

2019-07-01

# Uncertainty associated with the leaching of aerosol filters for the determination of metals in aerosol particulate matter using collision/reaction cell ICP-MS detection

Clough, R

<http://hdl.handle.net/10026.1/13640>

---

10.1016/j.talanta.2019.02.067

Talanta

Elsevier

---

*All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.*

# Uncertainty associated with the leaching of aerosol filters for the determination of metals in aerosol particulate matter using collision/reaction cell ICP-MS detection

Robert Clough<sup>1\*</sup>, Maeve C. Lohan<sup>1a</sup>, Simon J. Ussher<sup>1</sup>, Malcolm Nimmo<sup>1</sup> and Paul J. Worsfold<sup>1</sup>

<sup>1</sup>Biogeochemistry Research Centre, School of Geography, Earth and Environmental Sciences, Plymouth University, Plymouth, PL4 8AA, United Kingdom.

<sup>a</sup>Currently at Ocean and Earth Sciences, National Oceanography Centre Southampton, University of Southampton, SO14 3ZH Southampton, United Kingdom

## Keywords

Uncertainty, aerosol, leach, ICP-MS, cobalt, iron, lead, vanadium

## Abstract

High quality observational data with a firm uncertainty assessment are essential for the proper validation of biogeochemical models for trace metals such as iron. Typically concentrations of these metals are very low in oceanic waters and ICP-MS is therefore a favoured technique for quantitative analysis. Uncertainties in the measurement step are generally well constrained, even at sub-nM concentrations. However the measurement step is only part of the overall procedure. For the determination of trace metal solubilities from aerosols in the surface ocean, sample collection on a filter paper followed by leaching is likely to make a significant contribution to the overall uncertainty. This paper quantifies the uncertainties for key trace metals (cobalt, iron, lead and vanadium), together with aluminium as a reference element, for a controlled, flow through laboratory leaching procedure using filters collected from three different sites (Bermuda, Heraklion and Tel-Shikmona) and water, glucuronic acid and desferrioxamine B as leachants. Relative expanded uncertainties were in the range of 12 – 29% for cobalt, 12 – 62% for iron, 13 – 45% for lead and 5 – 11% for vanadium. Fractional solubilities for iron ranged from  $0.2 \pm 0.1\%$  to  $16.9 \pm 3.5\%$ .

## 1. Introduction

Atmospheric deposition is an important source of micro-nutrients to open ocean environments and data have been reported for, e.g. the North Atlantic [1], the central Atlantic [2], the North Pacific [3] Mediterranean Sea [4]. The availability of Fe (and other trace metal micronutrients) from atmospheric aerosols plays an important regulatory role in the growth, biomass and species composition of phytoplankton over large areas of the surface ocean [5-9]. Therefore the fractional solubility of trace elements from aerosol particulate matter is a key parameter in many biogeochemical and climate change models [10] and hence it is important that data from different sources are comparable and that uncertainties are quantified.

A wide variety of leachants have been used to assess the fractional solubility, and hence potential bioavailability, of Fe and other trace elements from aerosol samples collected on suitable filter media. These include high purity water (HPW), low iron seawater and aqueous solutions of ammonium acetate, sodium bicarbonate, ammonium formate and desferrioxamine B [11]. In addition the aerosol contact time with the leachant has been varied by the use of both batch and flow through type experiments. The use of these different methods for assessing the aerosol trace metal bioaccessible fraction has led to data that are not necessarily comparable. Therefore, it has been recommended that aerosol solubility investigations include a common and simple extraction method, such as rapid flow through exposure to HPW, to produce data sets that are comparable [11].

The experiments described here followed this recommendation by using a rapid flow through leach procedure with HPW as the leachant; for additional information two further leachants, desferrioxamine B, a strong Fe binding ligand, and glucuronic acid, a weak Fe binding ligand, were also studied. Aerosol samples from three different locations (Tudor Hill, Heraklion and Tel-Shikmona), having different trace metal compositions and solubilities due to varying anthropogenic influences, were used. The four metals investigated were cobalt, iron, lead and vanadium (plus aluminium as a reference element) and these were chosen to represent a range of natural and anthropogenic elements for which uncertainty data for the measurement process (flow injection with solid phase preconcentration and detection by collision/reaction cell quadrupole ICP-MS) have already been reported [12].

