

Atmospheric fluxes of soluble nutrients and Fe: more than three years of wet and dry deposition measurements at Gran Canaria (Canary Islands).

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10 Highlights

- This continuous set of wet deposition (WD) data represents one of the few available in the Atlantic and the first one in the Canary Region for Fe, N and P.
- Solubility of Fe is a function of aerosol origin: highest values in anthropogenic and chemical aging aerosols.
- WD contribute to more than 50% of soluble inputs of limiting nutrients such as Fe and N.
- 15 • Atmospheric nutrients could enhance marine nitrogen fixation mainly in summer months.

Abstract. Dust inputs to the oligotrophic waters of the subtropical North Atlantic are of significant importance to the biogeochemistry of the region. In this work, we present fluxes of particles, soluble elements (H^+ , major ions, Fe and organic ions) in dry deposition (DD) and wet deposition (WD) samples collected between September 2012 and April 2016. Positive Matrix Factorization Model (PMF) indicated four dominant factors influencing the elemental concentrations: marine, crustal and two anthropogenic. Soluble Fe fluxes appear to be affected predominantly by aerosol particle type, with higher values observed at lower dust loading. Although WD fluxes made up only a small fraction of total particle fluxes (12%), they represented an important input of soluble Fe and other nutrients such as nitrate (more than 50% of total amount deposited). This significant contribution to total deposition fluxes may have important consequences for primary production in the surface ocean. Mineral dust is the primary source of soluble atmospheric P to the north Atlantic, which is a region that is already P stressed. Our data show that DD dominates the total flux of soluble P to this area (~87% of the total flux) and it may have a bigger impact in the diazotroph communities during the summer months when the water column is more stratified and nutrient inputs from deeper water are restricted.

30 Keywords

Soluble nutrients

Deposition fluxes

Soluble iron

Aerosol

35 Dust

Eastern subtropical North Atlantic

1 Introduction

Mineral aerosols are the focus of increasing scientific attention due to their direct effect on the radiative budget and their important role in biogeochemical cycles [e.g. *Arimoto, 2001; Hu et al., 2017; Jickells et al., 2005; Zou et al., 2019*]. North Africa contains some of the world's largest sources of soil dust [*J. M. Prospero et al., 2001*], resulting in a westward flow of material over the North Atlantic Ocean accounting for some 30-50% of global dust output [*d'Almeida, 1986; Schütz et al., 1981*]. This mineral dust transport is the principal source of soluble atmospheric P, Fe and Si in the North Atlantic subtropical region [*A.R. Baker et al., 2006; N Mahowald et al., 2008*]. There are some data for aerosol and rainfall chemical composition in some islands in the Atlantic: Tenerife [*Castillo et al., 2017*], Barbados [*J. M. Prospero et al., 1996*], Bermuda [*Tian et al., 2008*] and Cape Verde [*Fomba et al., 2014*]; but only long-term chemical characterisation of total deposition (wet + dry) in samples collected in the Mediterranean [e.g. *Guieu et al., 2010; Vincent et al., 2016*]. On the whole, there is limited availability of island sampling locations [*Kadko et al., 2020*]

Situated close to the African continent and within the “dust belt” [*J.M. Prospero and Lamb, 2003*], the Canary Islands are affected by two large sources of aeolian soil dust: the desert regions of the Sahara and the Sahel. The islands are thus an ideal location to study the impact of African dust episodes in the subtropical North Atlantic Ocean [*Gelado-Caballero et al., 2012*]. Some studies have observed a significant increase in primary production and a change in diatom and mesozooplankton biomasses in the oligotrophic waters to the north of the Canary Islands after a Saharan dust storm [*Franchy et al., 2013*]. This is in agreement with dust addition experiments in which a wide range of impacts was observed across different microbial groups, including phytoplankton, heterotrophic bacteria, and diazotrophs [e.g. *Guieu et al., 2014*]. However, to date there have been few long-term aerosol studies in the Canary Region [*Gelado-Caballero et al., 2012; Rodríguez et al., 2015*], and data available from oceanographic research cruises which have crossed the region, generally as part of larger transects of the Atlantic Ocean, is limited in both temporal and spatial resolution [e.g. *A. R. Baker and Jickells, 2017; Powell et al., 2015*]. Obtaining deposition values from remote ocean regions is difficult [*Anderson et al., 2016*] and research cruises offers only a brief snapshot of aerosol loading [*Kadko et al., 2020*].

The deposition fluxes of atmospheric materials to the ocean have in general been estimated from data obtained via land-based sampling, due to the difficulties associated with the long-term measurement of aerosol concentrations and deposition fluxes at sea [*Duce, 1991; J. M. Prospero et al., 1996*]. Estimates have also been made using atmospheric models [e.g. *Ginoux et al., 2001; Zender et al., 2003*]. Mean trace metal deposition to the ocean is estimated by assuming that trace metals

constitute a fraction of dust mass equal to their estimated abundance in the upper continental crust and by assuming a certain value for fractional solubility [Duce *et al.*, 1991; N M Mahowald *et al.*, 2005]. As a result, comparisons between model results and in-situ measurements have shown significant discrepancies between the predicted and measured fluxes [e.g. Zender *et al.*, 2003]. Satellites have an extensive and spatial temporal coverage which can be used to characterize and quantify dust transport [Yu and Zhang, 2013], but are still unable to detect WD below the clouds [van der Does *et al.*, 2020]. Hence, long-term in-situ sampling together with high quality solubility measurements for metals and other species of interest are key to constraining global dust models and associated estimates of trace metal inputs to the oceans.

In this work, we present a data set of more than 3 years of Total Suspended Particles (TSP), DD and WD fluxes at Tafira station located in Gran Canaria, (Canary Islands). Soluble elements were extracted from the deposition samples immediately following collection and soluble ions and Fe deposition fluxes were used to estimate fluxes to the Region. Values obtained for Fe were compared with previously estimated data in the area given after analysing aerosol samples collected on filters. Moreover, as part of a long-term study of aerosol concentration, composition and deposition fluxes in the Canary Islands, measurements made in this work at Tafira, Gran Canaria, Spain, were used to augment the dataset [Gelado-Caballero *et al.*, 2012; López-García *et al.*, 2017; López-García *et al.*, 2013].

2 Methodology

2.1. Sampling site and collection methods.

Tafira (TF) station (28° 06' N, 15° 24' W; 269 m a.s.l) is an urban background site subject to anthropogenic influence and situated within the marine boundary layer (<1800 m a.s.l) (see Figure 1). A Total Suspended particles (TSP) concentration Time-series has been recorded since 1 December 2003 [Gelado-Caballero *et al.*, 2012; López-García *et al.*, 2013]. High volume (60 m³ h⁻¹) aerosol collectors (MCV, model CAV-A/M) were used to collect aerosol samples for TSP in air on glass fibre filters (Whatman GF/A). TSP concentrations were measured following the procedure described in Gelado-Caballero *et al.* [2012]. To minimize the risk of sample contamination, exposed filters were transferred to individual zip-lock plastic bags immediately after collection and subsequently handled under a laminar flow clean bench.

