



## 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(III) 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 each element 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.

### INTRODUCTION

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

Metal ions, non-metallic anions, and their inorganic derivatives (oxides, salts, etc.) are among the PM constituents (Brito *et al.*, 2018; Meng *et al.*, 2013; Popoola *et al.*, 2018) which are considered to be co-responsible for PM toxicity, likely because of the oxidative stress which several chemical

species may induce in cellular tissues (Meng *et al.*, 2013; Liu *et al.*, 2018; Yang *et al.*, 2019). If PM is in contact with environmental or physiological solutions, the substances contained in the particles may be released, thus becoming bio-accessible and potentially toxic to living organisms and human tissues. For this reason, a very large number of papers have been or are being published in which the release of selected elements from PM to simulated physiological fluids was investigated (Benetello *et al.*, 2018; Catalani *et al.*, 2018; Dehghani *et al.*, 2018; Gao *et al.*, 2018; Hernández-Pellón *et al.*, 2018; Huang *et al.*, 2018; Kastury *et al.*, 2018a, b; Nie *et al.*, 2018; Pelfrène and Douay, 2018; Wiseman *et al.*, 2018; Berlinger *et al.*, 2019; Du *et al.*, 2019; Hernández-Pellón *et al.*, 2019; Luo *et al.*, 2019; Tang *et al.*, 2019; Xing *et al.*, 2019). For a list of older references see the review by Mukhtar and Limbeck (2013). In these literature studies, the elemental solubility at equilibrium has been obtained. Solubilities depended on the element, on the season, on which species were loaded on the particle, on the distance of the sampling site from the element source, on the PM size, on the solution pH, and on pre-existing components in aqueous solution (Benetello *et al.*, 2018; Dehghani *et al.*, 2018; Gao *et al.*, 2018; Hernández-Pellón *et al.*, 2018; Kastury *et al.*, 2018a, b; Pelfrène and Douay, 2018; Hernández-Pellón *et al.*, 2019; Xie *et al.*, 2019; Xing *et al.*, 2019).

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Another information which has been sought in the literature, even if much less often than equilibrium solubility, was the kinetics of the solubilisation process (Desboeufs *et al.*, 1999; Desboeufs *et al.*, 2005; Hsu *et al.*, 2005; Joshi *et al.*, 2009; Armiento *et al.*, 2013; Huang *et al.*, 2016; Dufka and Dočekal, 2018). The rate by which a given element is released from the PM can be as relevant as the solubility at equilibrium, because this data would allow to model also the timing of the releasing process, especially when the contact between PM and aqueous phase does not last for long times. Very different kinetic results were reported: for example, leaching was found to be complete in timescales spanning from few minutes to 2 h (e.g., Desboeufs *et al.* (1999, 2005), Hsu *et al.* (2005)), but other authors found that some elements reached equilibrium only after several hours (Joshi *et al.*, 2009; Huang *et al.*, 2016) or even few days (Armiento *et al.*, 2013). The release kinetics was shown to be affected by solution pH (Desboeufs *et al.*, 1999, 2005) and in general it is expected to depend on the same factors affecting equilibrium solubility, so that no general conclusions can be drawn about any element. Indeed, kinetic data reported in the literature are still scarce, and studies on this matter should lead to a better knowledge of the complex phenomena occurring when PM is in contact with an aqueous phase.

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

## EXPERIMENTAL

### Chemicals

The reagents used were hydrochloric acid (Aldrich 37%), sulphuric acid (95–97%, Fluka), nitric acid (68.5–69.5%, Aristar for trace analysis, VWR), zinc acetate dihydrate (99.5% min, Riedel de Haën), methanol (99.9%, VWR), EDTA disodic salt (Carlo Erba), ammonium nitrate (99% min, Merck), ammonia (30–33%, Sigma Aldrich), eriochrome black T (EBT, Sigma Aldrich), sodium chloride (99.5% min, Analar Normapur), Rhenium standard for ICP (1001 ± 5 mg L<sup>-1</sup>, 2% HNO<sub>3</sub>, Sigma Aldrich), Germanium standard for ICP (1005

