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Validation of a continuous flow method for the determination of soluble iron in atmospheric dust and volcanic ash



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ABSTRACT

Iron is an essential micronutrient for phytoplankton growth and is supplied to the remote areas of the ocean mainly through atmospheric dust/ash. The amount of soluble Fe in dust/ash is a major source of uncertainty in modeling-Fe dissolution and deposition to the surface ocean. Currently in the literature, there exist almost as many different methods to estimate fractional solubility as researchers in the field, making it difficult to compare results between research groups. Also, an important constraint to evaluate Fe solubility in atmospheric dust is the limited mass of sample which is usually only available in micrograms to milligrams amounts. A continuous flow (CF) method that can be run with low mass of sediments (< 10 mg) was tested against a standard method which require about 1 g of sediments (BCR of the European Union). For validation of the CF experiment, we run both methods using South American surface sediment and deposited volcanic ash. Both materials tested are easy eroded by wind and are representative of atmospheric dust/ash exported from this region. The uncertainty of the CF method was obtained from seven replicates of one surface sediment sample, and shows very good reproducibility. The replication was conducted on different days in a span of two years and ranged between 8 and 22% (i.e., the uncertainty for the standard method was 6–19%). Compared to other standardized methods, the CF method allows studies of dissolution kinetic of metals and consumes less reagents and time (< 3 h). The method validated here is suggested to be used as a standardized method for Fe solubility studies on dust/ash.

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1. Introduction

Iron is an essential micronutrient in the ocean for the growth of phytoplankton and is strongly linked to climate *via* the impact of iron limitation on the ability of marine biomass to assimilate CO₂ [1–3]. The deposition and dissolution of continental dust as well as volcanic ashes is the major atmospheric input path of Fe into ocean areas far from continents [4,5]. Most of the Fe in dust/ash is highly refractory (primary found in the form of aluminosilicates and/or volcanic glass) and only a tiny proportion of atmospheric Fe is soluble in natural water (e.g., rain, fresh or ocean waters) [6].

The amount of soluble Fe in a dust/ash sample is an operationally-defined ratio of the dissolved Fe concentration relative to the total Fe contained in the bulk sample [7], and is a major source of uncertainty in modeling-Fe dissolution and deposition to the surface ocean [8,9]. Previous work has shown a considerable range (0.001–80%) in Fe solubility estimates [6,10,11].

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One of the contributing factor to this wide range of Fe solubility is the diverse range of techniques used [8,12–14]. Moreover, an important restriction to evaluate Fe solubility in atmospheric dust is the limited mass of sample which is usually only available in micrograms to milligrams amounts. This forces researchers in this field to use soil/sediment samples as a surrogate for dust [15–17]. The main advantage of using soil/sediment samples is that they are available in large quantities (grams to kilograms), requirement of most metal extraction techniques. However, this approach neglects an important mechanism of dust generation with regard to fractionation effects from wind erosion during the conversion of soil to dust that occurs during the processes of saltation and sandblasting [18]. Furthermore, to obtain a reliable dust sample from soils it is necessary to employ size-sorting techniques which are time consuming and eventually can modify the textural and the chemical composition of the samples. On the other hand, the advantage of using real dust samples is that they can usually represent the average composition of sediments from different and remote source areas which ultimately better characterize the true atmospheric input to the ocean [19].

Currently there are many dust monitoring programs worldwide seeking to characterize dust fluxes and also the textural, chemical and isotopic composition of the atmospheric dust load [19–21].

Important gaps of knowledge exist on the total amount of bioavailable Fe in dust [22] and most of the information on this subject comes from studies performed on top soil samples [7,10,15–17,23–25] rather than dust. Dust collectors at the monitoring sites could accumulate only a few milligrams of dust after several days of sampling or even after severe dust storms thus limiting the accessibility of samples for different analytical purposes. Furthermore, in the last SOLAS (Surface Ocean-Lower Atmosphere Study) Open Science Meeting (Seattle, 2012) a discussion group on “Impacts of dust and ash on ocean productivity” highlighted the existence of different type of methods to estimate fractional Fe solubility in dust/ash materials and the necessity of standardization of techniques to ensure coherence and quality control of the data (<http://www.solas-int.org/news/bulletin/bulletin80webpage.html>).

