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Estimating chemical composition of atmospheric deposition fluxes from mineral insoluble particles deposition collected in the western Mediterranean region

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Abstract. In order to measure the mass flux of atmospheric insoluble deposition and to constrain regional models of dust simulation, a network of automatic deposition collectors (CARAGA) has been installed throughout the western Mediterranean Basin. Weekly samples of the insoluble fraction of total atmospheric deposition were collected concurrently on filters at five sites including four on western Mediterranean islands (Frioul and Corsica, France; Mallorca, Spain; and Lampedusa, Italy) and one in the southern French Alps (Le Casset), and a weighing and ignition protocol was applied in order to quantify their mineral fraction. Atmospheric deposition is both a strong source of nutrients and metals for marine ecosystems in this area. However, there are few data on trace-metal deposition in the literature, since their deposition measurement is difficult to perform. In order to obtain more information from CARAGA atmospheric deposition samples, this study aimed to test their relevance in estimating elemental fluxes in addition to total mass fluxes. The elemental chemical analysis of ashed CARAGA filter samples was based on an acid digestion and an elemental analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and mass spectrometry (MS) in a clean room. The sampling and analytical protocols were tested to determine the elemental composition for mineral dust tracers (Al, Ca, K, Mg and Ti), nutrients (P and Fe) and trace metals (Cd, Co, Cr, Cu, Mn, Ni, V and Zn) from simulated wet deposition of dust analogues and traffic soot. The

relative mass loss by dissolution in wet deposition was lower than 1 % for Al and Fe, and reached 13 % for P due to its larger solubility in water. For trace metals, this loss represented less than 3 % of the total mass concentration, except for Zn, Cu and Mn for which it could reach 10 %, especially in traffic soot. The chemical contamination during analysis was negligible for all the elements except for Cd, which has a very low concentration in dust. Tests allowed us to conclude that the CARAGA samples could be used to estimate the contents of nutrients and trace metals in the limits of loss by dissolution. Chemical characterization of CARAGA deposition samples corresponding to the most intense dust deposition events recorded between 2011 and 2013 has been performed and showed elemental mass ratios consistent with the ones found in the literature for Saharan dust. However, the chemical analysis of CARAGA samples revealed the presence of some anthropogenic signatures, for instance high Zn concentrations in some samples in Lampedusa, and also pointed out that mineral dust can be mixed with anthropogenic compounds in the deposition samples collected on Frioul. Results showed that the chemical analysis of CARAGA ashed samples can be used to trace the origins of elemental deposition. The elemental atmospheric fluxes estimated from these chemical analyses of samples from the CARAGA network of weekly deposition monitoring constitute the first assessment of mass deposition fluxes of trace metals and P during intense dust deposition events at the scale of the western Mediter-

anean Basin. The mass fluxes strongly depend on the distance from dust sources and the most intense events, while proximity from anthropogenic sources strongly impacted the mass fluxes of Zn and Cu at Lampedusa and Frioul.

1 Introduction

The Mediterranean Basin is a receptor for the deposition of particles emitted in surrounding coastal urban areas and continents. These deposited particles can have both natural (e.g. Saharan dust and biogenic emissions) and anthropogenic origins (e.g. Loÿe-Pilot and Martin, 1996; Kanakidou et al., 2011). Atmospheric inputs supply as much nutrients as riverine inputs in the Mediterranean and are less confined to coastal waters (e.g. Moon et al., 2016; Richon et al., 2017). They play a significant role in marine nutrient cycles during the Mediterranean water stratification period, i.e. from May to September. This is the case for P and N macronutrients (Loÿe-Pilot et al., 1990; Pulido-Villena et al., 2010) and Fe micronutrients (Bonnet and Guieu, 2006). Saharan dust deposition is also considered an input of trace metals, such as Co, Ni, Mo, Mn, Zn and Cd, for the Mediterranean Sea, which play an essential role in phytoplanktonic activity (Morel and Hudson, 1985). For instance, N₂ fixation and growth of diazotrophs could be controlled by dust inputs of trace metals (Ridame et al., 2011).

The ADIOS programme, based on a network of deposition measurements with a common protocol deployed over the same period at nine stations throughout the basin, provides key information for studying the spatial variability of nutrients and trace metals deposited in the Mediterranean area, but it was limited to only 1 year (June 2001–May 2002) with a monthly resolution that cannot isolate high-deposition events (Guieu et al., 2010). The measured elemental fluxes show a high spatial variability and suggest that the dust-derived Fe deposition is higher in the north-western basin. For P deposition, the measurements seem to indicate a longitudinal gradient with significantly lower values in the eastern Mediterranean Basin, attributed equally to dust and anthropogenic inputs. However, due to the high temporal variability of desert dust events transported over the Mediterranean Basin, it is difficult to conclude much from a 1-year data set of the chemical elements associated with dust. To do that, a long-term and large-scale deposition sampling network is required (Schulz et al., 2012). In order to obtain a long time-series of deposition mass fluxes at several sampling sites, a CARAGA (Collecteur Automatique de Retombées Atmosphériques insolubles à Grande Autonomie) collector has been developed (Laurent et al., 2015) and implemented at five sites in the western Mediterranean region (Vincent et al., 2016). This collector has up to 6 months autonomy without human intervention. To do that, only the insoluble fraction of total deposition is sampled on filters, excluding the soluble

fraction of the deposition, which can be difficult to preserve over months.