± 2 mg L<sup>-1</sup>, 2% HNO<sub>3</sub>, Sigma Aldrich), Terbium standard for ICP (1002 ± 5 mg L<sup>-1</sup>, 2% HNO<sub>3</sub>, Sigma Aldrich), calibrating standard solution CCS-5 for ICP (100.00 ± 0.70 µg mL<sup>-1</sup> 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>, Inorganic Ventures), and calibrating standard solution IV-ICPMS-71A (10 ± 0.08 µg mL<sup>-1</sup> of Ag, Al, As, 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, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, Zn, Inorganic Ventures). HCl was distilled to 6 M prior use. All solutions were prepared and diluted using ultrapure water obtained with a Millipore Plus System (Milan, Italy, resistivity 18.2 Ω cm<sup>-1</sup>).

### Instrumentation and Procedure

The teflon filters (PALL, fiberfilm, Ø 47 mm, 2.0 µm pore size) were conditioned for 24 h inside a Q-Box3 Momo Line box at 20 ± 1°C and at 50 ± 5% relative humidity, and then they were loaded on a Aircube He pump equipped with a PM<sub>2.5</sub> certified selector (CEN standard method UNI-EN 14907). PM<sub>2.5</sub> sampling was performed on each filter for 24 h (from 9am to 9am of the following day) at a constant flow rate of 2.3 m<sup>3</sup> h<sup>-1</sup>. The sampling campaign was performed from the 22<sup>th</sup> January to the 21<sup>st</sup> February 2018, and 18 filters have been collected. The exact sampling days are reported in Table S1 (Supporting information). Sampling (outdoor) location was the sixth floor of the Department of Chemical Sciences, which is close to the city centre of Padua (Italy). Additional details about the sampling facility can be found elsewhere (Giorio *et al.*, 2013). The amounts of PM<sub>2.5</sub> collected in all sampling days are reported in Table S1; these values were obtained from the Agency for Environmental Protection in the Veneto Region (ARPAV, <http://www.arpa.veneto.it/>), which performs daily measurements to evaluate air quality in Padua and in other cities. Among all ARPAV sampling sites, results from "PD-Mandria" were considered, as this site is the closest to the Department of Chemical Sciences. The other environmental parameters measured by ARPAV during the same sampling days (pollutant concentrations and weather-related values) are reported in Table S2.

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

### Kinetic and Equilibrium Solubility Measurements

A glass filter holder was built to perform kinetic/solubility measurements (Fig. S1 in the Supporting Information). It comprises a *ca.* 15 cm long haft, and a *ca.* 5 cm wide and 1 cm tall cylinder. The lower part of the cylinder is folded to allow the insertion of the filter and avoid its accidental removal once the experiment is started. The lateral part of the cylinder has eight holes to allow the leaching substances to quickly dissolve within the bulk solution. The filter holder was put in the fridge (4°C) before use to assure that it would not heat the 5°C solution once immersed.

The solvent used for the leaching experiments was a

$5.3 \cdot 10^{-6}$  M  $\text{H}_2\text{SO}_4$  solution containing also  $10 \mu\text{g L}^{-1}$  of internal standards for ICP-MS ( $^{72}\text{Ge}$ ,  $^{159}\text{Tb}$ ,  $^{183}\text{Re}$ ) and  $9.4 \cdot 10^{-6}$  M  $\text{HNO}_3$ , and it had a computed pH equal to 4.7. For each experiment, the solvent (100 mL) was loaded into a water-jacketed cell (Metrohm) having a volume capacity of 150 mL. A constant stirring (200 rpm) and temperature ( $5.0 \pm 0.1^\circ\text{C}$ ) were set and maintained by a magnetic stirrer and a Haake F3 cryostat, respectively. A 3/4 piece of filter was loaded in the holder and inserted in the cell: this moment represented time = 0 for kinetic experiments. Twenty-two samples withdrawals (3 mL each, representing the minimum volume requirement for ICP-MS analysis) were performed at the following times (min): 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 45, 60, 90, 120, 240, 360. The starting volume was chosen to assure that the filter remained immersed in the solvent till the last withdrawal was performed. Each withdrawn sample was transferred to 15 mL Falcon tubes, previously washed with *ca.* 0.01 M HCl (2 mL), rinsed with water and left to dry. Tubes were added with conc.  $\text{HNO}_3$  (150  $\mu\text{L}$ ) to obtain a matrix (3.45% w/w  $\text{HNO}_3$ ) which was similar to the standard solutions and best suitable for the ICP-MS analysis. The tubes were closed and kept in the fridge ( $T = 4^\circ\text{C}$ ) until analysis via ICP-MS. The cell and the filter holder were washed with conc.  $\text{HNO}_3$  and then rinsed with water after each experiment.