In this study a continuous flow (CF) method to evaluate Fe release from dust/ash during atmospheric transport was validated. The proposed flow system require less time and small amounts of sediment (less than tens of milligrams) and utilizes common reagents (e.g., Milli-Q water and nitric acid) available in every laboratory and that minimizes the matrix effects. Data obtained with the CF method was validated by comparing with data obtained from a standard method (The Standard, Measurements and Testing Programme, SM & T—formerly BCR of the European Union), which recommend a series of approaches to be used for single or sequential extraction of metals from soil/sediments matrices [26–28].

2. Material and methods

2.1. Reagents

All chemicals were analytical grade and de-ionized water (Milli-Q, $18 \text{ m}\Omega \text{ cm}^{-1}$) was used. Glassware and containers were cleaned overnight with HNO_3 (4 M) and then rinsed several times with ultrapure water. The extractions were performed by using poly-propylene centrifuge tubes.

Different solutions were employed for the experiments. Solution A: 25 mL of glacial acetic acid (was making up to 1L with de-ionized water (0.43 M). Solution B: 0.5 M hydroxylamine hydrochloride was prepared weighing 34.75 g of hydroxylamine hydrochloride and dissolving with de-ionized water. Nitric acid (2 M) was added in order to obtain a pH of 2.0 and made up to 1 L with de-ionized water. This solution was prepared daily. Nitric acid solutions: 1% 10% and 30% V/V were prepared from appropriate dilution of ultrapure nitric acid.

2.2. Apparatus

Dissolved Fe concentrations obtained from different experiments were measured by using graphite furnace atomic absorption spectrometer (GFAAS) Buck 210, equipped with an autosampler. In order to evaluate the accuracy of the standard method of extraction and the GFAAS measurements, the procedure was applied to a certified reference material (BCR-701, certified by the Community Bureau of Reference). Results varied between $\pm 6\%$ related to certified values for the different stages of extractions.

Total Fe was analyzed at commercial labs (Actlabs, Canada). Samples were digested by means of the alkaline fusion method ($\text{Li}_2\text{B}_4\text{O}_7$, 1050°C , with HNO_3 digestion) and analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (detection limit=0.01%, and uncertainty based on one relative standard deviation of replicates was 3%). The validity of the results was checked with NIST 694, 696 and 1633b carried out along with sample analysis.

The continuous flow system is provided with a Gilson® Minipuls 3 peristaltic pump as propulsion system and a Rheodyne selection valve. All the reaction coils were made of PTFE tubing. The extraction columns consist of a piece of tygon tube.

2.3. Sampling and samples preparation

Since 2004 our group has been monitoring dust and volcanic ash transported in the atmosphere of southern of South America (SSA). The main objectives of this research program is to estimate

Table 1

Available Fe from souther South American top soils ($< 63 \mu\text{m}$) using two extraction techniques. All data are expressed in $\mu\text{g g}^{-1}$.

