

Supporting Information

Metal ion release from fine particulate matter sampled in the Po Valley to an aqueous solution mimicking fog water: kinetics and solubility

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Table S1: values of PM_{2.5} on each filter (given by ARPAV).

Filter (sample)	day	PM_{2.5} Mandria-PD (µg/m³)
1	22/01/18	46.0
2	23/01/18	56.7
3	24/01/18	78.7
4	25/01/18	98.0
5	26/01/18	93.0
6	29/01/18	48.7
7	30/01/18	47.3
8	31/01/18	50.0
9	05/02/18	31.0
10	08/02/18	52.7
11	09/02/18	42.3
12	13/02/18	27.3
13	14/02/18	43.3
14	15/02/18	64.3
15	16/02/18	78.0
16	19/02/18	22.0
17	20/02/18	29.7
18	21/02/18	26.7

Table S2: values of environmental parameters measured by ARPAV in the same days as those of the 18 samples of Table 1S. Columns represent the concentrations of CO, NO, NO₂, NO_x, O₃ and PM10, atmospheric pressure (*P*), solar radiation (rad), rain, average outdoor temperature (*T*), relative humidity (RH), wind speed (w.s.), wind main direction (w.d.), and mixing layer height (m.l.h.).

day	CO (mg/m ³)	NO (µg/m ³)	NO ₂ (µg/m ³)	NO _x (µg/m ³)	O ₃ (µg/m ³)	PM10 (µg/m ³)	<i>P</i> (mbar)	rad (W/m ²)	rain (mm)	<i>T</i> (°C)	RH (%)	w.s. (m/s)	w.d. ^(*) (sect)	m.l.h. (m)
22/01/18	0.54	63.4	62.8	160	9.30	55.0	1010	78.9	0.00	3.83	79.4	0.70	180	108
23/01/18	0.93	102	66.1	222	8.18	65.7	1020	77.9	0.00	3.08	84.6	0.63	129	144
24/01/18	0.93	131	71.7	272	8.96	85.7	1030	81.5	0.00	3.83	86.3	0.44	218	180
25/01/18	0.89	98.4	70.8	222	2.13	110	1020	26.3	0.00	4.08	92.1	0.52	190	74.5
26/01/18	0.97	90.5	60.7	199	4.43	108	1020	37.2	0.00	4.50	92.8	0.65	160	132
29/01/18	0.61	36.7	54.3	111	1.65	73.0	1030	20.8	0.00	3.71	100	0.48	187	56.2
30/01/18	0.55	22.2	44.1	78.6	3.35	64.7	1020	11.8	0.00	4.88	98.7	0.66	200	86.0
31/01/18	0.53	33.9	45.7	97.4	1.57	59.3	1010	16.6	0.00	5.63	98.5	0.58	132	126
05/02/18	0.46	33.4	53.9	105	17.8	32.0	1020	74.7	0.00	4.71	72.3	1.69	104	361
08/02/18	0.65	53.1	54.3	136	3.13	63.0	1010	56.9	0.00	6.04	92.5	0.51	205	177
09/02/18	0.67	57.0	49.1	136	12.1	50.3	1010	60.5	0.00	4.63	91.3	0.63	259	289
13/02/18	0.49	26.7	47.7	88.8	19.3	31.0	1010	86.9	0.00	2.17	77.9	0.92	175	250
14/02/18	0.63	68.1	58.7	163	19.4	51.0	1010	124	0.00	1.63	77.9	0.71	159	331
15/02/18	0.76	86.8	71.4	205	9.00	74.0	1020	78.3	0.00	1.50	80.6	0.52	184	225
16/02/18	0.82	80.3	68.6	192	7.57	87.7	1020	91.4	0.00	2.58	82.3	0.60	210	146
19/02/18	0.29	3.70	34.7	40.4	39.2	25.0	1010	75.6	0.00	2.92	68.1	2.19	154	452
20/02/18	0.47	14.0	44.9	66.6	23.2	33.3	1010	45.9	0.00	3.29	70.4	1.53	105	221
21/02/18	0.39	10.7	34.1	50.6	35.8	30.3	1000	41.0	0.00	4.79	67.4	2.63	87.4	443

(*) sector of main wind direction according to ARPAV maps



Figure S1: filter-holder used during the kinetic/solubility measurements.