A check test was performed to confirm that the leaching elements were able to diffuse enough from the filter holder, thus avoiding erroneous results due to inhomogeneous solutions. Test (blank) filters loaded with a *ca.* 1 M zinc acetate solution (few droplets) prepared in methanol and left to dry under vacuum for some hours at  $100^\circ\text{C}$  were used. 10 sample withdrawals (6 mL each) were performed every 1 min from the cell. Each test sample was transferred to 15 mL Falcon tubes, added with ammonium/ammonia buffer (1 mL) at pH 10 (0.509 g  $\text{NH}_4\text{NO}_3$  + 2.070 g  $\text{NH}_3$  dissolved in 5 mL water) and with the indicator (*ca.* 0.1 g, taken from a mixture of 0.05 g EBT + 10 g NaCl) and titrated with 0.02 M EDTA. The equivalence volume of EDTA became identical for all test solutions starting from the 2 min withdrawal, which therefore was considered to be both the homogenisation timing and the time resolution of the kinetic measurements.

Blanks were collected after *ca.* 1 h stirring from tests in which a) only the solvent, b) the solvent and the filter holder, c) the solvent, the filter holder and a conditioned filter, were inserted in the cell. These blanks were then analysed by ICP-MS. Other two blanks containing either 0.01 M HCl or 150  $\mu\text{L}$   $\text{HNO}_3$  in 3 mL water were also analysed. These blanks evidenced significant contaminations for a few elements due to the procedure (see below).

#### Measurements of Total Elemental Content

For each of the 18 filters (1/4 pieces), the total elemental content was determined by two subsequent analytical steps. In the first step, each filter was put in a 15 mL Falcon tube and added with 3.45% w/w  $\text{HNO}_3$  (3 mL) containing also an internal standard for ICP-MS ( $^{159}\text{Tb}$   $10 \mu\text{g L}^{-1}$ ). Tubes were closed and heated at bain-marie ( $100^\circ\text{C}$ ) for 2 h. The solutions obtained were removed from the tubes, added with the three water aliquots (100  $\mu\text{L}$  each) previously used to rinse

the filters, and they were subjected to the ICP-MS analysis. In the second step, 3 mL of conc.  $\text{HNO}_3$  were added to each tube containing a filter, then the tube was closed and heated at bain-marie ( $100^\circ\text{C}$ ) for 1 h. At the end, samples were diluted with water containing also an internal standard for ICP-MS ( $^{72}\text{Ge}$   $10 \mu\text{g L}^{-1}$ ) to obtain 3.45% w/w  $\text{HNO}_3$  solutions which were subjected to another ICP-MS analysis.

#### ICP-MS Analysis

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

It was possible to determine concentration values for the following elements, either only for the total elemental content, or also for the kinetic/solubility measurements: Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sr, V, W, and Zn. The instrumental detection limit (LOD) and quantification limit (LOQ) for each element were determined as described previously (Badocco *et al.*, 2015; Roverso *et al.*, 2015), and they are reported in Table S3. Values for B, Lu, P, Si were excluded due to anomalies in the calibration graphs (due to high LODs in the case of B, P and Si), whereas results for Cl and Hg were discarded as they showed strong memory effects. The signals of Au, Be, Br, 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, Tm, U, Y, Yb, detected in the samples resulted practically identical to those detected in the blanks, therefore also these elements were not further considered. Ca, Mg, Na, and Ni were not determined due to contamination of blank filters.