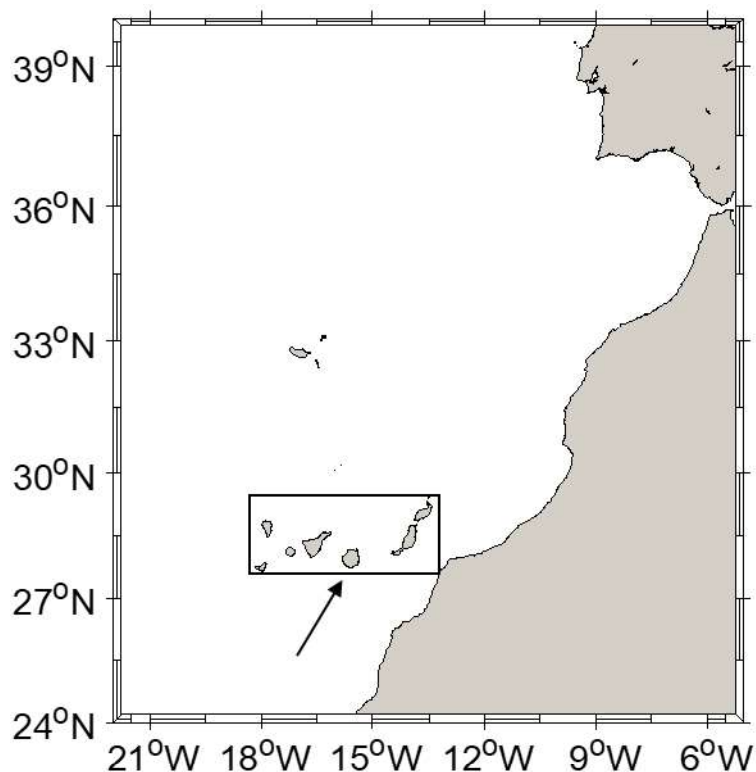


Figure 1. Canary Islands (delimited by the rectangle) and Gran Canaria Island (indicated with the arrow)

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For deposition measurements, an automatic wet and dry sampler (ARS 1000, MTX Italy) with acid cleaned polyethylene cylindrical containers having a surface area of 490 and 660 cm², respectively, was used. The instrument is equipped with a rain sensor. The containers and their lids were cleaned with 10% HCl before each replacement. They were rinsed with ultrapure (Milli-Q) water the same day and dried in a laminar flow cabinet. Containers were kept closed until they were placed in the sampler and the recovered sample container was covered with an acid-cleaned lid during transport to the lab. Dry deposition (DD) samples were collected throughout the period from September 2012 to April 2016 at Tafira, in 92 samples representing average time periods of 11 days; soluble elements were analysed in DD samples from February 2013. Wet deposition (WD) samples were collected after each rainfall over the same period (n=125) representing average sampling periods of 2 days.

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We consider that this deposition method for collecting particles is sufficiently accurate and that no significant resuspension seems to occur. This was shown in the data from an experiment that took place over a 3-year period in which two samplers were used simultaneously, with one of them modified to maintain a constant volume of water during the collection time [López-García *et al.*, 2013]. No relationship was found between dry deposition fluxes and meteorological conditions (such as wind speed), the volume of the deposition container, or the number of days sampled. Although both systems showed

105 consistent results with no significant differences in the estimation of total flux, the use of wet plates increased the uncertainty in the measurements and the complexity of the sampling method.

In this work, DD refers to the deposition of particles or gases from the atmosphere through the direct delivery of mass to the surface (i.e. via non-precipitation) [e.g. *Dolske and Gatz*, 1985] and WD to deposition via rain droplets that scavenge particles and gases from the atmosphere [e.g. *Tai et al.*, 2017]. WD includes ‘rainout particles’ (serving as cloud-
110 condensation nuclei or undergoing capture by cloud water) and ‘washout particles’ (i.e. removal of below-cloud particles by raindrops as they fall) [*Chate et al.*, 2003]. Since atmospheric nitrogen exists in the particulate phase and gaseous species, wet deposition will include both washed-out particulate and gaseous nitrogen.

2.2. Sample processing and chemical analysis

The collected aerosols were quantified by gravimetry after filtering. Membrane filters were dried and weighed to an accuracy
115 of ± 0.01 mg (using a Sartorius CP225D analytical balance). They were washed with 0.1 M hydrochloric acid (Suprapure, Merck) prior to use. The weight of particles collected in the filters was used to estimate the deposition during the sampling period.

For DD samples, 150 mL of Milli-Q water was added to the bucket to try to wash all the particles deposited on the walls. The bucket was placed in an orbital shaker for 15 minutes to extract all the soluble elements, then a portion of the sample
120 was used to measure pH with the rest filtered in an acid-cleaned Millipore Sterifil filtration system fitted with a Nuclepore filter (47 mm diameter and 0.2 μm pore size). WD samples were filtered and analysed immediately following the rain event and the same filtration method was used. The aqueous sample collected in the system after filtering was divided and placed in different acid cleaned bottles for soluble major ion analysis, nanomolar nutrient analysis and Fe analysis. After taking the sample for analysis, the portion used for pH measurements was filtered. To ensure all particles were collected, more Milli-Q
125 was used to rinse the containers and that sample was also filtered. IC samples were measured after collection, nanomolar nutrient samples were frozen (-20°C) until analysis and Fe samples were acidified to pH ~ 1.8 by the addition of $2 \mu\text{L mL}^{-1}$ HCl (Panreac Hiperpur Plus grade).

The pH of unfiltered samples of wet and dry deposition was measured with a combined electrode (Aquatrode Plus, Metrohm) at 25°C . The electrode was calibrated with single-use sachets of buffer solutions pH 4, 7, and 9 (Metrohm),
130 traceable to primary pH value reference materials of the NIST and the PTB, with a calibration slope $> 97\%$. The pH measured in the DD suspensions in Milli-Q water does not reflect that of any liquid water contained in the DD particles and is used here only as an important parameter for the chemical characterization of the DD suspensions in line with that of the WD solutions.

Procedural blanks were produced using 150 mL of Milli-Q water and following the same protocol as that for samples. Major
135 ion and nanomolar nutrient values were lower than 3% of the sample values, for soluble Fe values were 4% of mean sample values. No particles were detected in the filters after filtering the blank sample.

Soluble major ions were determined using two ion chromatographs (883 Basic IC Plus, Metrohm), a Metrosep ASupp 4 column for anion separation (fluoride, acetate, formate, chloride, bromide, nitrite, nitrate, phosphate, sulphate, and oxalate) and a Metrosep C4 column for cation separation (sodium, ammonium, potassium, calcium and magnesium) with a detection limit of $1 \mu\text{g L}^{-1}$. Because most of the phosphate concentrations in wet and dry deposition samples were below the detection limits of the IC, a nanomolar nutrient system was used. The nanomolar nutrient system comprising liquid waveguide capillary cells connected to a conventional segmented-flow autoanalyser and using miniaturised spectrophotometers. This approach achieves a LOD of 0.8 nM phosphate. [Patey *et al.*, 2008].

