

# 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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## Abstract

Metals are among the key aerosol components exerting adverse health effects. Their toxic properties may vary depending on their chemical form and solubility, which can be affected by aqueous processing during aerosol atmospheric lifetime. In this work, fine particulate matter (PM<sub>2.5</sub>) was collected in the city centre of Padua in the Po Valley (Italy), during a winter campaign. Part of the sampling filters were used to measure the kinetics by which metal ions and other elements can leach from PM<sub>2.5</sub> to an aqueous solution mimicking fog water in the winter in temperate climate regions (pH 4.7, 5 °C). The leaching process was interpreted by a first order kinetics, and the fitting of the experimental data allowed to obtain the leaching kinetic constants and the equilibrium concentrations (*i.e.* at infinite time) for all elements. The remaining filter parts were mineralised, through two subsequent extraction steps, and the extracts were analysed by ICP-MS to gain the total elemental content of PM for a large number of elements. We found that elements can leach from PM with half times generally between 10-40 minutes, which is a timescale compatible with atmospheric aqueous processing during fog events. For instance, aluminium in PM<sub>2.5</sub> dissolved with an average  $k = 0.0185 \text{ min}^{-1}$ , and  $t_{1/2} = 37.5 \text{ min}$ . Nevertheless, a fraction of the elements was immediately solubilised after contact with the extraction solution suggesting that metal ion solubilisation may already had started during particle lifetime in the atmosphere.

## Keywords

Metals; PM<sub>2.5</sub>; fog; leaching kinetics; urban air quality; ICP-MS

## 31 **Introduction**

32 Particulate matter (PM), and especially its fine fraction (PM<sub>2.5</sub>), existing in the atmosphere is  
33 considered to cause severe and different toxic effects on humans, including respiratory (Kowalska et  
34 al., 2019) and cardiovascular diseases (Du et al., 2019), nephrotoxicity (Hsu et al., 2005), diabetes (Lao  
35 et al., 2019), fetal distress in pregnant women (Liu et al., 2019), allergy (Dedele et al., 2019), autism  
36 (Kaufman et al., 2019), decreased fertility (Xia et al., 2019), and cancer (Santibáñez-Andrade et al.,  
37 2017). Eye irritation, dry throat, runny nose, sneezing, cough, tiredness, irritability, difficulty  
38 concentrating, headache, dizziness, and skin irritation are other less serious, indeed annoying side  
39 effects of human exposure to PM (Nezis et al., 2019).

40 Metal ions, non-metallic anions, and their inorganic derivatives (oxides, salts, etc.) are among the PM  
41 constituents (Brito et al., 2018; Meng et al., 2013; Popoola et al., 2018) which are considered to be co-  
42 responsible of PM toxicity, likely because of the oxidative stress which several chemical species may  
43 induce in cellular tissues (Liu et al., 2018; Meng et al., 2013; Yang et al., 2019). If PM is in contact  
44 with environmental or physiological solutions, the substances contained in the particles may be  
45 released, thus becoming bio-accessible and potentially toxic to living organisms and human tissues. For  
46 this reason, a very large number of papers have been or are being published in which the release of  
47 selected elements from PM to simulated physiological fluids was investigated (Benetello et al., 2018;  
48 Berlinger et al., 2019; Catalani et al., 2018; Dehghani et al., 2018; Du et al., 2019; Gao et al., 2018;  
49 Hernández-Pellón et al., 2019, 2018; Huang et al., 2018; Kastury et al., 2018b, 2018a; Luo et al., 2019;  
50 Nie et al., 2018; Pelfrêne and Douay, 2018; Tang et al., 2019; Wiseman et al., 2018; Xing et al., 2019).  
51 For a list of older references see the review by Mukhtar and Limbeck (2013). In these literature studies,  
52 the elemental solubility at equilibrium has been obtained. Solubilities depended on the element, on the  
53 season, on which species were loaded on the particle, on the distance of the sampling site from the  
54 element source, on the PM size, on the solution pH, and on pre-existing components in aqueous  
55 solution (Benetello et al., 2018; Dehghani et al., 2018; Gao et al., 2018; Hernández-Pellón et al., 2019,  
56 2018; Kastury et al., 2018a, 2018b; Pelfrêne and Douay, 2018; Xie et al., 2019; Xing et al., 2019).

57 Another information which has been sought in the literature, even if much less often than equilibrium  
58 solubility, was the kinetics of the solubilisation process (Armiento et al., 2013; Desboeufs et al., 2005,  
59 1999; Dufka and Dočekal, 2018; Hsu et al., 2005; Huang et al., 2016; Joshi et al., 2009). The rate by  
60 which a given element is released from the PM can be as relevant as the solubility at equilibrium,  
61 because this data would allow to model also the timing of the releasing process, especially when the  
62 contact between PM and aqueous phase does not last for long times. Very different kinetic results were  
63 reported: for example, leaching was found to be complete in timescales spanning from few minutes to 2  
64 h (*e.g.* (Desboeufs et al., 2005, 1999; Hsu et al., 2005)), but other authors found that some elements  
65 reached equilibrium only after several hours (Huang et al., 2016; Joshi et al., 2009) or even few days

66 (Armiento et al., 2013). The release kinetics was shown to be affected by solution pH (Desboeufs et al.,  
67 2005, 1999) and in general it is expected to depend on the same factors affecting equilibrium solubility,  
68 so that no general conclusions can be drawn about any element. Indeed, kinetic data reported in the  
69 literature are still scarce, and studies on this matter should lead to a better knowledge of the complex  
70 phenomena occurring when PM is in contact with an aqueous phase.