The concentration values (in  $\mu\text{g L}^{-1}$ ) obtained by ICP-MS from kinetic/solubility measurements were corrected to the values which would have been obtained if no volume withdrawals were performed from the cell. The corrected concentration corresponding to the  $x^{\text{th}}$  withdrawal ( $c_x$ ) was obtained by the formula:

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

where  $V_0$  is the starting volume (0.1 L),  $c'_i$  is the experimental concentration obtained from the ICP-MS analysis after the  $i^{\text{th}}$  volume withdrawal ( $1 \leq i \leq x$ ), and  $V_i$  is the volume of solution after the  $i^{\text{th}}$  withdrawal ( $V_i - V_{i+1} =$

$3 \cdot 10^{-3}$  L). The first term of the numerator is the mass of element experimentally contained in the solution, and the summation represents the total amount of element which has been removed to perform all measurements before the  $x^{\text{th}}$  one.

Concentrations in air ( $\text{ng m}^{-3}$ ) for each element in each individual sample were obtained by calculating the mass (ng) of each element from the concentration in the extracts adjusted for the portion of filter analysed and dividing it by the volume of sampled air ( $\text{m}^3$ ). The soluble concentrations at  $t_{\infty}$  were estimated by averaging values obtained at  $t > 60$  min in the kinetic experiments, when a plateau concentration was reached. The soluble fraction was then calculated by dividing the soluble concentration at  $t_{\infty}$  by the total concentration of the element in each individual sample.