Soluble Fe was measured using a FiALab-3500 flow-injection analysis (FIA) system adapted to measure Fe using luminol chemiluminescence. Toyopeal AF-Chelate-650M resin packed into a 1 cm column (Global FIA) was used for pre-concentration and the reagents and elution acid were passed through 2.5 m of 0.7 mm ID FEP tubing in a water bath heated to 40°C before entering the detector. A custom flow cell was made by coiling approximately 40 cm of 0.7 mm ID FEP tubing inside a custom-made PVC cap with aluminium foil backing. This flow cell fitted directly onto the end of the (Hamamatsu) photomultiplier tube of the FiaLab-supplied detection unit. Stock luminol was prepared by dissolving 120 mg of luminol (Sigma 123072) and 100 mg K_2CO_3 (Sigma P5833) in 5 mL Milli-Q water. Working luminol solution was prepared by diluting 5 mL stock solution together with 60 μL triethylenetetramine (TETA, Sigma 90460) to 1 L with Milli-Q water. 0.96 M NH_4OH and 0.4 M HCl solutions were prepared by dilutions of concentrated solutions (Panreac Hiperpur grade). 0.3 M H_2O_2 solution was prepared by diluting 30% w/v H_2O_2 (Sigma TraceSelect Ultra). A peroxide spike solution was made by diluting 20 μL 30% w/v H_2O_2 (Sigma TraceSelect Ultra) with 10 mL Milli-Q water. The day before analysis, 1 $\mu\text{L mL}^{-1}$ of this solution was added to all samples and standards to ensure any dissolved Fe (II) is oxidised to Fe (III). Samples and standard solutions were acidified to pH ~ 1.8 by the addition of 2 $\mu\text{L mL}^{-1}$ HCl (Panreac Hiperpur Plus grade). Calibration was performed using 6 standards prepared in Milli-Q water containing 0 to 6 nM Fe. Standards were diluted from a 1000 ppm stock standard (Sigma TraceCERT 16596). Samples containing more than 6 nM Fe were diluted until they fell within the range of the calibration standards. Performance of the instrument was periodically verified by measuring GEOTRACES SAFe D1 and D2 reference seawater standards. Calibration standards for these runs were prepared in 0.2 μm filtered seawater. Analysis of reference seawater SAFe D1 (consensus value 0.67 ± 0.04 nM) gave 0.68 ± 0.12 nM and SAFe D2 (consensus value 0.933 ± 0.023 nM) gave 0.94 ± 0.13 nM. Soluble Fe was measured only in samples collected from October 2013 to November 2015.

2.3. Air mass identification

The origin of air masses for each day sampled was interpreted using 5-day isentropic back trajectories (finishing at altitudes of 750, 1500, 2000, 2500, 3000 and 3500 m in 6-hour steps) calculated twice a day (00:00 and 12:00 UTC) using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model [Draxler, 1999; Draxler and Hess, 1997; 1998; Stein *et al.*, 2016] and FNL meteorological dataset. Due to the weather conditions and the time the air masses from the African and European continents take to arrive at the island, we found that using 5-day isentropic back trajectories

170 represented better the origin of the sample collected. This is consistent with other authors in the Canary Region [Alonso-Pérez *et al.*, 2007; Díaz *et al.*, 2006; Gelado-Caballero *et al.*, 2012].

We have considered 4 geographic sectors according to the differences in mineralogy in the soils from the source regions [e.g. K V Desboeufs and Cautenet, 2005; Formenti *et al.*, 2008; Moreno *et al.*, 2006] and the origin patterns detected in soluble and total fractions in the samples collected as the long-term studies carried out in the island [Gelado-Caballero *et al.*, 2012; 175 López-García *et al.*, 2017; López-García *et al.*, 2013]. These sectors are: Sahara Desert (38°-20°N, 18°W-20°E), Sahel Desert (0°-20°N, 18°W-20°E), MAR (maritime aerosol, trajectories over the Atlantic Ocean) and EUR (European and maritime aerosol, trajectories that cross European continent and Atlantic Ocean). Some air masses originating from the Sahel Desert might also cross the Western Sahara Desert.

2.4. Positive Matrix Factorization Model (PMF)

180 We applied the PMF model of the EPA to identify the soluble elements major sources influencing the deposition samples in our station. The model reduces the large number of variables in complex analytical data sets to combinations of species called source types and source contributions. The source types are identified by comparing them to measured profiles. Source contributions are used to determine how much each source contributed to a sample. In addition, EPA PMF provides robust uncertainty estimates and diagnostics [Norris *et al.*, 2014]. The model was run for both WD and DD samples, we 185 assigned the median value to samples with a missing value and the Instrument Detection Limit (IDL) to those below the detection limit. Since we did not have the analytical uncertainty data for each observation we followed the recommendations of Ito *et al.*, [2004] and used 5% of the measured value plus IDL to avoid near zero uncertainty at very low values. The IDL units were transformed to units of flux using an average volume (150 mL), the area of the container (0.069 and 0.049 m² for DD and WD respectively) and the average number of days (1 day for WD and 7 days for DD). We applied 100 bootstrap 190 runs to the PMF base run with the lowest Q value. The final factor profiles were selected by comparing results with previous PCA (SPSS) analysis, running the model to several numbers of factors and examining the distribution of key source tracers across factors. We also selected the best statistical results: minimum Q (robust and true) which are critical parameters for PMF.

3 Results and Discussion

195 3.1 Characteristics of the sampling period.

HYSPLIT back trajectory analysis between September 2012 to April 2016 (see Table 1) showed similarities in frequency and seasonality to previous years [Gelado-Caballero *et al.*, 2012]. Air masses from the Sahara Desert were predominant during winter but represented a high proportion of samples across all seasons. An increase in air masses from the Sahel Desert was detected in summer and autumn. When compared with the long term study in the area [Gelado-Caballero *et al.*,

200 2012] an increase of more than 15% in air masses with a Saharan origin and a reduction in the number of anthropogenic air masses (EUR and MAR) in winter and spring were observed.

Table 1: Seasonal air mass classification using the Hysplit model for the period September 2012 to April 2016. Four origins were used: Marine, European, Sahara and Sahel.

| | EUR | MAR | Sahara | Sahara & Sahel |
|---------------|-------|-------|--------|----------------|
| Winter | 8.86 | 26.32 | 63.71 | 1.11 |
| Spring | 21.96 | 35.01 | 41.84 | 1.19 |
| Summer | 20.29 | 29.35 | 35.87 | 14.49 |
| Autumn | 14.29 | 35.99 | 35.16 | 14.56 |

205 *Winter (December to February-DJF), spring (March to May- MAM), summer (June to August-JJA) and autumn (September to November- SON)

Figure 2 shows values of TSP concentrations and WD and DD particle fluxes from September 2012 to April 2016. Average TSP concentration during this period was $35.5 \pm 55.2 \mu\text{g m}^{-3}$ ($29.6 \mu\text{g m}^{-3}$ geometric mean) with a minimum of $1.7 \mu\text{g m}^{-3}$ and a maximum of $1172.1 \mu\text{g m}^{-3}$. Data in the second and third quartiles were between 19.9 and $42.5 \mu\text{g m}^{-3}$. The average particle flux was $20.1 \pm 20.5 \text{ mg m}^{-2} \text{ d}^{-1}$ in the dry mode and $12.1 \pm 41.0 \text{ mg m}^{-2} \text{ d}^{-1}$ in the wet mode (for days with rainfall). WD corresponded to 11.8 % of the total particle flux collected during this period. Values measured in this work are smaller than those reported previously at the same station for the period 2004-2011 [*Gelado-Caballero et al.*, 2012; *López-García et al.*, 2013], by annual geometric means of TSP concentration from 2004 to 2008 were around $40 \mu\text{g m}^{-3}$ but in subsequent years reduced to around $30 \mu\text{g m}^{-3}$ (see supplementary material Figure S1 for the period 2004-2016). This reduction in the particle concentrations could explain a reduction in DD and WD values compared to previous years (see Figure S2 in the supplementary material). For WD values, an increase was detected for 2016, but it coincided with an increase of the amount of total rain (see Figure S3 in the supplementary material).