## **2. Experimental**

### **2.1 Sample collection**

Three different aerosol samples were selected for use in this study. These samples were collected from site A (Tudor Hill, Bermuda; 194 hour collection period); site B (Heraklion, Crete; 24 h collection period); and site C (Tel-Shikmona, Israel; 24 h collection period). Each aerosol sample was collected onto a Whatman 41 cellulose filter (20 x 25 cm) fitted to a high volume sampler. All collected aerosol samples were stored frozen until use. The entire filter paper from site A was available for this work whereas only a quarter of one filter was available from sites B and C.

### **2.2 Reagents**

Concentrated hydrochloric acid (HCl), SpA grade, concentrated hydrofluoric acid (HF) and concentrated nitric acid (HNO<sub>3</sub>), both UpA grade, were purchased from Romil (Cambridge, UK). Desferrioxamine B (DFB) and glucuronic acid (GLA) were purchased from Sigma Aldrich (Gillingham, Dorset, UK). All high purity water (HPW), 18.2 MΩ cm, was drawn from a Milli-Q system (Millipore, Watford, UK). Individual 10000 mg L<sup>-1</sup> elemental standards were purchased from Thermo Fisher Scientific (Loughborough, UK). All weighing was performed using an analytical balance (OH1602/C, Ohaus, Thetford, UK). The accuracy of the balance was checked daily before use using F1 Class certified weights (KERN, Albstadt, Germany). All pipettes used were calibrated daily before use. All facilities were managed under ISO 9001:2008 certification. To ensure low blank Fe concentrations all sample and reagent handling was undertaken in an ISO 14644-1 Class 5 laminar flow hood. Reagent and sample containers were made of low density polyethylene (LDPE; Nalgene, Thermo Fisher Scientific, UK) and were cleaned using established cleaning protocols for trace metals. Containers were immersed in ~ 1.1 M trace metal grade HCl (Fisher Scientific) for at least fourteen days. Subsequently, the containers were rinsed in copious amounts of HPW, filled with 0.01 M HCl and stored in double re-sealable plastic bags until use.

### **2.3 The flow through filtration procedure**

The experimental design for the leaching and total digestion of aerosol filter sub-samples is shown in Table 1 and a schematic diagram of the flow through filtration experiments is shown in Fig. 1. A dual vacuum filtration unit (Saville, QMX Laboratories, UK), fitted with a 0.2 µm pore size polycarbonate filters (Whatman Track Etched, Thermo Fisher Scientific, Loughborough, UK) to retain particulates. The pre-cleaned polycarbonate filters were

stored in 1 M HCl. Fresh filters were fitted before each leach procedure and the dual filter unit washed with 250 ml of HPW before use. Subsequently, each 20 mm diameter aerosol filter sub-sample was placed in the filter unit and leached with 100 mL of the appropriate leachant. The leachate was directly collected into a 125 mL LDPE bottle. This procedure was repeated a further three times, giving four flow through leach samples for aerosol sub-sample. This was followed by removal of the aerosol filter sub-sample to a separate 125 mL LDPE bottle containing 100 mL of leachate, which was left to stand for 24 h. After this time period the leachate was separated from the aerosol filter sub-sample by vacuum filtration. All leachates were acidified with concentrated HNO<sub>3</sub> to a final concentration of 2% v/v immediately after collection. Ten sub-samples were taken at random from the Tudor Hill aerosol sample for leaches using HPW, DFB and GLA. For the Heraklion and Tel-Shikmona aerosols only five sub-samples were taken due to the smaller amount of filter available although this does result in a doubling of the sampling density. Twenty samples were also taken from an unexposed W41 filter to give ten full procedural blanks for both the HPW and DFB leachants.