71 In this paper, the kinetics of the elemental release from PM<sub>2.5</sub> samples into a simulated fog water was  
72 investigated in order to study how the aqueous processing affects the solubility of the elements during  
73 aerosol lifetime in the atmosphere. The PM was collected during a winter season in the Po Valley  
74 (northern Italy), which is characterised by a significant air pollution during winter because it is an  
75 intensely urbanised area surrounded by complex orography. To the best of our knowledge, for the Po  
76 Valley no kinetic study of elemental release from PM has been hitherto performed. Whereas most of  
77 the above mentioned literature focused on kinetic measurements in physiological fluids or marine  
78 water, leaching experiments were here performed in an aqueous solution (with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> at pH  
79 = 4.7) and at a temperature (5 °C) which better resemble the typical winter environmental conditions of  
80 humid, foggy or rainy days in temperate climate regions including the Po Valley. The study was  
81 extended to as many elements as possible, and solubility and PM total element content were obtained as  
82 well. The latter was performed by using a two-step ICP-MS-based analytical procedure with the aim to  
83 detect also elements present at very low concentration.

## 85 **Experimental**

### 86 **Chemicals**

87 The reagents used were hydrochloric acid (Aldrich 37%), sulphuric acid (95-97%, Fluka), nitric acid  
88 (68.5-69.5%, Aristar for trace analysis, VWR), zinc acetate dihydrate (99.5% min, Riedel de Haën),  
89 methanol (99.9%, VWR), EDTA disodic salt (Carlo Erba), ammonium nitrate (99% min, Merck),  
90 ammonia (30-33%, Sigma Aldrich), eriochrome black T (EBT, Sigma Aldrich), sodium chloride  
91 (99.5% min, Analar Normapur), Rhenium standard for ICP (1001±5 mg/L, 2% HNO<sub>3</sub>, Sigma Aldrich),  
92 Germanium standard for ICP (1005±2 mg/L, 2% HNO<sub>3</sub>, Sigma Aldrich), Terbium standard for ICP  
93 (1002±5 mg/L, 2% HNO<sub>3</sub>, Sigma Aldrich), calibrating standard solution CCS-5 for ICP (100.00±0.70  
94 µg/mL of B, Ge, Hf, Mo, Nb, P, Re, S, Sb, Si, Sn, Ta, Ti, W, Zr, 1.2% (v/v) HF + 7.43% (v/v) HNO<sub>3</sub>,  
95 Inorganic Ventures), and calibrating standard solution IV-ICPMS-71A (10±0.08 µg/mL of Ag, Al, As,  
96 B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P,  
97 Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, Zn, Inorganic Ventures). HCl was distilled to 6 M  
98 prior use. All solutions were prepared and diluted using ultrapure water obtained with a Millipore Plus  
99 System (Milan, Italy, resistivity 18.2 Ω cm<sup>-1</sup>).

## 100 **Instrumentation and Procedure**

101 The teflon filters (PALL, fiberfilm, Ø 47 mm, 2.0 µm pore size) were conditioned for 24 h inside a Q-  
102 Box3 Momo Line box at  $20 \pm 1$  °C and at  $50 \pm 5\%$  relative humidity, and then they were loaded on a  
103 Aircube He pump equipped with a PM<sub>2.5</sub> certified selector (CEN standard method UNI-EN 14907).  
104 PM<sub>2.5</sub> sampling was performed on each filter for 24 h (from 9am to 9am of the following day) at a  
105 constant flow rate of 2.3 m<sup>3</sup>/h. The sampling campaign was performed from the 22<sup>th</sup> January to the 21<sup>th</sup>  
106 February 2018, and 18 filters have been collected. The exact sampling days are reported in Table 1S  
107 (Supporting information). Sampling (outdoor) location was the sixth floor of the Department of  
108 Chemical Sciences, which is close to the city centre of Padua (Italy). Additional details about the  
109 sampling facility can be found elsewhere (Giorio et al., 2013). The amounts of PM<sub>2.5</sub> collected in all  
110 sampling days are reported in Table 1S; these values were obtained from the Agency for Environmental  
111 Protection in the Veneto Region (ARPAV, <http://www.arpa.veneto.it/>), which performs daily  
112 measurements to evaluate air quality in Padua and in other cities. Among all ARPAV sampling sites,  
113 results from "PD-Mandria" were considered, as this site is the closest to the Department of Chemical  
114 Sciences. The other environmental parameters measured by ARPAV during the same sampling days  
115 (pollutant concentrations and weather-related values) are reported in Table 2S.

116 At the end of the sampling time, each filter was cut into two parts (3/4 and 1/4). The first part was used  
117 to perform kinetic and equilibrium solubility measurements, and the second one was used to determine  
118 the elemental total content. After PM sampling and before subsequent measurements, filters were  
119 stored in the refrigerator (−18 °C).

### 120 *Kinetic and equilibrium solubility measurements*

121 A glass filter holder was built to perform kinetic/solubility measurements (Figure 1S in the Supporting  
122 Information). It comprises a *ca.* 15 cm long haft, and a *ca.* 5 cm bride and 1 cm tall cylinder. The lower  
123 part of the cylinder is folded to allow the insertion of the filter and avoid its accidental removal once  
124 the experiment is started. The lateral part of the cylinder has eight holes to allow the leaching  
125 substances to quickly dissolve within the bulk solution. The filter holder was put in the fridge (4 °C)  
126 before use to assure that it would not heat the 5 °C solution once immersed.