Samples ^a	Geographic position		Fe_T	Solution A step 1 BCR	Solution B step 2 BCR	Total simBCR ^b	$\text{Fe}_{\text{simBCR}}/\text{Fe}_T$ (%)	De-ionized water step 1 CF	HNO_3 1% step 2 CF	Total CF ^c	FeCF/Fe_T (%)
	Longitud	Latitud									
1	20°40'S	66°40'W	38500	2.0 ± 0.3^d	463 ± 47	465 ± 47	1.21	21.5 ± 2.0	648 ± 17	670 ± 17	1.74
2	23°12'S	65°52'W	40425	4.0 ± 0.4	841 ± 51	845 ± 51	2.09	8.0 ± 1.0	696 ± 70	704 ± 70	1.74
3	24°39'S	67°47'W	62736	1.1 ± 0.3	499 ± 32	500 ± 32	0.80	31.0 ± 8.0	453 ± 34	484 ± 35	0.77
4	29°17'S	67°14'W	41265	2.9 ± 0.1	524 ± 26	527 ± 26	1.28	10.8 ± 0.3	481 ± 56	492 ± 56	1.19
5	29°20'S	67°00'W	42943	1.7 ± 1.0	851 ± 135	852 ± 135	1.98	10.0 ± 3.0	1019 ± 41	1029 ± 41	2.40
6	34°24'S	67°30'W	41474	2.9 ± 0.8	432 ± 127	435 ± 127	1.05	3.7 ± 1.7	408 ± 70	412 ± 70	0.99
7	42°49'S	65°08'W	27836	2.1 ± 1.0	1237 ± 252	1239 ± 253	4.45	36.9 ± 22.0	1140 ± 325	1177 ± 326	4.23
8	44°04'S	66°40'W	22870	0.4 ± 0.2	297 ± 66	298 ± 66	1.30	4.1 ± 0.3	291 ± 7	295 ± 7	1.29
9	47°01'S	67°15'W	38117	3.6 ± 1.9	566 ± 25	569 ± 25	1.49	3.5 ± 2.0	441 ± 36	445 ± 36	1.17
10	47°28'S	67°16'W	32033	25.9 ± 1.1	1305 ± 274	1331 ± 274	4.15	12.9 ± 3.0	1454 ± 288	1467 ± 288	4.58
11	48°40'S	69°08'W	19583	2.1 ± 1.0	545 ± 8	547 ± 8	2.79	2.3 ± 1.6	451 ± 121	453 ± 121	2.31
12	49°18'S	67°44'W	44971	4.4 ± 0.0	624 ± 13	628 ± 13	1.40	93.2 ± 84.0	484 ± 40	577 ± 93	1.28
13	41°58'S	71°30'W	12659	245.0 ± 12.7	719 ± 8	964 ± 15	7.61	18.9 ± 7.0	1008 ± 190	1027 ± 190	8.11
14	41°09'S	71°18'W	34271	66.1 ± 8.2	936 ± 52	1002 ± 52	2.92	36.0 ± 10.0	705 ± 81	741 ± 82	2.16
15	41°09'S	71°18'W	30774	65.5 ± 1.9	451 ± 68	516 ± 68	1.68	66.0 ± 4.0	566 ± 125	632 ± 125	2.05
16	41°01'S	70°16'W	31753	16.0 ± 12.0	89 ± 47	105 ± 48	0.33	22.4 ± 12.0	95 ± 37	118 ± 39	0.37
17	38°55'S	69°14'W	32662	11.5 ± 0.1	523 ± 47	534 ± 47	1.64	27.0 ± 5.0	396 ± 67	423 ± 67	1.30
18	39°01'S	67°34'W	30074	22.8 ± 8.6	531 ± 28	554 ± 29	1.84	25.0 ± 12.0	606 ± 131	631 ± 131	2.10

Fe_T is the mass percentage of total Fe in the bulk sample.

^a Samples 1 to 11: top soil ; samples 12 to 18 : volcanic ash.

^b Simplified BCR scheme.

^c Continuous flow.

^d SD: All standard deviation for $n=3$ replicates except sample#7 $n=6$ replicates.

fluxes of dust/ash to the ocean and to collect samples for characterizing these materials in terms of mineralogical/chemical/isotopic composition and grain-size distribution [19]. Additionally, we currently have more than 50 top soil samples collected from the “arid diagonal” of SSA which are being characterized using similar approaches. Top soil samples, representing the most important potential dust sources in this part of the globe [19,29,30], were collected from the first 5 cm of the surface of arid and semi-arid terrains covering a distance of ~4000 km from southern Bolivia (~21°S) to Tierra del Fuego (~53°S). For this work we selected 11 top soils samples representing the three main dust sources in southern South America and 7 volcanic ash samples from recent Andean volcanic eruptions (Hudson, 1991, Chaitén, 2008, and Puyehue, 2011) (Table 1). Samples represent diverse environmental and geological setting ensuring different chemical and mineralogical compositions.

Samples were dried overnight at 40 °C before weighing [31]. It was observed that during long range transport atmospheric dust particles of up to 70 µm can be carried over long distances from the source (> 2000 km) [19]. Furthermore, the solubility of iron in sediments is likely controlled by the particle-size and the mineralogical composition [32]. The selected samples were sieved with a 63 µm plastic mesh.