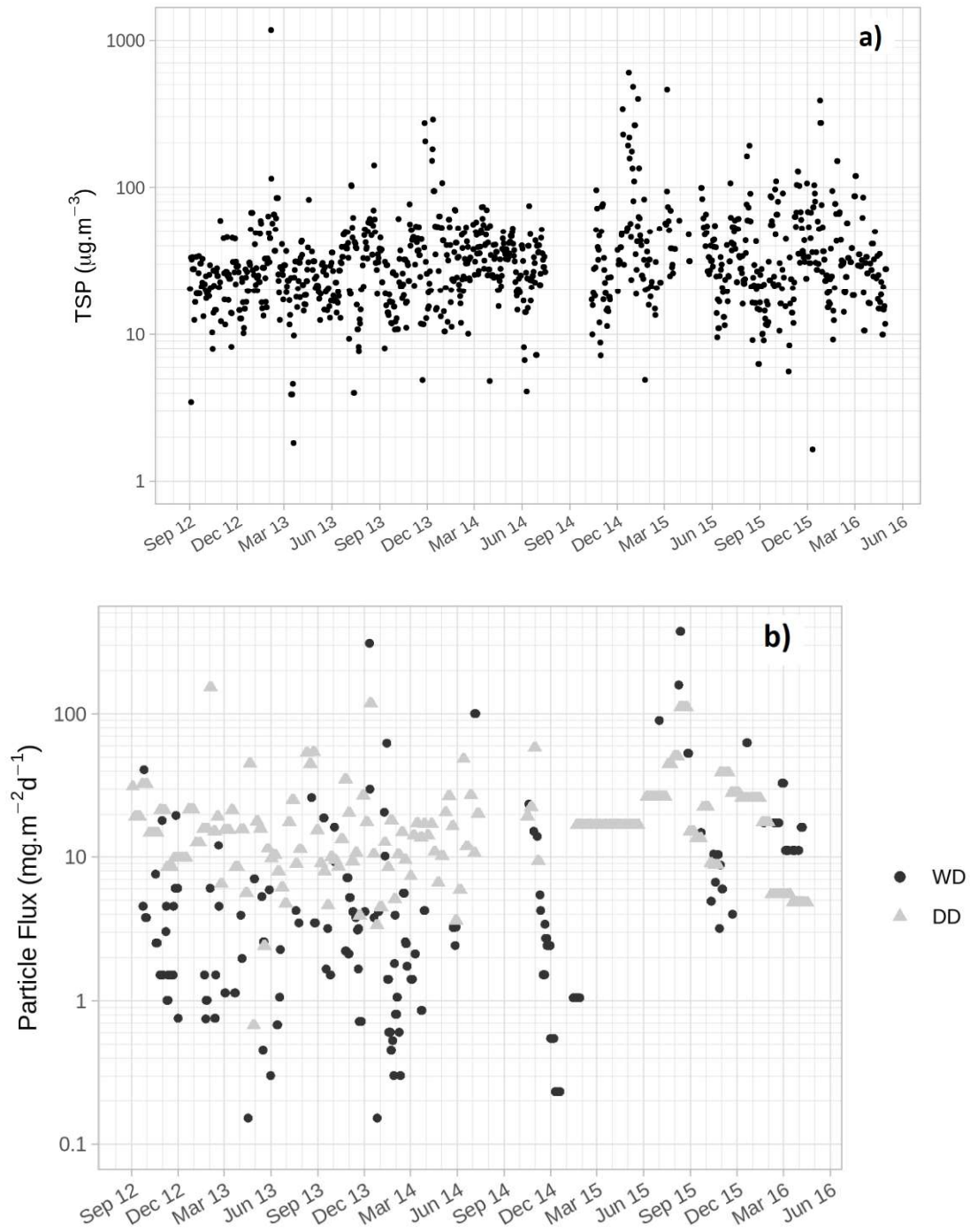


Figure 2: a) TSP concentrations and b) particle fluxes (wet and dry) for the period.

3.2 Characterisation of soluble elements

The average pH in the DD samples was 6.03 ± 0.49 (range: 4.40 – 7.61) with higher values in samples with high dust load. In WD samples, the average pH was 5.29 ± 0.70 (range: 4.16 – 8.83) with higher values in samples collected during an African dust outbreak. This was expected because dust events are considered alkaline events ($\text{pH} > 5.6$) due to the high calcareous content of the Saharan dust. Some studies have shown the increase of pH and calcium content in the rain during dust outbreaks [e.g. *Avila et al.*, 1998].

Average values of soluble element fluxes for DD and WD samples for the whole period are shown in Table 2. In general, WD values show a larger variability compared to DD, possibly due to longer sampling periods in the dry fraction. Dust outbreaks last for 3 days on average while the sampling period for DD samples was 7 days or longer, which is likely to have resulted in some high values during dust events being averaged over the whole sampling period. Moreover, the frequency and intensity of WD events are more variable and samples represented a short period (generally 1 day).

Table 2. Average of fluxes of soluble elements and standard deviation (SD) from September 2012 to April 2016.

Values for WD represent average values for days with rain. Element

| | DD ($\mu\text{mol m}^{-2} \text{d}^{-1}$) | | WD ($\mu\text{mol m}^{-2} \text{d}^{-1}$) | |
|-----------------------------------|--|-----------|--|-----------|
| | Average | <i>SD</i> | Average | <i>SD</i> |
| F^- | 0.28 | 0.24 | 1.24 | 1.84 |
| $\text{C}_2\text{H}_3\text{OO}^-$ | 1.80 | 2.80 | 16.13 | 23.68 |
| HCOO^- | 2.24 | 2.66 | 19.17 | 30.29 |
| Cl^- | 182.62 | 125.60 | 909.31 | 946.68 |
| Br^- | 0.08 | 0.07 | 1.34 | 1.51 |
| NO_3^- | 7.85 | 2.88 | 35.31 | 43.60 |
| SO_4^{2-} | 15.94 | 8.69 | 58.04 | 58.74 |
| nss- SO_4^{2-} | 3.17 | 2.87 | 17.23 | 24.75 |
| $\text{C}_2\text{O}_4^{2-}$ | 0.71 | 0.50 | 0.87 | 1.06 |
| PO_4^{3-} | 0.23 | 0.16 | 0.28 | 0.45 |
| Na^+ | 166.46 | 125.25 | 830.12 | 884.99 |
| NH_4^+ | 2.37 | 2.52 | 58.29 | 75.18 |
| K^+ | 4.70 | 2.50 | 21.40 | 19.43 |
| Mg^{2+} | 17.25 | 12.12 | 81.98 | 89.52 |
| Ca^{2+} | 24.57 | 14.64 | 40.15 | 47.82 |
| Fe | 0.0085 | 0.0059 | 0.0415 | 0.0342 |

Non-sea-salt sulphate (nss- SO_4^{2-}) is estimated by subtracting sea-salt SO_4^{2-} from the total SO_4^{2-} , where the sea-salt component is inferred from Na^+ concentrations and the constant $\text{SO}_4^{2-}/\text{Na}^+$ ratio in seawater (0.252 from Millero and Sohn [1992]). Nss- SO_4^{2-} corresponds to 18% and 33% approximately of the total SO_4^{2-} in the DD and WD, respectively, indicating that total sulphate is mainly associated with marine aerosols.