127 The solvent used for the leaching experiments was a  $5.3 \cdot 10^{-6}$  M H<sub>2</sub>SO<sub>4</sub> solution containing also 10  
128 µg/L of internal standards for ICP-MS (<sup>72</sup>Ge, <sup>159</sup>Tb, <sup>183</sup>Re) and  $9.4 \cdot 10^{-6}$  M HNO<sub>3</sub>, and it had a  
129 computed pH equal to 4.7. For each experiment, the solvent (100 mL) was loaded into a water-jacketed  
130 cell (Metrohm) having a volume capacity of 150 mL. A constant stirring (200 rpm) and temperature  
131 ( $5.0 \pm 0.1$  °C) were set and maintained by a magnetic stirrer and a Haake F3 cryostat, respectively. A  
132 3/4 piece of filter was loaded in the holder and inserted in the cell: this moment represented time = 0  
133 for kinetic experiments. Twenty-two samples withdrawals (3 mL each, representing the minimum

134 volume requirement for ICP-MS analysis) were performed at the following times (min): 0, 2, 4, 6, 8,  
135 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 45, 60, 90, 120, 240, 360. The starting volume was chosen to  
136 assure that the filter remained immersed in the solvent till the last withdrawal was performed. Each  
137 withdrawn sample was transferred to 15 mL Falcon tubes, previously washed with *ca.* 0.01 M HCl (2  
138 mL), rinsed with water and left dry. Tubes were added with conc. HNO<sub>3</sub> (150 μL) to obtain a matrix  
139 (3.45% w/w HNO<sub>3</sub>) which was similar to the standard solutions and best suitable for the ICP-MS  
140 analysis. The tubes were closed and kept in the fridge ( $T = 4\text{ }^{\circ}\text{C}$ ) until analysis via ICP-MS. The cell  
141 and the filter holder were washed with conc. HNO<sub>3</sub> and then rinsed with water after each experiment.

142 A check test was performed to confirm that the leaching elements were able to diffuse enough from the  
143 filter holder, thus avoiding erroneous results due to inhomogeneous solutions. Test (blank) filters  
144 loaded with a *ca.* 1 M zinc acetate solution (few droplets) prepared in methanol and left dry under  
145 vacuum for some hours at 100 °C were used. 10 sample withdrawals (6 mL each) were performed  
146 every 1 min from the cell. Each test sample was transferred to 15 mL Falcon tubes, added with  
147 ammonium/ammonia buffer (1 mL) at pH 10 (0.509 g NH<sub>4</sub>NO<sub>3</sub> + 2.070 g NH<sub>3</sub> dissolved in 5 mL  
148 water) and with the indicator (*ca.* 0.1 g, taken from a mixture of 0.05 g EBT + 10 g NaCl) and titrated  
149 with 0.02 M EDTA. The equivalence volume of EDTA became identical for all test solutions starting  
150 from the 2 min withdrawal, which therefore was considered to be both the homogenisation timing and  
151 the time resolution of the kinetic measurements.

152 Blanks were collected after *ca.* 1 h stirring from tests in which *a)* only the solvent, *b)* the solvent and  
153 the filter holder, *c)* the solvent, the filter holder and a conditioned filter, were inserted in the cell. These  
154 blanks were then analysed by ICP-MS. Other two blanks containing either 0.01 M HCl or 150 μL  
155 HNO<sub>3</sub> in 3 mL water were also analysed. These blanks evidenced significant contaminations for a few  
156 elements due to the procedure (see below).

#### 157 *Measurements of total elemental content*

158 For each of the 18 filters (1/4 pieces), the total elemental content was determined by two subsequent  
159 analytical steps. In the first step, each filter was put in a 15 mL Falcon tube and added with 3.45% w/w  
160 HNO<sub>3</sub> (3 mL) containing also an internal standard for ICP-MS (<sup>159</sup>Tb 10 μg/L). Tubes were closed and  
161 heated at bain-marie (100 °C) for 2 h. The solutions obtained were removed from the tubes, added with  
162 the three water aliquots (100 μL each) previously used to rinse the filters, and they were subjected to  
163 the ICP-MS analysis. In the second step, each tube containing a filter was added with conc. HNO<sub>3</sub> (3  
164 mL, containing also the internal standards), then it was closed and heated at bain-marie (100 °C) for 1  
165 h. At the end, samples were diluted with water containing also an internal standard for ICP-MS (<sup>72</sup>Ge  
166 10 μg/L) to obtain a 3.45% w/w HNO<sub>3</sub> solutions which were subjected to another ICP-MS analysis.

#### 167 *ICP-MS analysis*

168 The elemental analyser was an ICP-MS Agilent series 7700x (Agilent Technologies International  
169 Japan, Ltd., Tokyo, Japan). The instrumental operating conditions were as follows: radiofrequency  
170 power 1550 W, RF matching 1.8 V, plasma gas (Ar) flow rate 15 L min<sup>-1</sup>, carrier gas (Ar) flow rate  
171 1.05 L min<sup>-1</sup>, He gas flow rate 4.3 mL min<sup>-1</sup>, CeO<sup>+</sup>/Ce<sup>+</sup> = 0.90%, nebuliser type: microflow PFA, spray  
172 chamber type: Scott Double Pass at 2 °C, sample introduction speed 0.1 mL min<sup>-1</sup>, internal diameter of  
173 nickel cone 1.0 mm, internal diameter of skimmer cone 0.5 mm, sampling depth 8.5 mm, dwell  
174 time/mass = 100. The isotopes <sup>72</sup>Ge, <sup>159</sup>Tb, and <sup>183</sup>Re were used as internal standards to monitor the  
175 instrumental drift. Quantification has been performed by means of the external calibration method.  
176 Overall 437 analyses (396 for kinetics/solubility + 36 for total elemental content + 5 blanks) were  
177 performed.