Table S3: Instrumental limit of detection (LOD, $\mu\text{g/L}$) and limit of quantification (LOQ, $\mu\text{g/L}$) for each element obtained by ICP-MS analysis.

element	LOD	LOQ
Al	0.58	1.93
As	0.76	2.53
Ba	0.18	0.60
Ca	2.70	9.00
Cd	0.03	0.10
Cr	0.06	0.20
Cu	0.25	0.83
Fe	0.45	1.50
K	40.8	136
Mg	2.45	8.17
Mn	0.11	0.37
Mo	0.03	0.10
Na	34.1	114
Ni	0.35	1.17
Pb	0.04	0.13
Rb	0.16	0.53
Sb	0.07	0.23
Sr	0.08	0.27
V	0.02	0.07
W	0.19	0.63
Zn	75.3	251

Table S4: Kinetic constants k (min^{-1}) obtained for each element and all 18 samples for which a marked kinetic behaviour was observed. The corresponding standard deviations, computed from the fitting, are given in brackets.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Al					0.008 (0.012)		0.067 (0.055)	0.002 (0.015)	0.036 (0.024)	0.041 (0.014)			0.0172 (0.0067)	0.0175 (0.0077)			0.0206 (0.0071)	
As																		
Ba				0.027 (0.018)				0.0353 (0.0095)	0.0252 (0.0073)	0.0245 (0.0088)	0.0113 (0.0034)		0.038 (0.010)	0.0317 (0.0070)	0.0191 (0.0077)		0.0181 (0.0037)	0.0165 (0.0064)
Cd		0.066 (0.030)		0.0150 (0.0083)				0.228 (0.040)	0.049 (0.023)	0.0222 (0.0099)	0.036 (0.011)		0.0236 (0.0050)	0.0525 (0.0090)	0.0128 (0.0076)		0.050 (0.022)	0.0240 (0.0092)
Cr											0.016 (0.010)	0.060 (0.035)	0.0062 (0.0032)	0.0094 (0.0028)	0.0055 (0.0045)		0.0076 (0.0037)	0.0066 (0.0097)
Cu			0.0145 (0.0067)			0.034 (0.036)		0.0160 (0.0097)	0.025 (0.010)	0.0232 (0.0085)			0.025 (0.012)	0.0195 (0.0048)	0.0040 (0.0036)	0.033 (0.013)		
Fe						0.0058 (0.0072)				0.019 (0.013)	0.0237 (0.0069)	0.202 (0.082)	0.0230 (0.0074)	0.031 (0.011)	0.056 (0.011)			0.0052 (0.0035)
K	0.032 (0.014)	0.044 (0.011)		0.89 (0.26)	0.0235 (0.0061)			0.249 (0.027)		0.0475 (0.0078)	0.191 (0.047)		0.135 (0.028)	0.0566 (0.0063)	0.098 (0.029)	0.029 (0.021)	0.043 (0.019)	0.077 (0.018)
Mn		0.056 (0.017)	0.145 (0.041)		0.0155 (0.0098)	0.271 (0.068)	0.040 (0.010)	0.175 (0.050)	0.32 (0.18)	0.0277 (0.0050)	0.0275 (0.0073)		0.0286 (0.0066)	0.0289 (0.0047)	0.051 (0.017)	0.0144 (0.0091)	0.0127 (0.0043)	0.0213 (0.0052)
Mo	0.0127 (0.0073)	0.0216 (0.0037)		0.040 (0.012)	0.023 (0.016)	0.7 (2.3)	0.047 (0.013)	0.188 (0.071)		0.0132 (0.0038)	0.027 (0.011)	0.0172 (0.0030)	0.0374 (0.0083)	0.0295 (0.0038)	0.0232 (0.0047)	0.067 (0.021)	0.0350 (0.0074)	0.0329 (0.0097)
Pb																		
Rb	0.046 (0.014)	0.065 (0.013)	0.122 (0.079)	0.059 (0.029)	0.0235 (0.0071)	0.221 (0.078)		0.264 (0.039)		0.172 (0.054)			0.045 (0.030)	0.048 (0.014)		0.089 (0.065)		0.323 (0.055)
Sb		0.0089 (0.0083)			0.0121 (0.0068)		0.0254 (0.0041)	0.157 (0.023)		0.0100 (0.0026)	0.0132 (0.0026)	0.0122 (0.0051)	0.0194 (0.0021)39	0.0077 (0.0021)	0.0279 (0.0059)		0.0343 (0.0055)	
Sr			0.035 (0.014)	0.036 (0.030)		0.050 (0.019)		0.002 (0.012)		0.0215 (0.0090)	0.0046 (0.0029)		0.0090 (0.0036)	0.0182 (0.0074)	0.0128 (0.0099)	0.0084 (0.0046)		0.0118 (0.0033)
V	0.061 (0.022)	0.0123 (0.0051)	0.060 (0.021)		0.022 (0.014)			0.348 (0.041)	0.024 (0.022)	0.0367 (0.0048)	0.0070 (0.0030)		0.0522 (0.0097)	0.0307 (0.0055)	0.039 (0.016)	0.0285 (0.0094)	0.0338 (0.0085)	0.0298 (0.0083)
W																		
Zn																		