### Statistical Analysis

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

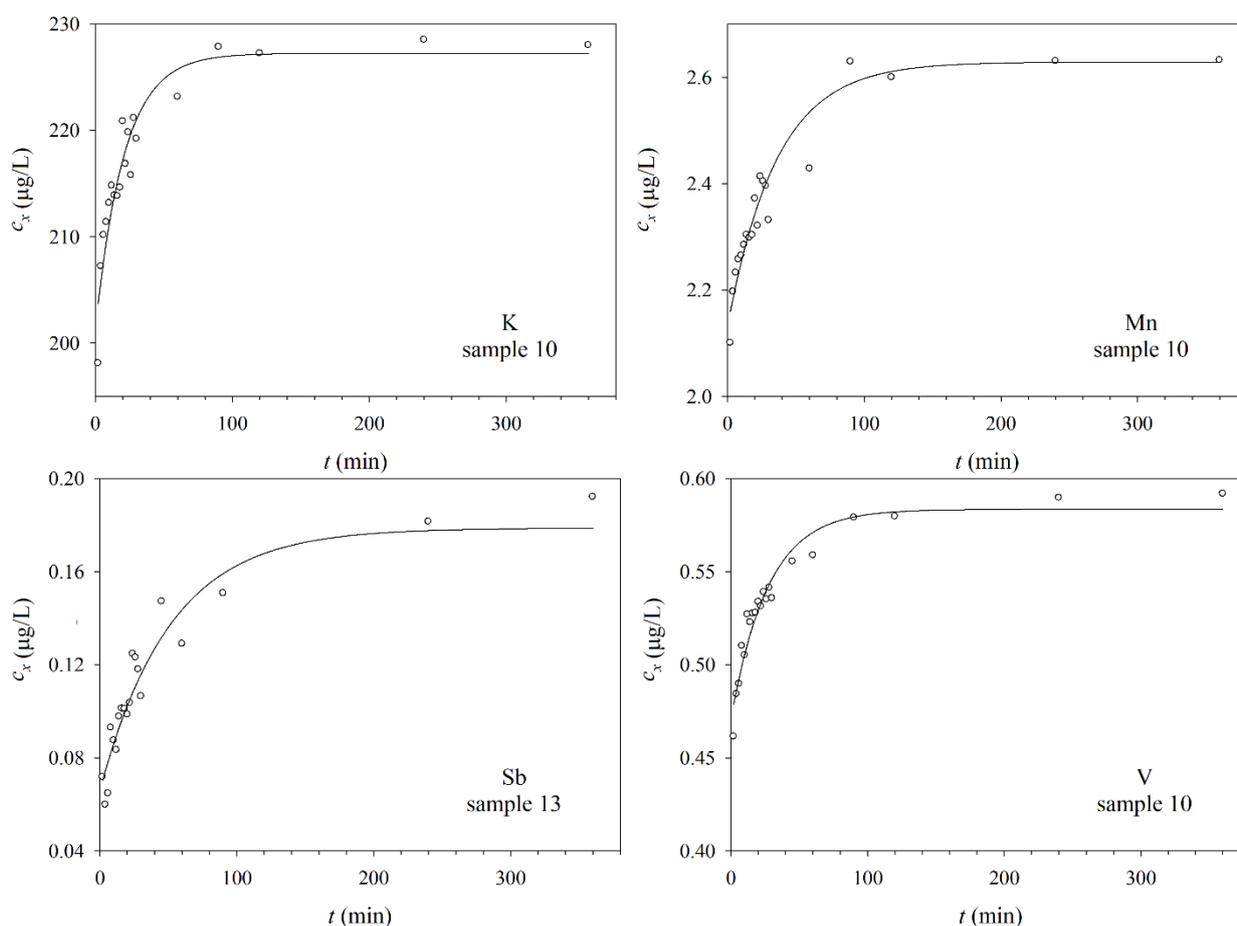
## RESULTS AND DISCUSSION

Some of the concentration-time profiles obtained during the kinetic experiments are shown in Fig. 1. Generally, the

elemental concentrations clearly increased over time, indicating that a leaching was occurring. According to our data, leaching appeared generally to stop after 1-2 hours; data was prudentially collected till 6 h, and in few cases (in particular for Sb, see Fig. 1) some further leaching was observed. Data collection was in any case ended after 6 h. For some of the analysed elements, observed concentrations were below the LOQ and no kinetic data could be obtained.

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

Even for elements which showed marked kinetic behaviours, kinetically non-significant concentration changes ( $p$ -value  $\geq 0.05$ ) were determined in a few samples. This result can be partly explained by noisy data, which, in some cases, has probably caused  $p$ -values being larger than 0.05.



**Fig. 1.** Experimental points and fitting lines (Eq. (3)) obtained in the kinetic measurements of elemental release from  $\text{PM}_{2.5}$ .

	Al	As	Ba	Cd	Cr	Cu	Fe	K	Mn	Mo	Pb	Rb	Sb	Sr	V	W	Zn
1	Green	White	Green	Green	Green	White	Green	Brown	Green	Brown	Brown	Brown	Brown	Brown	Brown	Green	Green
2	Green	White	Green	Brown	Green	White	Green	Brown	Green	Green							
3	Green	White	Green	Green	Green	White	Green	Brown	Green	Brown	Brown	Brown	Brown	Brown	Brown	Green	Green
4	Green	Green	Brown	Brown	Green	White	Green	Brown	Green	Green							
5	Brown	Green	Green	Green	Green	White	Green	Brown	Green	Green							
6	Green	White	Green	Green	Green	White	Green	Brown	Green	Brown	Brown	Brown	Brown	Brown	Brown	Green	Green
7	Brown	White	Green	Green	Green	White	Green	Brown	Green	Green							
8	Brown	White	Brown	Brown	Green	White	Green	Brown	Green	Green							
9	Brown	White	Brown	Brown	Green	White	Green	Brown	Green	Green							
10	Brown	White	Brown	Brown	Green	White	Green	Brown	Green	Green							
11	Green	White	Brown	Brown	Green	White	Green	Brown	Green	Green							
12	Green	White	Green	Green	Green	White	Green	Brown	Green	Green							
13	Brown	White	Brown	Brown	Green	White	Green	Brown	Green	Green							
14	Brown	White	Brown	Brown	Green	White	Green	Brown	Green	Green							
15	Green	Green	Green	Green	Green	White	Green	Brown	Green	Green							
16	Green	Green	Green	Green	Green	White	Green	Brown	Green	Green							
17	Brown	Green	Brown	Brown	Green	White	Green	Brown	Green	Green							
18	Green	White	Brown	Brown	Green	White	Green	Brown	Green	Green							