178 It was possible to determine concentration values for the following elements, either only for the total  
179 elemental content, or also for the kinetic/solubility measurements: Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K,  
180 Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sr, V, W, and Zn. The instrumental detection limit (LOD) and  
181 quantification limit (LOQ) for each element were determined as described previously (Badocco et al.,  
182 2015; Roverso et al., 2015), and they are reported in Table 3S. Values for B, Lu, P, Si were excluded  
183 due to anomalies in the calibration graphs (due to high LODs in the case of B, P and Si), whereas  
184 results for Cl and Hg were discarded as they showed strong memory effects. The signals of Au, Be, Br,  
185 Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, I, Ir, La, Li, Nb, Nd, Pd, Pr, Pt, Ru, Se, Sm, Ta, Te, Th, Tl,  
186 Tm, U, Y, Yb, detected in the samples resulted practically identical to those detected in the blanks,  
187 therefore also these elements were not further considered. Ca, Mg, Na, and Ni were not determined due  
188 to contamination of blank filters.

189 The concentration values (in µg/L) obtained by ICP-MS from kinetic/solubility measurements were  
190 corrected to the values which would have been obtained if no volume withdrawal were performed from  
191 the cell. The corrected concentration corresponding to the *x*<sup>th</sup> withdrawal (*c<sub>x</sub>*) was obtained by the  
192 formula:

$$193 \quad c_x = \frac{c_x V_x + \sum_{i=1}^x [c'_i (V_i - V_{i+1})]}{V_0} \quad (1)$$

194 where *V*<sub>0</sub> is the starting volume (0.1 L), *c*'<sub>*i*</sub> is the experimental concentration obtained from the ICP-MS  
195 analysis after the *i*<sup>th</sup> volume withdrawal (1 ≤ *i* ≤ *x*), and *V*<sub>*i*</sub> is the volume of solution after the *i*<sup>th</sup>  
196 withdrawal (*V*<sub>*i*</sub> - *V*<sub>*i*+1</sub> = 3 · 10<sup>-3</sup> L). The first term of the numerator is the mass of element experimentally  
197 contained in the solution, and the summation represents the total amount of element which has been  
198 removed to perform all measurements before the *x*<sup>th</sup> one.

199 Concentrations in air (ng/m<sup>3</sup>) for each element in each individual sample were obtained by calculating  
200 the mass (ng) of each element from the concentration in the extracts adjusted for the portion of filter  
201 analysed and dividing it by the volume of sampled air (m<sup>3</sup>). The soluble concentrations at *t*<sub>∞</sub> were

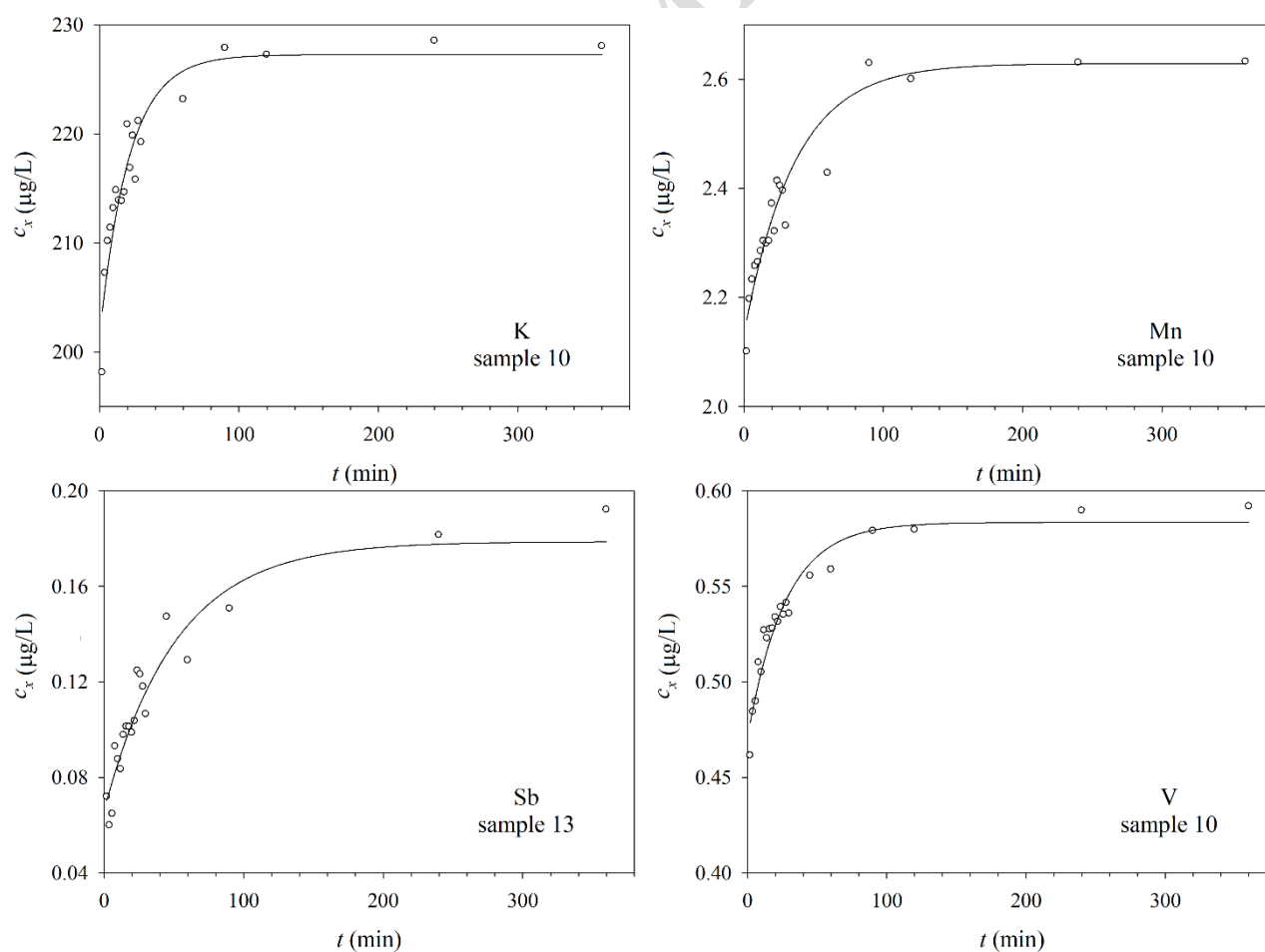
202 estimated by averaging values obtained at  $t > 60$  mins in the kinetic experiments, when a plateau  
203 concentration was reached. The soluble fraction was then calculated by dividing the soluble  
204 concentration at  $t_{\infty}$  by the total concentration of the element in each individual sample.