## **2.4 Total digestion of aerosol filter samples**

To determine the total amount of material contained on a filter sub-sample, ten sub-samples of the Tudor Hill aerosol and ten samples from an unexposed W41 filter were subjected to a heated, pressurised HF/HNO<sub>3</sub> digestion procedure [11, 13].

## **2.5 Elemental determinations**

An X Series 2 ICP-MS instrument (Thermo Scientific, Hemel Hempstead, UK) was used for all elemental determinations in the leachate and total digest samples. Due to the low signals expected for each analyte the instrument was configured and tuned for maximum stability. A micromist nebuliser (Glass Expansion, Melbourne, Australia), in natural aspiration mode, and a PC3 cyclonic spray chamber (Elemental Scientific, Omaha, USA) cooled to 5 °C were used to increase signal stability. Before each analytical session the instrument was tuned in standard mode, using a 10 µg L<sup>-1</sup> solution of Ba, Ce, Co, Li, In and U, and the performance checked to ensure that it was operating to the manufacturers specifications. The most abundant masses were used for all elements except for Pb, for which <sup>206</sup>Pb was used to avoid the potential for detector overload. Subsequently, to minimise the effect of polyatomic interferences, particularly the <sup>40</sup>Ar<sup>16</sup>O signal which is a polyatomic interferent for Fe, the instrument was tuned and operated in collision/reaction cell mode, with a cell gas of 7% H in He flowing at 3.6 mL min<sup>-1</sup>, to give a <sup>140</sup>Ce<sup>16</sup>O:<sup>140</sup>Ce ratio of ≤ 0.07%. The dwell time per isotope was set to 200 ms to ensure high precision

measurements. Data acquisition was by the PlasmaLab software of the ICP-MS instrument and the raw data exported to allow further off-line processing. Rhodium, indium and iridium were added to all calibration standards and samples, to a final concentration of 20 µg L<sup>-1</sup>, as internal standards to monitor and account for any instrumental drift. Multi-element calibration standards were prepared to produce six point calibration curves.

## 2.6 Measurement uncertainty

All uncertainty estimates were made by combining individual standard uncertainties using the numerical differentiation method of Kragten [14]. The equation used to calculate the analyte concentration in each leachate sample was used as the model for these calculations and is shown in Equation 1.

$$C_s = (I_s - I_B)/M \quad \text{Equation 1}$$

where  $C_s$  is the analyte concentration in the sample,  $I_s$  is the signal of the analyte;  $I_B$  is the signal procedural blank and  $M$  is the slope of the calibration curve. The standard uncertainty for  $I_s$  was calculated as the precision of three instrumental replicate measurements. The standard uncertainty for  $I_B$  was calculated from the standard deviation of the signal obtained for the procedural blanks ( $n = 10$ ). The uncertainty of the slope of the calibration curve was calculated using regression statistics [15]. Finally, the mass of metal released during each individual leach procedure was obtained by multiplying the found  $C_s$  value by the leachate volume after acidification,  $n = 10$  for leaches involving the Tudor Hill sample and  $n = 5$  for leaches of the Heraklion and Tel-Shikmona samples.

The uncertainty estimate for  $n$  procedural replicates was calculated by combining the between replicate ( $u_{\text{between}}$ ) and within replicate ( $u_{\text{within}}$ ) standard uncertainties according to error propagation laws [16] to give the standard uncertainty ( $u$ ) of the mass of metal solubilised by each leach procedure. Subsequently, this combined standard uncertainty was multiplied by a coverage factor,  $k$ , of 2, which approximates to the 95% confidence interval, to give the expanded uncertainty ( $U$ ), from which the relative expanded uncertainty ( $U_{\text{rel}}$ ) could also be calculated. For each leach procedure used,  $u_{\text{between}}$ , which could also be termed repeatability, was taken as the standard deviation of the mean of the amount of metal solubilised, whilst  $u_{\text{within}}$  was estimated by taking the mean of the standard uncertainties estimated for each replicate [17]. Thus, the sources of uncertainty arising from both the between leach variability and from each of the parameters in Equation 1 were accounted for.