**Fig. 2.** Diagram showing in which of the 18 samples element concentration was significantly ( $p$ -value  $< 0.05$ ) varying over time according to the Spearman test (brown), non-significantly ( $p$ -value  $\geq 0.05$ ) varying over time (green), or below LOQ (white).

It was decided to evaluate the kinetics for elements for which the concentration changes were significant in at least six samples.

Unexpected results were obtained for Pb, for which concentrations were decreasing over time rather than increasing. To the best of our knowledge, this behaviour was never described in literature. As a tentative explanation, it can be hypothesised that Pb was very rapidly released from PM once in contact with an aqueous solution, and then it reacted with other species released from the PM itself or contained in the solvent, forming insoluble products which cannot be detected by the ICP-MS analysis. For example,  $\text{Pb}^{2+}$  can form insoluble precipitates with several anions, such as halogenides, cyanide, sulphate, etc.

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

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

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

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

where  $A$  is the pre-exponential factor,  $k$  is the kinetic constant ( $k = rk'$ ), and  $c_e$  (defined as  $s/r$ ) represents the solution concentration at equilibrium ( $t = \infty$ ), i.e., the element solubility at the employed conditions (pH = 4.7,  $T = 5^\circ\text{C}$ ). For a summarising purpose, average values of  $k$  and  $t_{1/2}$  have been computed for each element, and they have been weighted using the uncertainty values obtained by the fitting procedure. Weighted average values of  $k$ , and  $t_{1/2}$  obtained for each element are reported in Table 1 while  $k$  values for each individual sample are reported in Table S4.

All kinetic constants obtained in this work were of the order of  $10^{-2}$  min. Values for Al, Cr, Sr were slightly lower than for other elements, whereas values for Cd and Rb were slightly larger. Al, Cr, Sr are of crustal origin, whereas Cd and Rb are of industrial and vehicular origin, and it is reasonable that the former elements have a more stable crystalline network, making these elements more refractory to solubilisation compared with Cd and Rb. This consideration explained solubility values obtained by Desboeufs *et al.* (2005), and might explain also the present kinetic results. Joshi *et al.* (2009) analysed 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,  $0.3\text{--}3 \cdot 10^{-2}$  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 those obtained in this work. However, some elements were reported to have a leaching kinetics only in the present work, and others only in the work of Joshi *et al.*, likely because of the different PM origin and different leaching solutions used. To the best of our knowledge, no other papers reported kinetic constants for PM leaching (for example, Desboeufs *et al.* (2005) reported only leaching rates).

Desboeufs *et al.* (2005, 1999) found that the dissolution rate of some elements followed a two-step process. During the first step the particle was hydrated, the element release was very quick (with a timing of a few minutes), and the rate increased with time. During the second step the rate decreased with time. For some other elements, conversely, only one step (the second one) was observed. Other studies observed only a single leaching step for all elements, and the rate was decreasing with time (Joshi *et al.*, 2009; Armiento *et al.*, 2013). It is worth noting that in the present experiments the values of  $c_x$  at time = 0 were generally larger than zero (Fig. 1), thus indicating that part of the elements has leached to the solution during the very few instants after the PM-water contact. Furthermore, Eq. (3) was generally not able to fit experimental data well unless the concentration values at time zero were excluded from the fitting set. These findings suggest that also in the present case two steps took place during the leaching experiments, but the first step was very