### 205 *Statistical analysis*

206 Correlation tests have been performed in R (v 3.4.1) by using the Spearman method (Field et al., 2012).  
207 A correlation was considered significant if the computed  $p$ -value was below 0.05. Final data reported in  
208 the tables were checked for outliers using the Tukey's rule.

## 211 **Results and discussion**

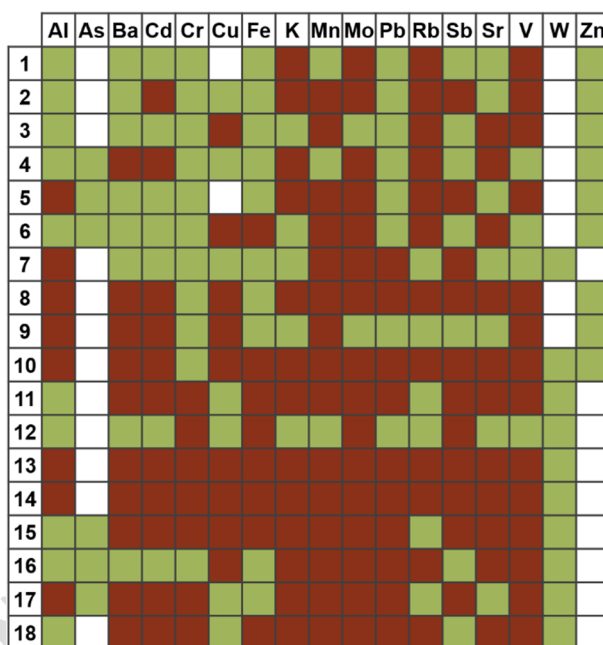
212 Some of the concentration-time profiles obtained during the kinetic experiments are shown in Figure 1.  
213 Generally, the elemental concentrations clearly increased over time, indicating that a leaching was  
214 occurring. According to our data, leaching appeared generally to stop after 1-2 hours; data was  
215 prudentially collected till 6 h, and in few cases (in particular for Sb, see Figure 1) some further leaching  
216 was observed. Data collection was in any case ended after 6 h. For some of the analysed elements,  
217 observed concentrations were below the LOQ and no kinetic data could be obtained.



219

220 **Figure 1. Experimental points and fitting lines (equation 3) obtained in the kinetic measurements of**  
 221 **elemental release from PM<sub>2.5</sub>.**  
 222

223 The occurrence of a time-dependent leaching was investigated for each element in each sample by  
 224 performing Spearman correlation tests: if *p*-value was below 0.05, it meant that the concentration for  
 225 the given element in the examined sample was varying significantly over time. Spearman correlation,  
 226 better than the more common Pearson one, is robust against outliers and is able to show correlations  
 227 also when the variables are not related linearly (Field et al., 2012), as it is the case in this work. Results  
 228 from the Spearman tests are given in Figure 2, which shows for each element which samples gave *p*-  
 229 values below 0.05, which samples gave *p*-values above 0.05, and which samples had concentration  
 230 below the LOQ.



232 **Figure 2. Diagram showing in which of the 18 samples element concentration was significantly (*p*-value <**  
 233 **0.05) varying over time according to the Spearman test (brown), non-significantly (*p*-value ≥ 0.05) varying over time**  
 234 **(green), or below LOQ (white).**  
 235  
 236

237 Even for elements which showed marked kinetic behaviours, kinetically non-significant concentration  
 238 changes (*p*-value ≥ 0.05) were determined in a few samples. This result can be partly explained by  
 239 noisy data, which, in some cases, has probably caused *p*-values being larger than 0.05. It was decided  
 240 to evaluate the kinetics for elements for which the concentration changes were significant in at least six  
 241 samples.