### 3 Results and Discussion

#### 3.1 Limits of quantitation for the elements studied

The rationale for selecting the four elements studied, namely Co, Fe, Pb and V, is that they represent a cross section of essential and anthropogenic elements for which the uncertainties associated with their measurement by collision cell - quadrupole ICP-MS (the detection method used in this work) have already been reported [12]. Data for aluminium, used for calculating element enrichment factors, are also provided to enable the calculation of enrichment factors. The limits of quantitation for each element, with each of the three leachants, are shown in Table 2. All sample data reported below have been blank subtracted.

#### 3.2 Amounts of each element leached and their associated uncertainties

The results for the absolute amounts of each element leached and their associated expanded uncertainties are presented in Table 3. The most comprehensive study was for the Tudor Hill, Bermuda aerosol sample. This sample was collected during a time period when the prevailing wind was from West Africa. The aim was to collect a Saharan dust sample which would subsequently have been weathered by marine processes as it was transported across the Atlantic Ocean. The amount of Fe solubilised increased as the ligand binding constant increased, giving 165, 249 and 287 ng for HPW, GLA and DFB respectively, although the latter two values are not statistically different within the uncertainty estimates shown in Table 3 which were all of similar magnitude (12-15%) This compares favourably with other studies, which used the same ligands but in a seawater matrix, where the variability was reported to be as high as 50% for one standard deviation [18]. For each of the other three metals discussed, there was no significant statistical difference (95% confidence interval) between the amount of metal leached and the leach solution composition Co (~1.2 ng), Pb (~2.1 ng) and V (~ 13 ng). However, the relative expanded uncertainties were greater for Co and Pb (an average of 23 and 18 % respectively) than for Fe whilst those estimated for V (11% relative) were of a similar magnitude to those obtained for Fe. In all cases the major uncertainty contribution was from the filter replicates ( $U_{\text{between}}$ ), which contributed > 90 %, with <10 % being due to the uncertainty associated with each individual measurement of  $C_s$  ( $U_{\text{within}}$ ).

The Heraklion, CR 12 and CR 13, and the Tel-Shikmona, IS 524 and IS 525, sample pairs were chosen as one sample from each pair (CR12 and IS 524) was collected when the air mass flow direction, and hence the aerosol particle source, was from an area of major anthropogenic activity. The other sample in each pair (CR 13 and IS 525) was collected

when the wind direction should have given ‘natural’ samples of mainly lithogenic composition. For both sampling locations the amount of metal solubilised from anthropogenically sourced aerosols was significantly higher than from ‘natural’ aerosols, which agrees with previous studies [18, 19]. For example, the amounts of Fe solubilised with a HPW leach were 400 and 3,600% higher for the anthropogenically sourced samples for the Heraklion and Tel-Shikmona sites respectively. Cobalt showed an increase of 370% for both sampling sites. The magnitude of  $U_{rel}$  was highly variable for the leaches of these samples. For V,  $U_{rel}$  was  $\leq 10\%$  whilst for the other metals it ranged from 12 – 29% for Co, 19 – 62 for Fe and 13 – 45% for Pb. Again the major uncertainty contribution was from  $U_{between}$ , which contributed  $> 85 \%$ , with  $< 15 \%$  from  $U_{within}$ .

The data from leach experiments is principally used to determine the fractional solubility of trace elements from dust dissolution in the surface ocean. The fractional solubility is defined as the ratio of the amount of an element released from a filter sub-sample during a particular leach procedure relative to the amount determined from a total digestion of another filter sub-sample of the same area. The ratios can be calculated from the data presented in Table 3. For example, the fractional solubility of Fe ranged from  $0.2 \pm 0.1\%$  for Site B (Heraklion CR 13) to  $16.9 \pm 3.5\%$  for Site C (Tel-Shikmona IS 524). For Site A (Tudor Hill) there was little difference between the fractional solubility with a water leach ( $2.5 \pm 0.4$ ) compared with a GLA leach ( $3.8 \pm 0.5$ ) or a DFB leach ( $4.3 \pm 0.6$ ). The uncertainties associated with these fractional solubilities were calculated using the standard approach for the propagation of errors [15].

