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/m$^3$) |
|-----------------|----------|----------------------------------|
| 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, NOx, 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/m³) | NO (µg/m³) | NO₂ (µg/m³) | NOx (µg/m³) | O₃ (µg/m³) | PM10 (µg/m³) | \(P\) (mbar) | rad (W/m²) | rain (mm) | \(T\) (°C) | RH (%) | w.s. (m/s) | w.d. (°) | 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        | 76.6       | 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, µg/L) and limit of quantification (LOQ, µg/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 | 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) |
| Ba | 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) |
| Cd | 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) | 0.0005 (0.0025) |
| Cu | 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) | 0.0005 (0.0025) |
| Fe | 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) | 0.0566 (0.0063) | 0.098 (0.029) | 0.029 (0.021) | 0.043 (0.019) | 0.077 (0.018) |
| K  | 0.056 (0.017) | 0.145 (0.041) | 0.155 (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) |
| Mn | 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 (0.0047) | 0.0232 (0.001) | 0.067 (0.021) | 0.0350 (0.0074) | 0.0329 (0.0097) |
| Mo | 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) |
| Pb | 0.0089 (0.0083) | 0.0121 (0.0068) | 0.0254 (0.0041) | 0.157 (0.025) | 0.0100 (0.0026) | 0.0132 (0.0026) | 0.0122 (0.0051) | 0.0194 (0.0021) | 0.0279 (0.0059) | 0.0343 (0.0055) |
| Rb | 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) |
| Sr | 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) |
| V  | 0.0089 (0.0083) | 0.0121 (0.0068) | 0.0254 (0.0041) | 0.157 (0.025) | 0.0100 (0.0026) | 0.0132 (0.0026) | 0.0122 (0.0051) | 0.0194 (0.0021) | 0.0279 (0.0059) | 0.0343 (0.0055) |
| W  | 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) |
| Zn | 0.0089 (0.0083) | 0.0121 (0.0068) | 0.0254 (0.0041) | 0.157 (0.025) | 0.0100 (0.0026) | 0.0132 (0.0026) | 0.0122 (0.0051) | 0.0194 (0.0021) | 0.0279 (0.0059) | 0.0343 (0.0055) |
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 | 1.79 | 0.936 | 1.74 | 2.09 | 2.68 | 0.558 | 1.25 | 0.600 |
| Sb    | 3.56 | 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