Values for fluxes of soluble N and Fe are in agreement with those given for the region [A.R. Baker et al., 2013; A.R. Baker et al., 2010] (values of soluble Fe in DD: $0.01 \mu\text{mol m}^{-2} \text{d}^{-1}$). Fluxes of soluble phosphate are higher than reported for the Eastern Atlantic 2b region in the DD fraction of $0.009 \mu\text{mol m}^{-2} \text{d}^{-1}$ [A.R. Baker et al., 2010] and higher than those reported in Barbados for the WD fraction of $0.021 \mu\text{mol m}^{-2} \text{d}^{-1}$ [Zamora et al., 2013]. However, the data in Baker et al. [2010] represent the average of a limited number of cruises (spaced over several years) and over a large area, where the dust and P concentrations were lower than those measured in this work. Moreover, Baker et al. [2010] values of deposited elements are estimated from aerosol samples collected on filters and using a model which incorporates wind speed and the effect of relative humidity on particle growth to calculate velocities [Slinn and Slinn, 1980] which may further explain the differences from this work. In Zamora [2013], samples were collected in the western Atlantic, where the observed dust concentration is likely to be lower than in the east owing to the increased distance from the dust sources.

Although WD fluxes constitute a small fraction of total particle fluxes, it represents a significant input of soluble elements such as Fe and nitrate (54.5 and 54.4 % respectively) (see Figure 3 for monthly deposition fluxes). One possible explanation could be the capacity of rain to scavenge finer particles, resulting in an increase in the soluble fraction for some chemical species that have significant anthropogenic sources. Numerous studies have noted the importance of scavenging (wash-out) in determining the final chemical composition of rainwater [K Desboeufs et al., 2010]. The low pH in the rain will increase the input of dissolved inorganic elements like phosphates and soluble Fe to the surface waters from the dust having a significant effect in the ocean biogeochemistry [Korte et al., 2018; Ridame et al., 2014].

For other elements such as phosphate and oxalate DD inputs are more important, showing that these elements are more related with the origin which in this case is crustal. These elements have a positive correlation with the particle fluxes (Pearson correlation for Oxalate were 0.87 and 0.4 for WD and DD, respectively; for phosphate were 0.53 and 0.57 for WD and DD, respectively). For more information, all monthly fluxes are included in Mendeley Data repository [Lopez Garcia et al., 2020] which were calculated by summing the daily flux values obtained in this work.

When comparing soluble Fe fluxes obtained in this work with values estimated from samples collected on filters at a higher altitude station in the island [López-García et al., 2017], lower values were registered for DD. These differences might be due to the large uncertainties of values from deposition velocities (Vd) and percentages of solubility applied for Fe. A wide range of values for the percentage of soluble iron have been reported (0.001-90%) possibly due to a combination of factors including mineralogy, composition and aerosol origin [A.R. Baker and Croot, 2010; A.R. Baker and Jickells, 2006; Shelley et al., 2018]. To illustrate the importance of the accuracy of the parameters used to calculate fluxes of Fe to the ocean, we also estimated the flux of soluble Fe using deposition velocities given by Duce et al. [1991] for large (2 cm s^{-1}) and small (0.1 cm s^{-1}) particles and using the average monthly TSP concentration measured in this work for the same sample period as the DD

samples. We also considered that total Fe is 4% of total dust [Gelado-Caballero *et al.*, 2012] and the solubility of Fe is 1% for larger particles and 10% for smaller and more anthropogenic influenced particles [López-García *et al.*, 2017] which is in good agreement with previous work [Bopp *et al.*, 2003; Wu and Boyle, 2002]. When comparing values obtained in this work with model estimation it seems that the values given by the model overestimate the amount of soluble Fe deposited (See
275 Figure S4-a in Supplementary Material). The same tendency was detected in our WD values when comparing with estimates following the method of Duce *et al.* [1991] (See Figure S4-b in supplementary material). Modelling wet deposition processes is difficult [Rasch *et al.*, 2001], but values presented here show the need for more experimentally determined wet and dry deposition data, of which there are currently very few [e.g. Sarthou *et al.*, 2003] and collection in the eastern tropical North Atlantic on cruises is further challenged due to the low precipitation rate [Powell *et al.*, 2015]. This seems to be particularly
280 important in this study area where our results suggest that WD of soluble Fe represents more than half of the total deposition, which is in agreement with other values reported for the North Atlantic Region. Baker *et al.*, [2013] calculated that soluble iron in the wet fraction represented more than 60% of the total input of soluble deposition in spring and autumn months, and a similar result was reported by Powell *et al.*, [2015] for autumn months but not for the rest of the year, possibly as a result of the low precipitation rate in the area and, thus, less probability of experiencing a rainfall event during the cruises.

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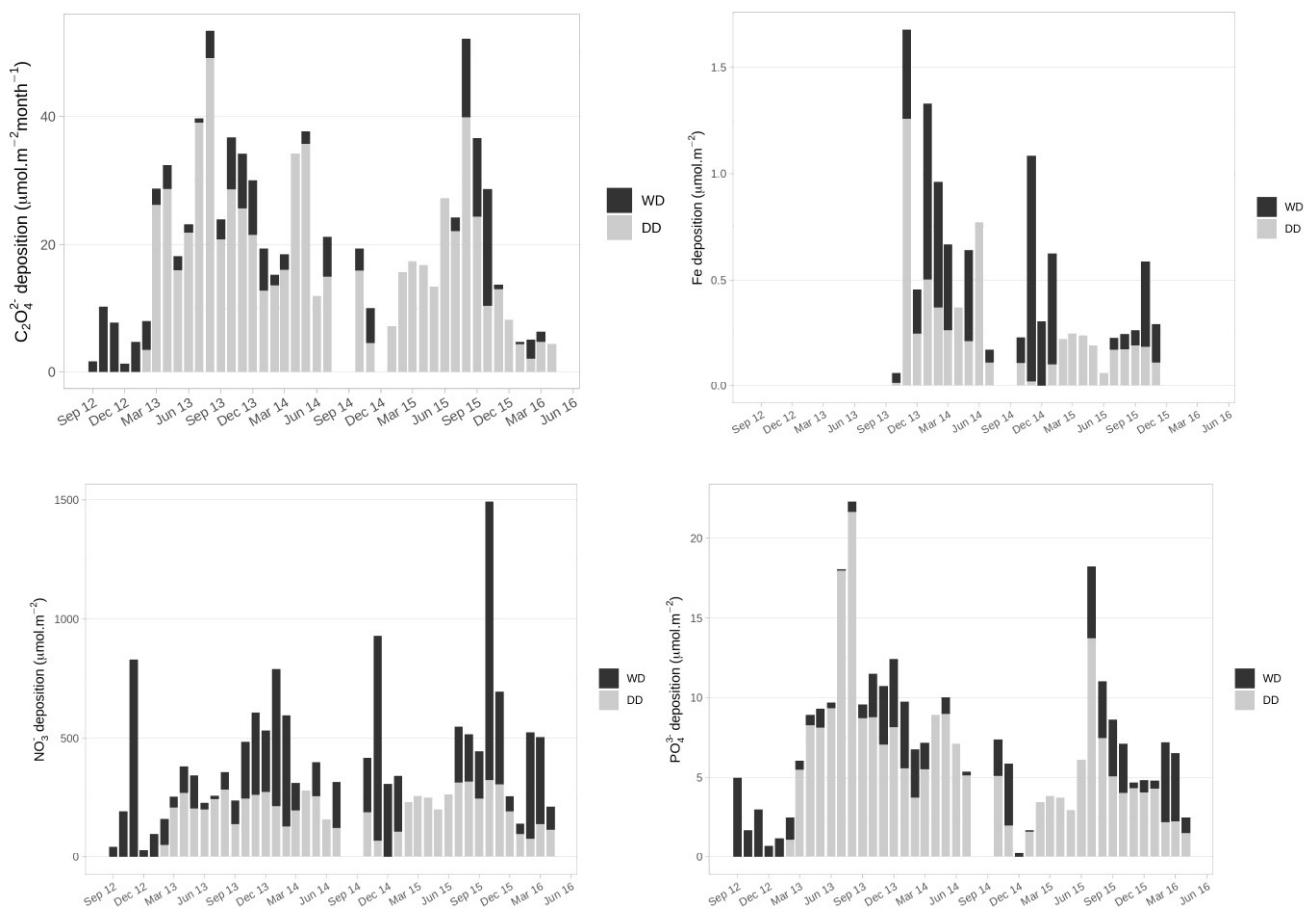