### 3.3 Factors contributing to the combined expanded uncertainties

There are a number of possible reasons, or combinations thereof, for the relatively high uncertainties estimated during this study for some sample types and/or leachants. The first cause could be that not all of the soluble material was leached during the flow through part of the procedure, i.e. leaches 1 – 4. However, for Fe, all of the readily soluble material was released from the particulate phase during the first leach with HPW, with a smaller amount released during the 24 h leach as shown in Table 4. Conversely, for the leaches using GLA and DFB, Fe was solubilised during all four flow through leaches and also during the 24 hour leach. The relative uncertainty estimate for each of these three leachants was very similar, 15, 12 and 13% for HPW, GLA and DFB respectively, which, combined with the different dissolution profiles for Fe, suggests that the leaching procedure was under control and not a major source of the variability observed. The second cause could be due to the

very low masses of metals, and hence concentrations in the leach solutions, solubilised. The cobalt data provides evidence against this hypothesis. With count rates as low as 4 per second (sample IS 525) for leaches, which was 10 times the blank signal,  $u_{\text{within}}$ , the internal precision, was typically <5% relative and hence a minor contributor to the overall uncertainty estimate. Indeed, data for two of the Mediterranean samples, CR1 3 and IS 524, exhibited very acceptable expanded uncertainties, especially for sub-nanogram quantities of material.

The final factor that could influence the estimated uncertainties is sample homogeneity. As noted,  $u_{\text{between}}$  was the major contributor to all of the uncertainty estimates. This suggests that the aerosol particulates were not evenly deposited across the filter paper during collection. The HF/HNO<sub>3</sub> digests, which solubilised all of the material contained on a filter sub-sample, gave relative expanded uncertainties of 7.1, 4.4, 5.7 and 5.6% for Co, Fe, Pb and V respectively. Data of this precision strongly indicates that the aerosol sample is homogeneously distributed over a filter paper. Therefore, the conclusion is that the proportion of readily soluble material is less homogeneously distributed over the filter paper. The data for the Heraklion and Tel-Shikmona samples has shown that anthropogenically derived particles contain a higher proportion of soluble material than predominantly lithogenically sourced samples. Anthropogenically produced particles are typically smaller in size than lithogenic particles, < 0.5 and 4 – 10  $\mu\text{m}$  respectively, and it has been postulated that this size difference could result in a greater heterogeneity for anthropogenic particles collected using commonly deployed high volume air samplers. Due to the low particulate mass contained on an exposed filter, approximately 2 mg per 20 mm diameter subsample, it has not been possible to determine the particle size distribution and provide further evidence of particulate heterogeneity.

#### **4. Conclusions**

Aerosol dust samples from different sources have been subjected to different leach procedures under tightly controlled experimental conditions. The data realised has shown that the trace metals under study are more readily solubilised from aerosols of a predominantly anthropogenic source than lithogenically dominated source aerosol. Furthermore, it has also been demonstrated that a greater proportion of Fe is solubilised when weak (GLA) and strong (DFB) Fe binding ligand based leachants are used compared with HPW alone. Whilst the actual amount of Co, Fe, Pb and V solubilised varied with the sample type and leachant used, the combined expanded uncertainty was

reasonably constant for each element. The major uncertainty contribution, >85%, in each case arose from the standard deviation of the amount of metal released by either ten or five full procedural replicates. This suggests that the soluble fractions, of Co, Fe, Pb and V are not homogeneously distributed on a collected aerosol sample. This finding has implications for studies that use only a small portion of an aerosol filter for dissolution work. The relative expanded uncertainty for the total amount of each metal contained on a filter paper was 7% or better. Therefore, for partial aerosol dissolution (i.e. leaching) studies, it is recommended that sufficient replication is undertaken to achieve a similar expanded uncertainty. This was the case for V in this work, and also for some of the data for Co, Fe, and Pb. Given the very small amounts of analyte being determined, which requires stringent blank control, and the fact that measurements are approaching absolute detection limits for a wide variety of instrumentation, it should be stated that a relative expanded uncertainty of 10 – 15% for partial dissolution studies is acceptable.