2.4. Procedure of the simplified sequential extraction (sBCR) scheme

Iron availability was determined in the selected samples by means of a sequential extraction of metals (BCR) which consist of four-step procedure [26]. In the first stage, the exchangeable fraction of metals is released from sediment and represents, according to the authors, the most bioavailable portion. The second stage released the reducible fraction of metals (e.g., bound to iron/manganese oxides). Metals from this fraction of the sediments can be released in nature through small changes in the redox potential (*Eh*). Bearing in mind that the oxidizable (stage 3) and the residual fractions (stage 4) are considered not readily bioavailable and non-available respectively, in this work we used a simplified BCR extraction scheme (sBCR) by using only steps 1 and 2 [33].

Following the BCR protocol [28], in the first stage of extraction 1 g of dried sample was weighed into a PTFE centrifuge tube and 40 mL of solution ‘A’ was added. This mixture was shaken at 30 rpm for 16 h at 22 ± 5 °C. After this time, the mixture was centrifuged at 3000g for 20 min; the supernatant was removed and then stored in a polyethylene bottle at 4 °C until analysis. The solid residue was rinsed twice and then shaken for 15 min with 20 mL of de-ionized water each time. In the second step, solution ‘B’ was added to the residue and the procedures was repeated as described above. In order to eliminate sources of variability, each batch of extractions involved at least three replicates and a blank.

2.5. Procedure of the continuous flow method

Fig. 1a, shows a scheme of the continuous flow system used in this work. Stream of Milli-Q water (pH~5) passes through four reactors (three replicates of the sample and one blank) during 20 min. The column for blank was prepared in identical conditions as the rest of the columns but without sample. It was observed that this time was enough for removing the easily available Fe from sediment/ash (Fig. 2). This agrees with previous similar studies on dissolution rates of Fe from dust showing that the highest rates are obtained in the first 10 min [15]. During this time, eight aliquots of 200 µL were taken at the outlet of the system. After this time, the selection valve (V) was switched to select the following solution (HNO₃ 1%; pH~2.0) which passed through the system during 120 min. In this case, twelve aliquots of solution of

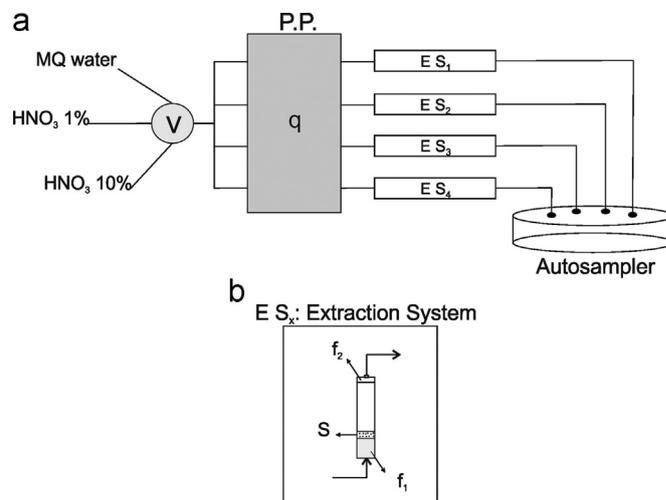


Fig. 1. (a) Scheme of the continuous flow system for dusts Fe solubility measurements. P.P.: Peristaltic pump; q: flow rate; V: selection valve; ES: extraction system (ES₁, ES₂, ES₃: replicates of sample; ES₄: blank); (b) SE_x: PTFE column; S: sample; f₁: filter of cellulose acetate tow; f₂: filter membrane (0.45 µm).

each replicates and the blank were collected at the end of the system. The same procedures were repeated by using HNO₃ at 10% V/V but the use of HNO₃ 30% V/V was discarded because it represents a very aggressive medium for the proposed objectives.

3. Results

3.1. Optimization of the continuous flow system

The CF method is inspired by those proposed by Desboeufs et al. and Jimoh et al. [15,34]. The first one employed an open-flow reactor with a single step extraction using de-ionized water acidified with H₂SO₄ to measured Fe dissolution rates in a Saharan loess sample. The second one employed flow injection analysis (FIA) developing a four-stage extraction scheme, using first de-ionized water and then nitric acid in sequences of 1, 10 and, 30% V/V (acid scheme). Jimoh et al. [33], compared results obtained for six metals (Fe not included) extracted from two standard reference materials using the same FIA system and the same reagents as the used in the two first stages of the standard BCR method. In their experiments also the same FIA system was used with an acid scheme. They concluded that whatever process they use (i.e. BCR, simplified BCR or acid scheme), the three methods give approximately the same information about metal availability.