Figure 3. Monthly fluxes of soluble elements: dry deposition (grey bars) and wet deposition (black bars).

*** Soluble Fe deposition were measured only from October 2013.**

****During September 2012 to January 2013 only wet deposition samples were measured.**

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3.3 Source identification

The results obtained with the PMF model in order to identify the sources, were physically interpretable, but some rotational ambiguity still exists since some factors included species that should not be related. This issue has been reported in other works with aerosol samples [e.g. Xie *et al.*, 1999]. Therefore, the commonly used natural physical constraints are insufficient to guarantee a unique, physically valid solution [Henry, 1987]. In this study, rotation was applied and the best solution was chosen after ensuring that no relation between factors existed. Based on the results selected for WD and DD samples, the primary constituents of each possible source are summarized in Table 3.

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Table 3 Composition of each of the factors identified in the PMF.

| Factor | Constituents- DD | Constituents- WD |
|--|--|--|
| 1- Marine | Cl ⁻ (81%), Br ⁻ (63%), NO ₃ ⁻ (24%), SO ₄ ²⁻ (66%), Na ⁺ (88%), NH ₄ ⁺ (51%), K ⁺ (71%), Mg ²⁺ (85%), Ca ²⁺ (24%) | Cl ⁻ (90%), F ⁻ (23%), Br ⁻ (94%), NO ₃ ⁻ (33%), SO ₄ ²⁻ (71%), Na ⁺ (91%), K ⁺ (81%), Mg ²⁺ (88%), Ca ²⁺ (64%), Fe (35%) |
| 2- Crustal | Fe (75%), PO ₄ ³⁻ (91%), F ⁻ (64%), Br ⁻ (21%), NO ₃ ⁻ (37%), C ₂ O ₄ ²⁻ (77%), NH ₄ ⁺ (47%), Ca ²⁺ (76%) | PO ₄ ³⁻ (91%), C ₂ O ₄ ²⁻ (93%), Ca ²⁺ (22%) |
| 3- Anthropogenic/ Local influence | NO ₃ ⁻ (36%), SO ₄ ²⁻ (23%), nss- SO ₄ ²⁻ (90%) | NO ₃ ⁻ (48%), SO ₄ ²⁻ (21%), nss- SO ₄ ²⁻ (94%), F ⁻ (46%), NH ₄ ⁺ (31%) |
| 4- Anthropogenic/Organic acids | C ₂ H ₃ OO ⁻ (84%), HCOO ⁻ (74%) | C ₂ H ₃ OO ⁻ (92%), HCOO ⁻ (90%), Fe (40%), NH ₄ ⁺ (52%) |

*Concentration (in percent) of each species contributing to each factor (in brackets).

**Only values of Factor contributions of elements higher than 20% are included.

315

Overall, the two PMF analyses show four main groups: marine, crustal and two anthropogenic.

The marine factor includes elements from sea spray (Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺). The Na/Cl ratios average 0.90 and 0.93 for DD and WD samples, respectively, indicating that they have a predominantly marine origin. As discussed in previous section, the sulphate component has mainly a marine origin. In our samples, ammonia is predominantly related with the marine fraction in the DD samples while in the WD samples, the anthropogenic and more local origins seem to influence more the results of the model which might be due to the wash-out effect of the rain. Anthropogenic ammonia emissions originate mainly from agriculture activities including soils, fertilizers and domesticated animals waste [e.g. Bouwman *et al.*, 1997], although traffic emissions are also important sources of ammonia in urban areas [e.g. Pandolfi *et al.*, 2012]. In addition, the station is also close to a field where potatoes are grown and fertilizer is applied twice per year during late spring and late autumn. This could also explain the higher concentrations of ammonium during those months.

The crustal factor includes calcium, phosphate and other species that are associated with mineral dust (such as oxalate). Oxalate has been suggested to have both anthropogenic and natural sources of its precursor gases [e.g. Rinaldi *et al.*, 2011] and, due to its polar nature and the alkaline nature of dust particles, these organic acids are preferentially transferred to the aerosol phase [e.g. Falkovich *et al.*, 2004]. In the DD results, nitrate, bromide, ammonia and fluoride are associated with these crustal elements which may indicate adsorption on to the particles during transport. Airborne fluoride exists in gaseous

and particulate forms emitted from both natural and anthropogenic sources (for example, fluoride-containing pesticides
335 contribute to the release of fluoride [Rodgers *et al.*, 2002] and can be transported over large distances [Sloof *et al.*, 1989].
This may explain the dominance of one source over others in the DD factors.

The anthropogenic factor also includes NO_3^- , SO_4^{2-} , non-sea-SO_4^{2-} . The presence of anthropogenic species like sulphate whose
non-sea salt fraction contributes more than 90% to this factor, suggests that it is mainly regional in origin. The most
important anthropogenic sources of sulphate are fossil fuel combustion for energy production, transport, and industrial
340 activities in big cities and their surroundings [e.g. Lee *et al.*, 2011]. In the case of NO_x , it is well known that traffic leads to
elevated concentrations of this component [e.g. Cuevas *et al.*, 2014] and due to the location of the sampling station, locally
produced NO_x could be washed from the air by the rain. Previous studies at station TF show higher concentrations of NO_x
than at a rural station [López-García *et al.*, 2017], principally in filter samples with marine and European origins.