## **Acknowledgements**

This work was financially supported by the EMRP via JRP-ENV05-REG1 (R.C.). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union. Writing of this manuscript was also supported by EU Horizon 2020 AtlantOS project SEP-210177333 (P.J.W, S.J.U. and M.C.L.) and Natural Environment Research Council (NERC) grant NE/H004475/1 (M.C.L.).

## References

- [1] C.S. Buck, W.M. Landing, J.A. Resing, Particle size and aerosol iron solubility: A high-resolution analysis of Atlantic aerosols, *Marine Chemistry*, 120 (2010) 14-24.
- [2] C.S. Buck, W.M. Landing, J.A. Resing, C.I. Measures, The solubility and deposition of aerosol Fe and other trace elements in the North Atlantic Ocean: Observations from the A16N CLIVAR/CO<sub>2</sub> repeat hydrography section, *Marine Chemistry*, 120 (2010) 57-70.
- [3] C.S. Buck, W.M. Landing, J. Resing, Pacific Ocean aerosols: Deposition and solubility of iron, aluminum, and other trace elements, *Marine Chemistry*, 157 (2013) 117-130.
- [4] M.J.M. Séguret, M. Koçak, C. Theodosi, S.J. Ussher, P.J. Worsfold, B. Herut, N. Mihalopoulos, N. Kubilay, M. Nimmo, Iron solubility in crustal and anthropogenic aerosols: The Eastern Mediterranean as a case study, *Marine Chemistry*, 126 (2011) 229-238.
- [5] J.M. Rose, Y. Feng, G.R. Ditullio, R.B. Dunbar, C.E. Hare, P.A. Lee, M. Lohan, M. Long, W.O. Smith Jr, B. Sohst, S. Tozzi, Y. Zhang, D.A. Hutchins, Synergistic effects of iron and temperature on Antarctic phytoplankton and microzooplankton assemblages, *Biogeosciences*, 6 (2009) 3131-3147.
- [6] F.M.M. Morel, A.B. Kustka, Y. Shaked, The role of unchelated Fe in the iron nutrition of phytoplankton, *Limnology and Oceanography*, 53 (2008) 400-404.
- [7] A.L. King, K. Barbeau, Evidence for phytoplankton iron limitation in the southern California Current System, *Marine Ecology Progress Series*, 342 (2007) 91-103.
- [8] J.H. Street, A. Paytan, Iron, phytoplankton growth, and the carbon cycle, in: A. Sigel, H. Sigel, R.K.O. Sigel (Eds.), 2005, pp. 153-193.
- [9] Y. Shaked, A.B. Kustka, F.M.M. Morel, A general kinetic model for iron acquisition by eukaryotic phytoplankton, *Limnology and Oceanography*, 50 (2005) 872-882.
- [10] R.U. Shelley, W.M. Landing, S.J. Ussher, H. Planquette, G. Sarthou, Regional trends in the fractional solubility of Fe and other metals from North Atlantic aerosols (GEOTRACES cruises GA01 and GA03) following a two-stage leach, *Biogeosciences*, 15 (2018) 2271-2288.
- [11] P.L. Morton, W.M. Landing, S.C. Hsu, A. Milne, A.M. Aguilar-Islas, A.R. Baker, A.R. Bowie, C.S. Buck, Y. Gao, S. Gichuki, M.G. Hastings, M. Hatta, A.M. Johansen, R.