242 Unexpected results were obtained for Pb, for which concentrations were decreasing over time rather  
 243 than increasing. To the best of our knowledge, this behaviour was never described in literature. As a  
 244 tentative explanation, it can be hypothesised that Pb was very rapidly released from PM once in contact  
 245 with an aqueous solution, and then it reacted with other species released from the PM itself or



246 contained in the solvent, forming insoluble products which cannot be detected by the ICP-MS analysis.  
 247 For example,  $\text{Pb}^{2+}$  can form insoluble precipitates with several anions, such as halogenides, cyanide,  
 248 sulphate, etc.

249 The kinetic data obtained during the experiments can be fitted by a suitable equation. Some of the  
 250 previous papers regarding leaching kinetics from PM did not treat their data, but they only verified the  
 251 leaching times (Armiento et al., 2013; Hsu et al., 2005) or showed the applicability of a new method  
 252 (diffusive gradients in thin film) for the analysis of PM (Dufka and Dočekal, 2018). In the other papers,  
 253 it was considered that the leaching rate determining step was the solubilisation from the PM surface, so  
 254 that a first order kinetic law should apply (Desboeufs et al., 1999; Huang et al., 2016; Joshi et al.,  
 255 2009). The same hypothesis was made here, and the following differential equation was considered:

$$\frac{dc_x}{dt} = k'(s_0 - rc_x) \quad (2)$$

257 where  $k'$  is the first order kinetic constant, and the term in brackets represents the concentration of the  
 258 given element on the PM surface at time  $t$ , which is equal to the surface concentration at  $t = 0$  ( $s_0$ )  
 259 minus the dissolved amount  $rc_x$  (where  $r$  is a constant which relates surface and solution  
 260 concentrations). By solving equation (2), the integral equation for the first order kinetics is obtained:

$$c_x = c_e - Ae^{-kt} \quad (3)$$

262 where  $A$  is the pre-exponential factor,  $k$  is the kinetic constant ( $k = rk'$ ), and  $c_e$  (defined as  $s/r$ )  
 263 represents the solution concentration at equilibrium ( $t = \infty$ ), *i.e.* the element solubility at the employed  
 264 conditions ( $\text{pH} = 4.7$ ,  $T = 5$  °C). For a summarising purpose, average values of  $k$  and  $t_{1/2}$  have been  
 265 computed for each element, and they have been weighted using the uncertainty values obtained by the  
 266 fitting procedure. Weighted average values of  $k$ , and  $t_{1/2}$  obtained for each element are reported in Table  
 267 1 while  $k$  values for each individual sample are reported in Table 4S.

268

269 **Table 1. Weighted averages of  $k$ , and  $t_{1/2}$  obtained for each element and all samples ( $N$ ) for which a marked**  
 270 **kinetic behaviour was observed. The corresponding standard deviations, computed for the weighted means, are**  
 271 **given in brackets.**

element	$k$ ( $\text{min}^{-1}$ )	$t_{1/2}$ (min)	$N$
Al	0.0185 (0.0036)	37.5 (7.3)	8
As	–	–	–
Ba	0.0192 (0.0019)	36.1 (3.6)	10
Cd	0.0271 (0.0029)	25.6 (2.7)	11
Cr	0.0079 (0.0016)	88 (18)	7
Cu	0.0135 (0.0023)	51.3 (8.7)	9
Fe	0.0143 (0.0025)	48.5 (8.4)	8
K	0.0478 (0.0032)	14.5 (1.0)	13
Mn	0.0247 (0.0020)	28.1 (2.2)	15
Mo	0.0226 (0.0015)	30.7 (2.0)	16

Pb	–	–	10
Rb	0.0463 (0.0050)	15.0 (1.6)	12
Sb	0.0140 (0.0011)	49.5 (4.0)	11
Sr	0.0098 (0.0016)	71 (12)	11
V	0.0218 (0.0019)	31.7 (2.7)	14
W	–	–	–
Zn	–	–	–