The Organic component includes formate and acetate ions whose precursors may have predominantly anthropogenic and
345 regional origins. Formic and acetic acids have different sources including direct emissions by vegetation [e.g. Talbot *et al.*,
1990], indirect formation via the oxidation of ethane and propene by ozone [Calvert and Stockwell, 1983], via the oxidation
of isoprene [Andreae *et al.*, 1987] and via the reaction of ozone with olefins [e.g. Calvert and Stockwell, 1983]. Soluble Fe is
presented in this component in the WD samples which might indicate the ability of electron donors of organic ligands and a
reductive ligand-promoted dissolution. This organic complexation on iron has been described in previous articles [e.g. Chen
350 and Grassian, 2013; Johnson and Meskhidze, 2011; Paris and Desboeufs, 2013]

In WD Fe appears to be confined to the marine and anthropogenic components, although it might have been expected to
show a greater relationship with other crustal elements like in the DD samples. When the soluble Fe content of particles is
plotted against the total particle flux (Figure 4), it shows that higher solubility values are associated with low dust
concentrations due to a greater relative contribution from anthropogenic sources and /or smaller particles, this same
behaviour has been observed in aerosol samples collected on filters [A.R. Baker *et al.*, 2006; Hsu *et al.*, 2010; López-García
355 *et al.*, 2017]. In WD the percentage of soluble Fe is higher for the same particle fluxes than DD samples. In these samples,
rain water had lower pH when compared to the Milli-Q water used for the DD extraction. Other processes occurring in
clouds and the washing out of smaller particles by raindrops must be considered. This will result in the deposition of smaller
particles with lower deposition velocities and higher solubility value due to either the size of the particles or their
anthropogenic origin and therefore composition [e.g. Pavese *et al.*, 2012]. This process of washing out, to a first
360 approximation, does not appear to be related to the quantity of rain in each event, since when wash ratios are calculated (see
Figure S5 in the supplementary material), it can be seen that as the precipitation quantity increases there is no further
increase in the amount of particles deposited. Therefore, a more thorough study will be necessary to find the variables that
control this process (such as the height of clouds, droplet size, and so on).

365

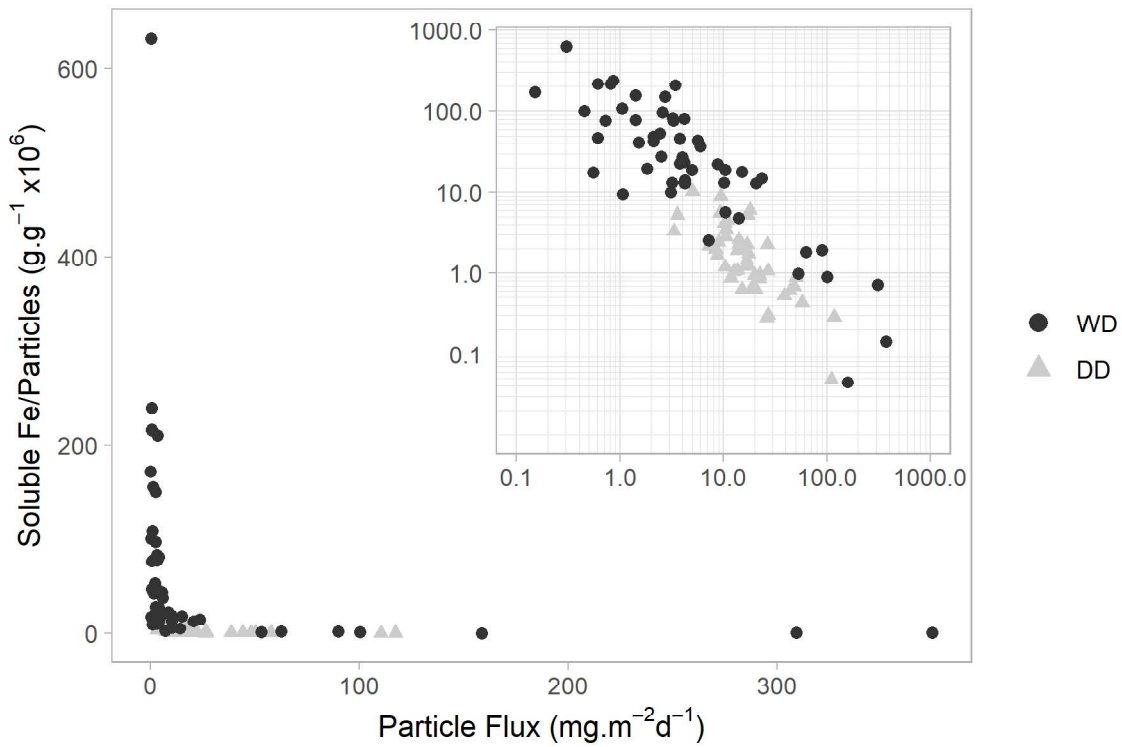


Figure 4. Fluxes of soluble Fe – vs Fluxes of particles for WD (white triangles) and DD (black triangles). The inset shows the values plotted with a logarithmic scale.

370

3.4 Seasonality.

The average seasonal dry and wet deposition of soluble NO_3^- , NH_4^+ , PO_4^{3-} , Fe, Ca^{2+} and oxalate are shown in Table 4. Values for NH_4^+ , NO_3^- , and Fe in DD are in agreement with those given for the North Atlantic Ocean [Powell *et al.*, 2015].

375 However, NO_3^- and NH_4^+ , values for WD were higher than those reported by Powell *et al.* [2015] indicating a possible local anthropogenic influence which is in line with the results of the PMF.

380

Table 4. Seasonal average dry (DD) and wet (WD) deposition fluxes of soluble elements.

| | | Fluxes of soluble elements ($\mu\text{mol m}^{-2} \text{d}^{-1}$) | | | | | | | | |
|------------|-----------|---|-----------------|-----------------|--------------------|-----------------------------|-------------------------|--------|-------|--|
| | | Fe | NO_3^- | NH_4^+ | PO_4^{3-} | $\text{C}_2\text{O}_4^{2-}$ | nss- SO_4^{2-} | N:P | P:Fe | |
| DJF | DD | 0.0115 | 6.73 | 3.25 | 0.15 | 0.43 | 4.68 | 68.11 | 21.14 | |
| | WD | 0.0070 | 8.57 | 11.92 | 0.07 | 0.10 | 15.79 | 575.77 | 5.18 | |
| MAM | DD | 0.0098 | 7.49 | 2.91 | 0.19 | 0.70 | 2.52 | 57.75 | 19.70 | |
| | WD | 0.0026 | 3.19 | 9.78 | 0.03 | 0.05 | 9.76 | 248.86 | 4.51 | |
| JJA | DD | 0.0052 | 8.71 | 1.28 | 0.40 | 1.03 | 3.13 | 39.70 | 78.79 | |
| | WD | 0.0007 | 3.39 | 3.68 | 0.04 | 0.12 | 24.57 | 144.28 | 54.29 | |
| SON | DD | 0.0072 | 8.61 | 2.28 | 0.21 | 0.69 | 3.24 | 61.24 | 29.44 | |
| | WD | 0.0077 | 15.17 | 23.54 | 0.09 | 0.23 | 18.69 | 389.63 | 9.79 | |

385 *Winter (December to February-DJF), spring (March to May- MAM, summer (June to August-JJA) and autumn
(September to November- SON)

Fluxes of PO_4^{3-} and oxalate were at their greatest during summer, in agreement with other measurements in the subtropical
390 North Atlantic region [Powell *et al.*, 2015], and correlated with a crustal factor of the PMF. It is probable that these particles
are deposited predominantly from those that are transported in summer at higher altitudes [Joseph M. Prospero *et al.*, 2014].
The presence of oxalate and other organic acids like formate and acetate will act as electron donors in the photo-reduction of
Fe(III) to the more biologically available Fe(II) [e.g. Siffert and Sulzberger, 1991] and might increase its solubility in
seawater [Smoydzin and von Glasow, 2007].