- Losno, C. Mead, M.D. Patey, G. Swarr, A. Vandermark, L.M. Zamora, Methods for the sampling and analysis of marine aerosols: Results from the 2008 GEOTRACES aerosol intercalibration experiment, *Limnology and Oceanography: Methods*, 11 (2013) 62-78.
- [12] R. Clough, H. Sela, A. Milne, M.C. Lohan, S. Tokalioglu, P.J. Worsfold, Uncertainty contributions to the measurement of dissolved Co, Fe, Pb and v in seawater using flow injection with solid phase preconcentration and detection by collision/reaction cell - Quadrupole ICP-MS, *Talanta*, 133 (2015) 162-169.
- [13] M.P. Fishwick, P.N. Sedwick, M.C. Lohan, P.J. Worsfold, K.N. Buck, T.M. Church, S.J. Ussher, The impact of changing surface ocean conditions on the dissolution of aerosol iron, *Global Biogeochemical Cycles*, 28 (2014) 1235-1250.
- [14] J. Kragten, Tutorial review. Calculating standard deviations and confidence intervals with a universally applicable spreadsheet technique, *The Analyst*, 119 (1994) 2161-2165.
- [15] J.N. Miller, J.C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, Sixth ed., Pearson, London, 2010.
- [16] S.L.R. Ellison, M. Rosslein, A. Williams, L.A. Konopel'ko, A.V. Garmash, EURACHEM/CITAC Guide: Quantifying Uncertainty in Analytical Measurement, *Journal of Analytical Chemistry*, 58 (2003) 191.
- [17] C.S.J. Wolff Briche, C. Harrington, T. Catterick, B. Fairman, Orthodox uncertainty budgeting for high accuracy measurements by isotope dilution inductively coupled plasma-mass spectrometry, *Analytica Chimica Acta*, 437 (2001) 1-10.
- [18] M. Thompson, S.L.R. Ellison, Dark uncertainty, *Accreditation and Quality Assurance*, 16 (2011) 483-487.
- [19] A.M. Aguilar-Islas, J. Wu, R. Rember, A.M. Johansen, L.M. Shank, Dissolution of aerosol-derived iron in seawater: Leach solution chemistry, aerosol type, and colloidal iron fraction, *Marine Chemistry*, 120 (2010) 25-33.

Table 1. Experimental design for the leaching and total digestion of 20 mm diameter aerosol filter sub-samples punched from Whatman 41 20 x 25 cm cellulose filters.

Site	Site A (Tudor Hill, Bermuda; 194 h collection period)				Site B (Heraklion; 24 h collection)	Site C (Tel-Shikmona; 24 h collection)
Matrix	Site A sub-sample	Site A sub-sample	Site A sub-sample	Site A sub-sample	Site B sub-sample	Site C sub-sample
Leachant	H <sub>2</sub> O	Desferrioxamine B (DFB)	Glucuronic acid (GLA)		H <sub>2</sub> O	H <sub>2</sub> O
Digestant				HF/HNO <sub>3</sub>		
Number of sub-samples	10	10	10	10	5	5
Number of filter blanks	10	10		10		

Table 2. Limits of quantitation (defined as the blank signal + 10 x the standard deviation of the blank signal) for the elements studied with each of the three leachants used. Data are calculated from the mean and s.d. of 10 full procedural blanks for each leach/digest procedure. Blanks are in absolute amounts for a non-acid washed filter taken from box of filters at the University of Plymouth.

Leachant	Co	Fe	Pb	V	Al
	pg	ng	pg	pg	ng
H <sub>2</sub> O	42	34	221	156	55
GLA/DFB	24	14	299	61	129
HF/HNO <sub>3</sub> digests	5	103	44	10	174

Table 3. The absolute amounts of Co, Fe, Pb, V and Al released from aerosol samples during various leach procedures. U = Expanded uncertainty ( $k = 2$ ),  $U_{rel}$  = relative expanded uncertainty. Results for the total digestion of Site A aerosol samples are also shown.