272

273 All kinetic constants obtained in this work were of the order of  $10^{-2}$  min. Values for Al, Cr, Sr were  
274 slightly lower than for other elements, whereas values for Cd and Rb were slightly larger. Al, Cr, Sr are  
275 of crustal origin, whereas Cd and Rb are of industrial and vehicular origin, and it is reasonable that the  
276 former elements have a more stable crystalline network, making these elements more refractory to  
277 solubilisation compared with Cd and Rb. This consideration explained solubility values obtained by  
278 Desboeufs et al. (2005), and might explain also the present kinetic results. Joshi et al. (2009) analysed  
279 PM samples collected in Singapore, and they obtained  $k$  values ( $\text{min}^{-1}$ ) in the range  $0.2\text{-}0.6 \cdot 10^{-2}$  for Al,  
280  $0.3\text{-}3 \cdot 10^{-2}$  for Cr,  $0.1\text{-}2 \cdot 10^{-2}$  for Fe,  $0.3\text{-}6 \cdot 10^{-2}$  for Mn, and  $0.3\text{-}4 \cdot 10^{-2}$  for V, which were in line with  
281 those obtained in this work. However, some elements were reported to have a leaching kinetics only in  
282 the present work, and others only in the work of Joshi et al, likely because of the different PM origin  
283 and different leaching solutions used. To the best of our knowledge, no other papers reported kinetic  
284 constants for PM leaching (for example, Desboeufs et al. (2005) reported only leaching rates).  
285 Desboeufs et al. (2005 and 1999) found that the dissolution rate of some elements followed a two-step  
286 process. During the first step the particle was hydrated, the element release was very quick (with a  
287 timing of few minutes), and the rate increased with time. During the second step the rate decreased with  
288 time. For some other elements, conversely, only one step (the second one) was observed. Other studies  
289 observed only a single leaching step for all elements, and the rate was decreasing with time (Armiento  
290 et al., 2013; Joshi et al., 2009). It is worth noting that in the present experiments the values of  $c_x$  at time  
291  $= 0$  were generally larger than zero (Figure 1), thus indicating that part of the elements has leached to  
292 the solution during the very few instants after the PM-water contact. Furthermore, equation (3) was  
293 generally not able to fit experimental data well unless the concentration values at time zero were  
294 excluded from the fitting set. These findings suggest that also in the present case two steps took place  
295 during the leaching experiments, but the first step was very quick and comparable to the time resolution  
296 of the kinetic measurements (*ca.* 2 min); therefore, it could not be detected. The fact that a fraction of  
297 the elements is released immediately after contact with water may indicate that an aqueous phase  
298 processing of the particles had already happened during their atmospheric lifetime either because they  
299 were in a deliquescent state or because of the presence of fog.

Other than  $c_e$ , the total elemental concentration which can dissolve from the PM ( $c_T$ ) was determined for each sample. These measurements have been performed by subjecting the filters to two subsequent digestions: a first one, employing hot diluted (3.45 % w/w)  $HNO_3$ , and a second one in which hot concentrated  $HNO_3$  was used. The latter condition represented a strong acidic and oxidising digestion which is expected to solubilise all elemental species present in PM, whereas the former was a milder procedure which might be non-exhaustive. A milder digestion was performed because the samples obtained in this way did not need any dilution prior to the ICP-MS analysis, thus elements at very low concentrations may be better detected than after a hot acid digestion that requires dilution to 3.45%  $HNO_3$  before analysis. The concentrations obtained after a mild digestion are shown in Table 5S. Values obtained after the two successive procedures, which represent total concentration,  $c_T$ , are reported in Table 2.

311

312 **Table 2. Values of total concentration,  $c_T$  (ng/m<sup>3</sup>), obtained for each element and all 18 samples.**  
 313 **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	107	43.1	40.8	2804*	45.8	106	46.2	1375*	101	42.5	87.2	77.7	48.7	52.0	47.6	69.5	4839*	400
As	0.816	0.833	2.03	1.39	1.33	1.38	0.896	1.26	1.18	1.04	0.886	0.693	0.868	1.10	1.23	1.90	100*	4.68*
Ba	27.0*	8.66	8.49	2409*	8.15	6.32	4.59	9.13	6.87	6.83	7.29	5.48	7.42	10.2	8.54	6.15	60.5*	6.03
Cd	0.327	0.290	0.322	0.675	0.531	0.385	0.262	0.491	0.250	0.335	0.656	0.149	0.318	0.422	0.490	0.194	0.265	0.127
Cr	9.58	4.73	3.99	15.6*	3.68	4.13	2.92	6.32	23.5*	3.47	2.91	2.39	3.47	7.23	4.01	3.90	5.03	2.43
Cu	36.9	30.0	42.2	39.6	76.7*	22.6	14.2	18.7	14.8	19.0	13.9	8.75	23.9	19.7	23.1	8.48	12.3	7.78
Fe	551	329	341	1003*	639	384	172	354	353	250	325	168	352	511	558	568	727	155
K	1186	832	830	1541	1525	941	581	979	527	589	824	392	744	822	1504	305	917	255
Mn	14.6	12.8	11.7	21.5	14.3	40.3*	7.41	10.5	6.19	11.1	7.88	5.19	7.49	14.2	12.6	3.87	9.60	4.47
Mo	3.32	11.0*	4.80	4.59	2.21	2.48	1.36	2.21	0.845	1.48	1.09	2.48	1.32	3.50	3.24	0.435	0.817	0.569
Pb	10.5	13.9	11.6	21.9*	11.1	16.2	6.95	10.7	4.90	9.34	5.21	3.34	5.14	7.96	10.0	9.78	20.7*	4.93
Rb	2.24	2.09	2.05	3.78*	3.02	2.29	1.37	2.05	1.38	1.41	1.96	0.974	1.85	2.18	2.98	0.736	2.42	0.678
Sb	3.76	1.77	2.70	4.48	3.76	2.15	1.74	4.37	1.81	2.10	2.74	1.07	2.07	1.84	2.69	1.40	17.7*	3.43
Sr	1.93	1.90	1.25	14.3*	1.30	1.13	1.05	1.73	1.36	1.40	1.37	1.36	1.54	1.76	2.05	1.70	7.28*	1.69
V	2.15	1.38	1.39	1.69	1.74	0.650	0.616	1.54	0.354	1.66	0.973	0.336	0.437	0.711	0.636	0.201	0.519	0.247
W	0.220	0.276	0.239	0.306	0.187	0.185	0.165	0.211	0.106	0.204	0.117	0.089	0.106	0.159	0.202	0.043	0.191	0.304
Zn	88.8	71.5	75.2	458	274	177	50.1	84.0	126	71.9	46.9	33.4	67.5	121	297	494	349	29.8

314 \*Suspected outliers according to Tukey's rule.