395 In general, seasonal values of WD for all species were at their greatest during the autumn and winter months, coinciding with
periods of significant rain events. This will have a significant effect in the region since the rain will wash out small particles
and the low pH of the solution will increase the dissolution of nutrients like P and Fe from the aerosol deposited. This effect
has been reported in seeding experiments in oligotrophic waters in the North Atlantic Ocean [Korte *et al.*, 2018] and in the
Mediterranean Sea [Pulido-Villena *et al.*, 2010; Ridame *et al.*, 2014] which showed that ‘wet’ dust increases the
400 concentration of nutrients in the waters. Rain also appears to increase the deposition of other components with a more local
and anthropogenic origin such as NO_3^- , NH_4^+ and nss- SO_4^{2-} which do not have a clear seasonal trend.

In the case of the seasonal values of DD for soluble Fe, the greatest values correspond to periods with the highest
atmospheric particle concentrations and where air masses from the North of Africa are more abundant (Table 1). This
increase in the winter samples can be related with the increase of solubility in samples with a Saharan origin as has been
405 previously described in samples collected in the island [López-García *et al.*, 2017]. As previously discussed, the

anthropogenic fraction exhibits greater solubility and has a strong influence on overall flux values during the raining season (autumn-winter).

When comparing nutrient ratios with Redfield Ratios [Ho *et al.*, 2003], we can see that WD and DD samples are depleted in P during all seasons although this depletion is less during the summer months where there is a higher African dust input that increases P fluxes. N:P ratios are higher in WD than DD showing the washing out rain process and the input from the gas fraction of N. P:Fe has opposite tendency, because the amount of Fe increased in the WD during the raining seasons.

3.5 Implications for the biogeochemistry of the region.

Values of dissolved nutrients measured in the Canary Region are very low: nitrate+nitrite less than 30 nM most of the year (maximum of 120 nM), phosphate around 100 nM year round (samples collected in seasonal cruises to the European Station of Time-Series in the Oceanic of Canary Islands-ESTOC and in the surrounding coastal areas of Gran Canaria Island during 2014-2018, unpublished data); and Fe values less than 0.4 nM [Rijkenberg *et al.*, 2008; Sarthou *et al.*, 2003]. Therefore, these values suggest that N is the limiting nutrient in this region, contrary to suggestions of P-limitation throughout the North Atlantic [Wu *et al.*, 2000] but in agreement with other studies in the Canary Region [Mills *et al.*, 2004; Moore *et al.*, 2008]. Nitrogen limitation of primary production accentuates the potential importance of diazotrophy throughout this region which is co-limited by Fe and P [Mills *et al.*, 2004]. Dust will not only bring N, P and Fe but also other micronutrients including Mo, Mn, V and Co [e.g. Bellenger *et al.*, 2011] and viable airborne diazotrophs that may enhance N₂ fixation [e.g. Rahav *et al.*, 2018].

Consistent with the hypothesis of iron or phosphorus limitation of diazotrophy, N₂ fixation has been observed to respond positively to the addition of Saharan dust to natural water samples from the eastern subtropical Atlantic [Mills *et al.*, 2004; Moore *et al.*, 2013]. Since soluble P is the limiting factor in the dust deposited, we can estimate how much these P inputs obtained in this work ($0.24 \pm 0.16 \mu\text{mol m}^{-2} \text{d}^{-1}$), will represent in the total N₂ fixation in a year in the Canary Region (assuming an 80,000 km² box ranging from 24° N to 30° N and 300 to 400 km off Northwest Africa coast [Ratmeyer *et al.*, 1999]). At a Redfield Ratio N:P of 16:1 [Ho *et al.*, 2003], and assuming that 100% of the P is used to support N₂ fixation, atmospheric deposition could support a N₂ fixation rate of $10.7 \times 10^7 \text{ mol N yr}^{-1}$. This can be compared with values calculated for the region ($\sim 2.9 \times 10^7 \text{ mol N yr}^{-1}$) by Luo *et al.* [2012]. Thus, for this region as a whole, P deposited in dust can support at most 2.5 times the annual N₂ fixation. This number might seem large but there are some factors, which may reduce the availability of the dust nutrients: characteristics of the aerosol (wet or dry deposition, amount of dust, source, composition, aging, particle size [e.g. A.R. Baker and Jickells, 2006; Croot *et al.*, 2004; Shi *et al.*, 2011]), physical and biogeochemical conditions of the seawater (temperature, stratification, turbulence, concentration of ligands, pH [e.g. Gledhill and Buck, 2012]), biological influences from bacteria and phytoplankton and grazing effects [e.g. Barbeau *et al.*, 1996] and possibly the number and status of the diazotrophs.

The inputs of soluble nutrients should have a greater impact during summer months when the mixed layer is shallower and the supply of nutrients from deep waters is impeded by greater stratification. Relationships between *Trichodesmium*, a major diazotroph in the region, blooms in the south of Gran Canaria and dust events during summer have been observed [Benavides and Aristegui, 2020]. However, it must be considered that *Trichodesmium* has patchy distributions based on a variety of environmental controls, in addition to nutrient availability. Among *Trichodesmium* blooms, nutrient assimilation is non-uniform, with physiological differences in Fe and dust scavenging based on morphology.

4 Conclusions

Long-term aerosol monitoring in the Canary Islands reveals the importance of the evaluation of the impact of aerosols on the biogeochemistry of the Canary Basin. Air masses with an African origin represent approximately 50% of all days and are an important supply of nutrients and trace metals to the region. N_2 fixation could be enhanced by the addition of Saharan dust and our estimations showed that it could have a big effect in the diazotrophy mainly in summer months. Also, some evidence supports that dust is a trigger for *Trichodesmium* blooms in the Canary Region.

Soluble elements showed four main origins: marine, crustal, and two anthropogenic. Anthropogenic components represent the effect of the dust transport and adsorption of some components during it and some regional influence. The crustal component includes elements that arrive with the dust and increase their concentration in the soluble fraction when there is an increase in the amount of particles. Organic acids are related with the chemical aging processes which indicates that they are adsorbed on to the dust particles during transport. These components will help to increase the solubility of some elements when acting as electron-donors.

Soluble Fe fluxes appear to be affected predominantly by aerosol particle type, with higher values observed at lower dust loading. Soluble Fe depositions are significant during autumn and winter months when there is an increase in days with rain. The soluble Fe associated with wet deposition represents more than 50% of the total flux when particle deposition represents only 12% of the total flux. Data for the region based on dry and wet deposition flux models tend to overestimate soluble Fe fluxes. Our results suggest that there is a need to apply corrections to the methods used to estimated soluble fluxes as well as give more consideration to the influence of small particles.

Author contribution

PLG and MDGC planned the experiment. PLG, MDP and MDGC collected and analysed samples. All authors contributed with analysis and interpretation of data; and reviewing and editing the final manuscript.

Competing interest

The authors declare that they have no conflict of interest.

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