The CF system used in this work was optimized by a univariant method; those values of each variable that have the maximum signal and a high analytical reproducibility were considered the best values. A top soil sample from a Patagonian ephemeral lake (Sample 7, Fig. 2a) was used as a control sample for the optimization of the system. The length of the column was tested between 50 to 160 mm (reactor SE_x, Fig. 1b) and different inner diameters were proved (3, 5, and 8 mm). After several trials, was observed that the appropriate inner diameter and longitude for ES_x was 5 mm and 140 mm, respectively. It was observed that longer reactors increased the pressure in the system and promoted loss of material in the tubing connectors. In order to avoid the loss of sediment and to obtain a clear solution for subsequent GFAAS analyses, the reactor was sealed at both ends (f₁ and f₂, Fig. 1b). For the inlet section (f₁), different materials were tested as sealants; cotton, spun glass and cellulose acetate tow [35]. The conclusion is that cellulose acetate tow is the best suited for the experiments. In order to minimize the background, cellulose acetate tow was

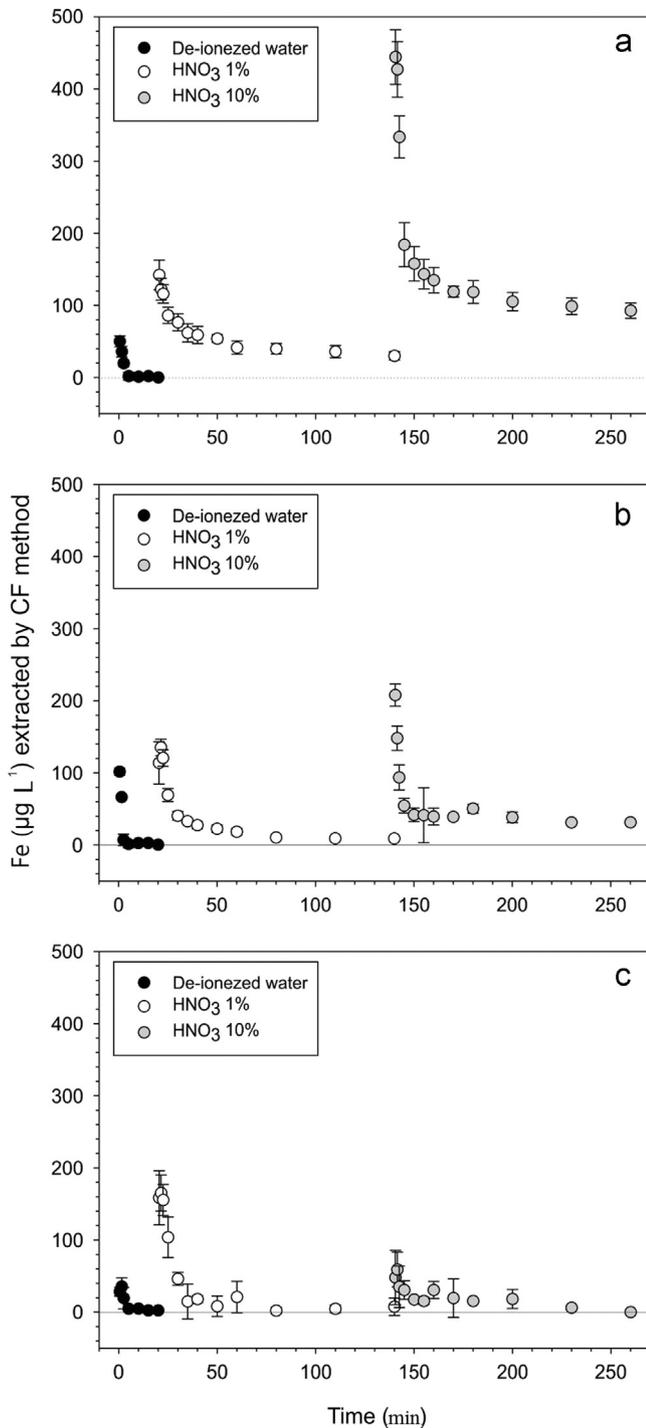


Fig. 2. Examples of Fe dissolution from top soil samples (a) and (b) and volcanic ash (c) using a continuous flow system. Error bars represent the standard deviation of 7 replicates (a) and 3 replicates (b) and (c).