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

element	$k$ (min <sup>-1</sup> )	$t_{1/2}$ (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	–	–	–

quick and comparable to the time resolution of the kinetic measurements (*ca.* 2 min); therefore, it could not be detected. The fact that a fraction of the elements is released immediately after contact with water may indicate that an aqueous phase processing of the particles had already happened during their atmospheric lifetime either because they 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<sub>3</sub>, and a second one in which hot concentrated HNO<sub>3</sub> 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<sub>3</sub> before analysis. The concentrations obtained after a mild digestion are shown in Table S5. Values obtained after the two successive procedures, which represent total concentration,  $c_T$ , are reported in Table 2.

The comparison between Tables S5 and 2 indicates that most elements solubilised in a complete manner (> 90%) also in hot diluted HNO<sub>3</sub> (mild digestion). This solvent thus simultaneously allowed to quantitatively solubilise most elements from PM and to measure concentration values close to the LOD. Only Al, and only in some samples, was not completely solubilised in diluted HNO<sub>3</sub>; the determination of its total amount in PM required a second analytical step with a digestion in concentrated HNO<sub>3</sub>.

Median values of soluble metal ions and total element content are reported in Table 3. Benetello *et al.* (2018) analysed the PM<sub>2.5</sub> of Padua sampled in the year 2012–2013: results

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

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

### Conclusions and Perspectives

In this work, leaching kinetics and equilibrium solubility were evaluated for elements leaching from PM to an environmentally relevant aqueous solution mimicking fog water. A two-step analytical procedure allowed also to analyse the total content of a larger number of elements than those generally detected in the literature. Equilibrium solubility and total elemental content can allow to evaluate the fraction of each element which can solubilise from the PM. The results of our kinetic experiments showed also that a fraction of the elements was immediately released in the aqueous solution (at time = 0), and a slower release following a first-order kinetic took place simultaneously. Kinetic measurements gave constants of the order of 10<sup>-2</sup> min<sup>-1</sup>, from which it is calculated that elements can leach from PM with half times of 10–40 minutes. This timing is compatible with the atmospheric lifetime of clouds and fogs (Xue *et al.*, 2006; Ervens and Volkamer, 2010; Maalick *et al.*, 2016) and it should be taken into account if the leaching of elements

**Table 2.** Values of total concentration,  $c_T$  ( $\text{ng m}^{-3}$ ), obtained for each element in all 18 samples. 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

\* Suspected outliers according to Tukey's rule.

**Table 3.** Median concentrations of elements in sampled air ( $\text{ng m}^{-3}$ ) obtained for each element in all samples. Median values of soluble concentrations at  $\text{pH} = 4.7$  and  $T = 5^\circ\text{C}$  at  $t_\infty$ , median values of total concentrations (individual values reported in Table 2), and median % of soluble fraction  $S$  at  $t_\infty$  (standard deviations in brackets\*) are reported. Total concentrations reported by Benetello *et al.* (2018) (average annual values) and by Armiento *et al.* (2013) (range of given values) are also reported here for comparison.

	Soluble concentration ( $\text{ng m}^{-3}$ ) (this study)	Total concentration ( $\text{ng m}^{-3}$ ) (this study)	$S_{t_\infty}$ (%) (this study)	Total concentration ( $\text{ng m}^{-3}$ ) Benetello <i>et al.</i> (2018)	Total concentration ( $\text{ng m}^{-3}$ ) Armiento <i>et al.</i> (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	22.8–60.98

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

from PM to atmospheric aqueous phases is modelled. The fact that a fraction of the elements was released immediately after contact with water may indicate that an aqueous phase processing of the particles had already happened during their atmospheric lifetime either because they were in a deliquescent state or because of the presence of fog. As suggested by Scheinhardt *et al.* (2013) and Tapparo *et al.* (2020) this atmospheric aqueous phase processing may be dependent on

particle chemical composition so more studies are now needed to investigate the underlying mechanisms of atmospheric processing affecting solubilisation kinetics of metals.

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## SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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