Mn	ng/m^3	11	0.25	11	0.63	6.1	0.076	9.1	1.0	16	1.3	20	1.1
Mo	ng/m^3	3.1	0.11	4.3	0.14	3.8	0.34	5.8	1.2	15	1.5	16	1.1
Ni	ng/m^3	5.7	0.45	7.1	0.57	5.5	0.24	4.1	1.3	20	1.2	24	2.5
Pb	ng/m^3	3.3	0.16	3.7	0.12	5.1	0.093	3.4	0.37	4.8	0.27	3.9	0.59
Rb	ng/m^3	0.79	0.074	0.76	0.082	0.83	0.045	0.46	0.070	0.80	0.056	0.67	0.084
Sb	ng/m^3	1.1	0.014	0.75	0.0042	0.57	0.0057	1.2	0.070	1.0	0.044	0.54	0.062
Sn	ng/m^3	2.3	0.082	1.8	0.14	2.3	0.14	1.0	0.085	2.4	0.094	1.2	0.12
Sr	ng/m^3	2.9	0.28	3.5	0.47	2.4	0.19	4.1	0.44	4.2	0.51	3.1	0.44
Ti	ng/m^3	4.6	0.12	4.4	0.48	7.2	0.44	3.7	0.41	7.2	0.41	8.1	0.72

Table S3. Certified values for the SRM 1515 (apple leaves) used and accuracy obtained by SRM (ng mg^{-1}).

Apple leaves SRM 1515					
		Certified value		Accuracy obtained	
	UoM	Mean	Std Dev	Mean	Std Dev
Ba	ng/mg	49	2	41	0.98
Cd	ng/mg	0.013	0.002	0.014	0.001
Cr	ng/mg	0.3*	-	0.36	0.07
Cu	ng/mg	5.6	0.24	5.8	0.25
Fe	ng/mg	83	5	99	0.4
Mn	ng/mg	54	3	57	0.83
Mo	ng/mg	0.095*	-	0.11	0.03
Ni	ng/mg	0.91	0.12	1.2	0.3
Pb	ng/mg	0.47	0.024	0.51	0.08
Rb	ng/mg	10	0.82	9.3	0.21
Sb	ng/mg	0.013*	-	0.016	0.003
Sn	ng/mg	0.2*	-	0.32	0.04
Sr	ng/mg	25	3	28.7	0.2

* = values of these elements have to be considered as informative concentrations.

Figure S1. SEM micrograph (a) and respective EDX spectrum (b) of a steel particle (Fe, Ni and Cu) sampled near the steel plant.

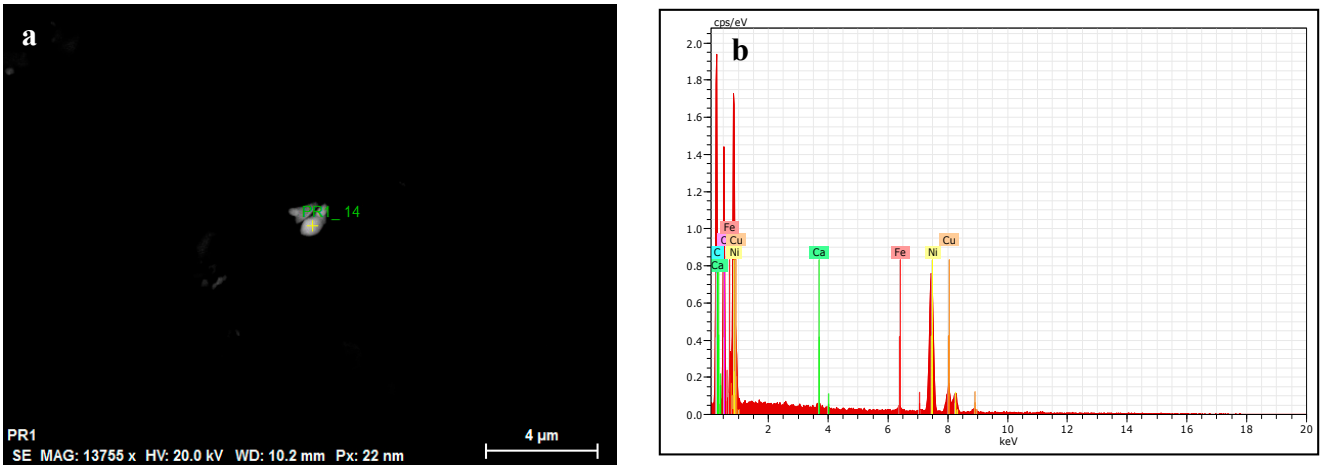

Table S1.1: limits of detection (LODs) of the concentrations (µg/L) detected in river water samples of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations, Table S1.2: limits of detection (LODs) of the concentrations (µg/L) detected in PM_{10} samples, of the water-soluble and insoluble fraction of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations, Table S1.3: limits of detection (LODs) of the concentrations (µg/L) detected in washed and unwashed *A. donax* leaves of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations, Table S2.1: mean values and standard deviations calculated between monthly values of element concentrations detected in unwashed *A. donax* leaves at the six monitoring sites, Table S2.2: mean values and standard deviations calculated between monthly values of element concentrations detected in washed *A. donax* leaves at the 6 monitoring sites, Table S2.3: mean values and standard deviations calculated between monthly values of element concentrations detected in river water samples at the six monitoring sites, Table S2.4: mean values and standard deviations calculated between monthly values of interpolated concentrations of water-soluble fraction

of PM_{10} elements at the six monitoring sites, Table S2.5: mean values and standard deviations calculated between monthly values of interpolated concentrations of insoluble fraction of PM_{10} elements at the six monitoring sites, Table S2.6: mean values and standard deviations calculated between monthly values of interpolated concentrations of the total fraction of PM_{10} elements at the six monitoring sites, Table S3: Certified values for the SRM 1515 (apple leaves) used and accuracy obtained by SRM (ng mg^{-1}). Figure S1: SEM micrograph (a) and respective EDX spectrum (b) of a steel particle (Fe, Ni and Cu) sampled near the steel plant.