previously washed with HNO₃ 5% and rinsed several times with de-ionized water. For the outlet section (f2) was employed commercial filters of 0.45 µm membrane, 13mm diameter (Millipore). The flow rate of the extracting solution was tested between 0.5 and 1.8 mL min⁻¹ and it was concluded that the best flow rate is obtained at 1.0 mL min⁻¹, considering the reproducibility and higher sample throughput.

Different masses of sample inside the column were tested between 2 and 10 mg. The optimum amount finally used for each

experiment was ~5 mg because it was the lowest amount of sample that provides reproducible results.

Aliquots of 200 µL of emerging solution were collected into PTFE wells. The selection of each extracting solutions is performed by a selection valve (V) (see Fig. 1a).

3.2. Reproducibility of the continuous flow method

The uncertainty of the CF method was compared with the uncertainty derived from the standard method (sBCR). The reproducibility (RSD) was estimated from seven individual experiments by applying the standard and the CF methods on sample 7 (Table 1). The replication was conducted on seven different days in a span of two years. For all steps, results show that the standard method has a RSD range between 6 and 19% while the uncertainty of the CF method ranges between 8 and 22% (Fig. 2) indicating that the proposed method has very good reproducibility, even considering that these samples. Moreover, it is important to highlight that in the period in which the study was made, many changes have occurred; e.g., temperature changes, changes of reagents for preparation of standards, changes of lamps and graphite furnaces in the GFAAS, etc.

3.3. Validation of the continuous flow method for Fe determinations

The same group of samples used for the sBCR method was also employed to evaluate the continuous flow (CF) method. Data of Fe extracted normalized to the total Fe concentration of each sample (%) from both methods were compared by using a *paired t-test* analysis [36,37]. In this test, differences between the paired data are considered and the mean value should not differ statistically of 0. A value $t_{\text{calculated}}=0.15$ was obtained and compared with a tabulated value $t_{(17,0.05)}=2.11$. The test indicates that as $t_{\text{calculated}}$ is much less than the tabulated value, the null hypothesis ($H_0: \delta_0=0$, δ_0 is the ideal difference) cannot be rejected at 0.05 significant levels. Therefore, it is concluded that there is no significant difference between both methods for the quantification of easily available iron in sediment/ash samples.

On the other hand, a *joint hypothesis test* for slope and intercept was applied to the group of data [36]. In Fig. 3 (inset 'a'), the residuals of Y versus X variable are represented. Data indicates that the residuals are randomly scattered within a horizontal band with similar number of positive and negative values. The random

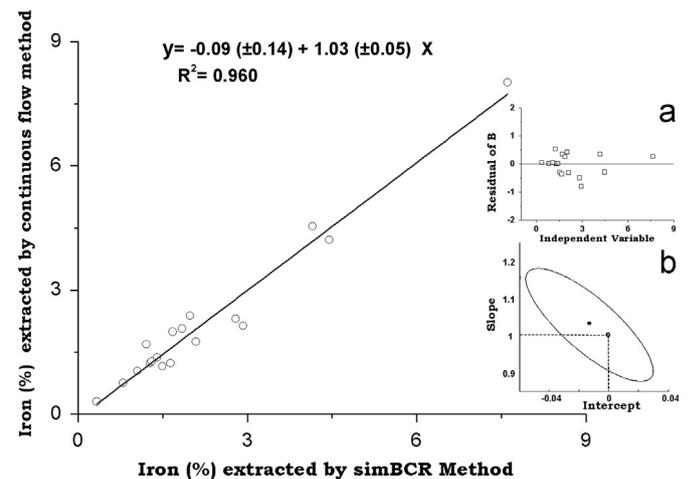


Fig. 3. Comparison of the percentage of Fe extracted from sediment/ash by means of a continuous flow (CF) and a simplified BCR (sBCR) methods. Data indicate a significant correlation between both methods ($p < 0.05$). Statistic analyses (insets (a) and (b)) further indicate no significant differences between the involved methods.