315

316 **Table 3. Median concentrations of elements in sampled air (ng/m<sup>3</sup>) obtained for each element in all samples.**  
 317 **Median values of soluble concentrations at pH = 4.7 and T = 5 °C at  $t_\infty$ , median values of total concentrations**  
 318 **(individual values reported in Table 2), and median % of soluble fraction S at  $t_\infty$  (standard deviations in brackets\*)**  
 319 **are reported. Total concentrations reported by Benetello et al. (2018) (average annual values) and by Armiento et al.**  
 320 **(2013) (range of given values) are also reported here for comparison.**

	Soluble concentration (ng/m <sup>3</sup> ) (this study)	Total concentration (ng/m <sup>3</sup> ) (this study)	$S_{T=\infty}$ (%) (this study)	Total concentration (ng/m <sup>3</sup> ) Benetello et al. (2018)	Total concentration (ng/m <sup>3</sup> ) Armiento et al. (2013)
Al	9.68	73.6	12 (66)	273	
As	< LOD	1.20	28 (28)	0.5	0.33 - 0.81
Ba	2.99	7.79	37 (55)	12	
Cd	0.183	0.325	62 (26)		0.06 - 0.38
Cr	1.60	4.00	26 (65)		1.09 - 2.75
Cu	3.09	19.3	22 (13)	8	8.64 - 22.47
Fe	38.4	354	14 (15)	150	128.9 - 975.2

K	661	827	91 (30)	455	
Mn	4.24	10.8	44 (13)	6	
Mo	0.741	2.21	40 (22)		
Pb	3.19	9.89	39 (30)	9	5.57 - 14.53
Rb	1.58	2.05	88 (19)		
Sb	0.499	2.42	20 (10)	2.2	
Sr	0.848	1.62	41 (113)		
V	0.430	0.681	52 (27)	1.2	
W	0.009	0.189	15 (8)		
Zn	8.61	86.4	102 (80)	40	22.08 - 60.98

\*standard deviations reflect the high sample-to-sample variability

321

322 The comparison between Tables 5S and 2 indicates that most elements solubilised in a complete  
 323 manner (> 90%) also in hot diluted HNO<sub>3</sub> (mild digestion). This solvent thus simultaneously allowed to  
 324 quantitatively solubilise most elements from PM and to measure concentration values close to the  
 325 LOD. Only Al, and only in some samples, was not completely solubilised in diluted HNO<sub>3</sub>; the  
 326 determination of its total amount in PM required a second analytical step with a digestion in  
 327 concentrated HNO<sub>3</sub>.

328 Median values of soluble metal ions and total element content are reported in Table 3.

329 Benetello et al. (2018) analysed the PM<sub>2.5</sub> of Padua sampled in the year 2012-2013: results are given as  
 330 well in Table 3 for comparison. Differences between values from Benetello et al. (2018) and those of  
 331 the present study were very modest. Also results of Armiento et al. (2013) were taken into account for  
 332 comparison; they analysed the PM<sub>2.5</sub> fraction collected in another Italian city (Rome) in the year 2011-  
 333 2012. These values, shown in Table 3, were even more similar to ours than those of Benetello et al.  
 334 (2018). It is also worth noting that in the present work the analysis and detection of more PM elements,  
 335 than in cited papers, was possible thanks to the two-step procedure developed for the ICP-MS analysis  
 336 of the total elemental content.

337 The soluble fractions of the elements which can dissolve at pH = 4.7 and  $T = 5$  °C represent the  
 338 fractions becoming potentially bio-accessible. Fractions ranged between *ca.* 10-20% for Cu, Fe, Sb, up  
 339 to 80-100% for alkali and alkaline earth metal ions, Cd, and Zn (Table 3).

340

### 341 **Conclusions and perspectives**

342 In this work, leaching kinetics and equilibrium solubility were evaluated for elements leaching from  
 343 PM to an environmentally relevant aqueous solution mimicking fog water. A two-step analytical  
 344 procedure allowed also to analyse the total content of a larger number of elements than those generally  
 345 detected in the literature. Equilibrium solubility and total elemental content can allow to evaluate the  
 346 fraction of each element which can solubilise from the PM. The results of our kinetic experiments

347 showed also that a fraction of the elements was immediately released in the aqueous solution (at time =  
348 0), and a slower release following a first-order kinetic took place simultaneously. Kinetic  
349 measurements gave constants of the order of  $10^{-2} \text{ min}^{-1}$ , from which it is calculated that elements can  
350 leach from PM with half times of 10-40 minutes. This timing is compatible with the atmospheric  
351 lifetime of clouds and fogs (Ervens and Volkamer, 2010; Maalick et al., 2016; Xue et al., 2006) and it  
352 should be taken into account if the leaching of elements from PM to atmospheric aqueous phases is  
353 modelled. The fact that a fraction of the elements was released immediately after contact with water  
354 may indicate that an aqueous phase processing of the particles had already happened during their  
355 atmospheric lifetime either because they were in a deliquescent state or because of the presence of fog.  
356 As suggested by Scheinhardt et al. (2013) and Tapparo et al. (2020) this atmospheric aqueous phase  
357 processing may be dependent on particle chemical composition so more studies are now needed to  
358 investigate the underlying mechanisms of atmospheric processing affecting solubilisation kinetics of  
359 metals.

360

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364

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