Sample	Leachant	Co	U	$U_{rel}$	Fe	U	$U_{rel}$	Pb	U	$U_{rel}$	V	U	$U_{rel}$	Al	U	$U_{rel}$
		ng	ng	%	ng	ng	%	ng	ng	%	ng	ng	%	ng	ng	%
Site A (Tudor Hill)	H <sub>2</sub> O	1.12	0.32	28	165	25	15	2.72	0.52	19	12.9	1.4	10	245	67	27
Site A (Tudor Hill)	GLA	1.26	0.28	22	249	30	12	1.91	0.26	13	15.5	1.7	11	392	75	19
Site A (Tudor Hill)	DFB	1.20	0.23	19	287	36	13	2.67	0.62	23	14.5	1.6	11	467	218	47
Site B (Heraklion CR 12)	H <sub>2</sub> O	1.80	0.29	16	60.4	11.6	19	31.8	14.2	45	39.3	2.7	6.9	247	88	26
Site B (Heraklion CR 13)	H <sub>2</sub> O	0.488	0.071	14	14.6	6.4	44	7.06	0.91	13	27.3	2.7	10			
Site C (Tel-Shikmona IS 524)	H <sub>2</sub> O	0.736	0.086	12	1115	225	20	5.26	0.99	19	13.0	0.70	5.4	2710	616	23
Site C (Tel-Shikmona IS 525)	H <sub>2</sub> O	0.203	0.058	29	31.0	19	62	6.46	2.5	38	5.89	0.43	7.2			
Site A (Tudor Hill)	HF/HNO <sub>3</sub> Digestion	2.38	0.17	7	6600	292	4	8.04	0.46	6	30.1	1.70	6	11283	515	5

Table 4: The amount of Fe and V released from aerosol samples during each leach for Site A samples. U = Expanded uncertainty (k = 2), U<sub>rel</sub> = relative expanded uncertainty.

Leachant		Co	U	U <sub>rel</sub>	Fe	U	U <sub>rel</sub>	Pb	U	U <sub>rel</sub>	V	U	U <sub>rel</sub>	Al	U	U <sub>rel</sub>
		ng	ng	%	ng	ng	%	ng	ng	%	ng	ng	%	ng	ng	%
H <sub>2</sub> O	1st leach	1.12	0.32		132	24.6		2.72	0.52		8.49	1.20		245	134	
H <sub>2</sub> O	2nd leach	<LOQ			<LOQ			<LOQ			1.76	0.60		<LOQ		
H <sub>2</sub> O	3rd leach	<LOQ			<LOQ			<LOQ			0.56	0.04		<LOQ		
H <sub>2</sub> O	4th leach	<LOQ			<LOQ			<LOQ			0.32	0.02		<LOQ		
H <sub>2</sub> O	5th leach	<LOQ			32.6	5.4		<LOQ			1.81	0.22		<LOQ		
H <sub>2</sub> O	Total	1.12		28	164.6		15	2.72		19	12.9		10	245		27
DFB	1st leach	1.20	0.24		124	19.6		2.67	0.62		8.95	1.10		467	436	
DFB	2nd leach	<LOQ			29.9	13.4		<LOQ			1.69	1.00		<LOQ		
DFB	3rd leach	<LOQ			17.6	1.6		<LOQ			0.84	0.38		<LOQ		
DFB	4th leach	<LOQ			44.7	26.2		<LOQ			0.58	0.20		<LOQ		
DFB	5th leach	<LOQ			71.1	7.6		<LOQ			2.43	0.34		<LOQ		
DFB	Total	1.20		19	287.1		13	2.67		23	14.5		11	467		47
GLA	1st leach	1.26	0.28		144	22.2		1.91	0.26		9.30	1.38		392	150	
GLA	2nd leach	<LOQ			26.7	12.0		<LOQ			1.96	0.86		<LOQ		
GLA	3rd leach	<LOQ			13.4	1.8		<LOQ			1.02	0.44		<LOQ		
GLA	4th leach	<LOQ			20.5	10.0		<LOQ			0.59	0.10		<LOQ		
GLA	5th leach	<LOQ			44.5	13.6		<LOQ			2.62	0.28		<LOQ		
GLA	Total	1.26		22	248.7		12	1.91		13	15.5		11	392		19

Figure caption

Schematic diagram of the procedure for the flow through filtration experiments.

Fig. 1.