sequence of positive and negative residuals point out the goodness fit with the lineal model. On the other hand, when the methods give the same results ideally, when regression analysis is applied the slope of the regression line should be 1 and the intercept should be 0. The existence of random errors leads to random deviations therefore, it must be statistically demonstrated that the slope and intercept estimated by the fit do not differ statistically of 1 and 0, respectively. A value $F_{\text{calculated}} = 2.51$ was obtained and the tabulated value is $F_{(0,05,2,16)} = 3.60$. As $F_{\text{calculated}}$ is lower than the tabulated value $F_{(0,05,2,16)}$, the null hypothesis $H_0: \beta_0 = 0$ and $\beta_1 = 1$ (β_0 , ideal interception and β_1 ideal slope) cannot be rejected. This result indicates that the CF method can be used for studying Fe dissolution from sediment/ash samples with a confidence level of 95%. In Fig. 3 (insets 'b'), the joint 95% confidence region obtained for β_0 and β_1 is shown. Point (0,1) lies within this region and it can be considered that the slope is 1 and the interception is 0.

4. Discussion

In order to obtain the amount of Fe released during the entire CF experiments, each dissolution curve (see the examples on Fig. 2) was integrated for each stage and normalized to the corresponding mass of sediments. Results of Fe extractions using both techniques can be seen in Table 1. Data indicate that after 140 min of a continuous flow with de-ionized water and HNO₃ 1% it is possible to match the total Fe concentration obtained from the sBCR method which is referred to as the most available metal fraction. Clearly, steps 3 and 4 used in the scheme original [34] are not necessary to evaluate the most mobile Fe fraction on sediments and volcanic ashes.

The time span of 140 min used during the CF experiments is within the range considered typical for weathering by rain and cloud water [15]. Also, the final solid/liquid ratio used in the experiments was 36 mg L⁻¹ which is consistent with the range observed in cloud conditions [22]. For most of the samples, we observed a fast Fe dissolution after 30–40 min of sediment contact with HNO₃ 1%. After this time the dissolved Fe concentration decreases at a slower rate (see some examples on Fig. 2a–c). Shi et al. [7] indicate the existence of an Fe pool that may consist of crystalline Fe oxide phases (i.e., goethite and/or hematite) which can release Fe for longer time period at a very slow rate (could be the case of sample 7 in Fig. 2a). Other cases (for example sample 3 and 17 in Fig. 2b and c) indicate that after 30–50 min of sediment contact with HNO₃ 1%, Fe concentration is close to zero. This is more evident in volcanic ash samples where glass shard is the dominant phase and Fe oxide phases are almost absent [38] (Fig. 2c).

Table 1 shows that the total Fe content in the studied materials ranged between 1.2 to 6.3%, similar to the range of values found in dust from different source regions [11,39] and highlights the representativeness of the materials used in the experiments. Data indicate that no correlation exists between the amount of available Fe released in both experiments and the total amount of Fe in top soil and ash samples. The percentage of extracted Fe from total Fe obtained by the two methods ranged between 0.3 to 8.0% for ash samples and between 0.8 to 4.5% for top soil samples. Using ammonium acetate (pH=4.7) as extracting solution, Baker et al. [40] obtained similar values from aerosol samples collected in the South Atlantic ocean. Furthermore, the dissolved Fe concentration relative to the total Fe contained in the bulk sample obtained by means of step 1 (0.05%) and step 2 (2.1%) (not shown in Table 1) are comparable to the values obtained from Saharan sediments using similar approaches [15,41].

The mean Fe released in step 1 represents 4% (sBCR) and 3.4% (CF) of the total amount extracted for each method. However,

individual analysis of data indicate that sediment samples 1 to 6 show Fe values systematically higher after de-ionized water treatment compared to the amount released using acetic acid (Table 1). In general, an opposite situation is observed for sediment/ash samples collected from Patagonia (i.e., samples 7 to 18). It is worth indicating here that surface sediments from this region are highly contaminated with volcanic ashes [42]. Comparable results were found in similar works [33,43,44]. Possible explanations for this could be associated to readsorption problems using batch experiments [43] and/or differences in the composition of the investigated materials [33]. Conclusions from these works can also be relevant to our results. However, it must be emphasized that readsorption problems in the CF method should be much less important than in sBCR (batch systems) because extraction time is greatly reduced and the possibilities of readsorption are minimized [43]. Moreover, step 1 of both methods achieved different results with a clear geographic control, suggesting that the compositional characteristic of the samples prevails over the methodological aspect. Ongoing investigations on the physical/chemical and mineralogical composition of the investigated samples will help to better constrain these observations.