Table S5: Concentration values (ng/m³) obtained for each element and all samples after PM dissolution in hot diluted (3.45 %) HNO₃. Uncertainties were of the order of 5%.

elem.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Al	54.0*	27.0	26.4	28.6	20.0	18.3	17.0	20.4	20.6	19.5	21.5	22.6	24.1	38.9	29.1	23.1	43.6*	23.6
As	0.570	0.621	0.797	0.965	1.10	1.12	0.642	0.912	0.381	0.614	0.573	0.429	0.547	0.750	0.899	0.451	0.450	0.364
Ba	9.82	7.22	7.17	7.90	6.86	5.21	3.89	5.86	5.42	4.83	5.82	4.20	5.61	8.46	7.22	3.14	3.76	2.81
Cd	0.322	0.290	0.322	0.527	0.438	0.385	0.262	0.491	0.250	0.335	0.656	0.149	0.318	0.422	0.490	0.144	0.197	0.127
Cr	8.22*	2.88	3.01	3.81	2.45	2.81	2.12	3.11	1.96	2.61	2.42	1.62	2.07	3.14	2.71	1.93	1.69	1.27
Cu	21.2	14.8	17.2	19.2	13.7	15.2	7.98	11.4	8.47	10.8	11.2	6.56	11.0	16.9	18.8	4.58	7.74	5.19
Fe	395	280	293	381	299	254	147	221	160	212	249	131	239	326	345	95.8	158	128
K	841	787	793	1398*	1162	930	566	722	517	494	714	389	687	803	1059	224	499	247
Mn	13.5	11.6	11.0	18.0	12.9	38.4*	5.78	9.41	5.29	10.5	7.50	4.91	6.94	13.4	11.6	2.98	4.84	4.28
Mo	2.93	8.00*	4.02	3.89	1.78	2.35	1.32	2.12	0.802	1.48	1.09	2.17	1.24	3.33	2.98	0.391	0.643	0.569
Pb	9.43	6.66	10.8	14.1	10.4	15.3	6.60	9.29	3.31	7.68	4.58	3.10	4.34	6.79	9.23	3.53	4.53	3.66
Rb	2.11	2.00	1.89	3.45*	2.92	2.23	1.31	1.67	1.29	1.21	1.79	0.936	1.74	2.09	2.68	0.558	1.25	0.600
Sb	3.36	1.77	2.46	4.00	3.63	2.11	1.74	4.37*	1.20	2.01	2.74	1.07	2.07	1.84	2.30	0.963	2.54	0.861
Sr	1.04*	1.15*	0.594	0.934	0.671	0.463	0.396	0.538	0.482	0.506	0.532	0.456	0.507	0.721	0.634	0.320	0.447	0.409
V	2.07	1.34	1.35	1.63	1.73	0.641	0.595	1.51	0.354	1.61	0.969	0.336	0.391	0.703	0.636	0.188	0.233	0.225
W	0.090	0.146	0.152	0.220*	0.100	0.098	0.078	0.124	0.063	0.117	0.074	0.046	0.063	0.115	0.115	<LOD	0.061	0.043
Zn	88.8	71.5	75.3	118	81.3	177*	50.1	80.3	76.5	71.9	46.9	33.4	47.6	75.7	78.8	28.0	67.8	29.8

*Suspected outliers according to Tukey's rule