4.1. Implications of the proposed continuous flow method for the study of Fe dissolution in atmospheric dust and volcanic ash

De-ionized water and HNO₃ solutions are common reagents available in laboratories, do not promote matrix effects [34] and are widely employed in studies of metal dissolution from atmospheric dust/ash [5,22] and citestherein. Several works have employed de-ionized water which has similar pH to that of non-acidified cloud water. However, this extracting solution has no buffer capacity and important pH changes are expected when batch experiments using dust/ash samples with different mineralogical characteristics are studied. Moreover, this requires that large amounts of water are employed during dissolution experiments [22]. The continuous flow methodology should minimize this problem as solutions are continuously renewed throughout the process.

Probably the most important chemical changes during atmospheric processing is the change of pH in the water droplets surrounding dust particles. In the atmosphere, the presence of SO_x and NO_x gases can be formed as a result of pollution and/or from natural processes. As the water droplets become saturated with CO₂ these gases will dissolve decreasing the pH of the water droplets [22]. According to thermodynamic modeling a pH of 2 or lower is often expected in the dust surface due to coating of HNO₃ and H₂SO₄ [45,46]. Similar pH values are expected during volcanic ash plume process [38]. Other important atmospheric processes promoting Fe dissolution from mineral dust include the photo-reduction and the aqueous complexation and chelating effect of organic ligands. The increase of Fe dust solubility in presence of organic species is of the same order of magnitude as the increase solubility of this metal by reactions with acidic species (HNO₃ or H₂SO₄) and by photochemical processing [47]. Although each potential synergetic effect of the different atmospheric process need to be estimated, a solution of HNO₃ 1% as used in the CF method is useful for examines the pool of soluble Fe that can be released from dust during cloud processing including the generation of acidic conditions, photoreduction effect and the presence of organic ligands.

5. Comments and conclusions

The solubility of Fe in continental dust and volcanic ash is a key aspect for developing a better understanding of the marine cycle

of Fe indirectly through its significant influence on phytoplankton growth and the carbon cycle. One main concern during dust/volcanic ash monitoring program is the restricted amount of material available for chemical/physical characterization of atmospheric particles which in some cases could represent dust storms or volcanic eruptions that ultimately can reach and fertilize extensive HNLC (High-Nutrient Low-Chlorophyll) oceanic regions. As a consequence of the large amount of sediments needed for following up the recipe of the diverse published techniques, most of the studies that focus on this issue usually employ surface sediments as surrogate of dust. Furthermore, dust Fe solubility reported in the literature varies across 3–4 orders of magnitude. This variation is not only explained by the employment of heterogeneous materials but also because different procedures are used in dust Fe solubility measurements (e.g., [12]).

The continuous flow method validated here can be used for the standardization of dust Fe solubility studies. The method was successfully tested on ~5 mg of different kinds of top soils and different volcanic ash samples. It can be used with confidence in real dust/ash samples. This method attempts to mimic the mechanism of Fe dissolution during cloud processing prior to the contact of sediment/ash with oceanic waters. The advantages of this methodology are that use common reagents available in many laboratories and do not promote matrix effects. It allows dissolution studies with small amount of samples and with high reproducibility. Avoids the propagation of errors due to the automatization of the process. Cross contamination and risk of personal procedural errors is prevented. Due to the characteristics of the flow systems no re-adsorption problems occur. It is appropriate for kinetics studies of metal's dissolution. The dissolution process can be follow in almost real time which is not possible through batch procedures. It consumes less reagents and time regarding the standard method which requires a minimum of 2 days. This continuous flow method provides similar information which is achieved in less than 3 h. Moreover, reagents, de-ionized water and HNO₃ 1%, ensure the solubility of the knowable Fe pool that could be released during atmospheric processing. This will permit improve the flux estimations of soluble Fe to the ocean.

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