Samples of atmospheric deposition have automatically been collected by CARAGA since 2011 at five sites: Le Casset (SE France), Corsica (France), Frioul (France), Mallorca (Spain) and Lampedusa (Italy). Measured total mass fluxes of atmospheric deposition and the weighing and ignition protocols used to quantify the mineral deposition are presented in Laurent et al. (2015) and Vincent et al. (2016). In the present study, we investigate the possibility of using the CARAGA ashed samples to estimate the elemental mass deposition flux of nutrients and trace metals. Firstly, we tested the elemental composition changes during the sampling and treatment protocol of deposition samples with aerosol analogues. Secondly, we estimated the nutrients and trace-metal fluxes of the most intense dust deposition events associated with dust events over the western Mediterranean Basin between 2011 and 2013.

2 Materials and methods

2.1 Sampling of insoluble deposition and total mass measurements

Weekly deposition samples were collected between 2011 and 2013 with CARAGA collectors at five stations in the western Mediterranean Basin presented in Fig. 1. The site positions were selected to cover the western basin by integrating east–west and north–south gradients:

1. Le Casset (44°59′ N, 6°28′ E, S-E France at 1850 m in altitude, rural area, ~170 km from sea shore) – a previous study on the composition of rainwater (Coddeville et al., 2002) showed that this site was highly influenced by the anthropogenic emissions and the crustal sources around the Mediterranean Basin and northern Africa. Other European areas (e.g. Italy) can influence the concentrations recorded at Le Casset.
2. Corsica (43°00′ N, 9°21′ E, France, at 75 m in altitude, 300 m from sea shore) – the chemical composition of aerosol on this site was studied during the ChArMEx campaign (June–August 2013) and the results showed the influence of elemental carbon-containing particles, issued in part from fossil fuel, biomass burning and ship traffic, sea-salt particles and secondary organic aerosol (Mallet et al., 2016; Arndt et al., 2017).
3. Frioul (43°16′30″ N, 5°18′28″ E, France, at 45 m in altitude, in front of Marseille (city of 1.57 million population according to INSEE 2012) – previous dry deposition measurements operated in the Frioul islands have shown, from lipid analyses, a significant contribution of terrestrial particles, plant debris and meat cooking residues in the deposited particles (Rontani et al., 2012).



Figure 1. Location of the CARAGA sampling sites in the western Mediterranean Basin: Le Casset, Corsica, Frioul, Mallorca and Lampedusa.

4. Mallorca (39°16' N, 3°03' E, Spain, at 7 m in altitude, 70 m from the seashore) – this site has never been used for atmospheric studies, so no information on the source influence is available.
5. Lampedusa (35°31' N, 12°37' E, Italy, at 45 m in altitude, ~ 20 m from the north-western coast). The site on Lampedusa is a station for climate observations, maintained by ENEA (the Italian Agency for New Technologies, Energy and Sustainable Economic Development). Various atmospheric parameters are monitored at this station: greenhouse gas concentrations, aerosol chemical and optical properties, total ozone and radiative budget (e.g. Artuso et al., 2009; Becagli et al., 2012; Gómez-Amo et al., 2013). The results show that the PM₁₀ concentrations are influenced by marine and ship emissions to which Saharan dust events in spring are added (Becagli et al., 2012; Mallet et al., 2016). Regarding trace-metal concentrations, Ni and V in the submicronic fraction are mainly due to heavy oil combustion associated with ship traffic (Becagli et al., 2012, 2017).

In the CARAGA collectors, dry and wet deposition are collected by a funnel (0.2 m²) over 1 week starting on Thursday at noon. At the end of the week, the funnel is rinsed with 250 mL of ultrapure water. Rinse water and rainwater pass through an AA Millipore[®] cellulose ester filter with a 0.8 μm porosity in order to collect the insoluble fraction of the deposition. A complete description of the CARAGA collector and sampling network can be found in Laurent et al. (2015) and Vincent et al. (2016). After being brought back to the laboratory, collected filters were ashed following a progressive increase in temperature up to 550 °C in order to destroy and vaporize the filter and organic matters. The mineral deposi-

tion mass, excluding volatile and organic matter, was estimated by weighing the ashed samples (Laurent et al., 2015), and the ashes were stored in acid-cleaned Eppendorf tubes.

From 2011 to 2013, 108 samples corresponding to the most intense weekly dust deposition samples were studied by Vincent et al. (2016), and a Saharan origin was identified for 107 selected samples by using satellite data and air mass trajectories. The selected samples account for 84, 78 and 73 % in mass of the total deposition in Lampedusa (37 samples), Mallorca (21 samples) and Corsica (11 samples), and it contributes for around 50 % in Frioul (21 samples) and Le Casset (17 samples). A complete description of the treatment and selection of samples can be found in Vincent et al. (2016).

2.2 Analytical protocol

In order to further obtain their elemental composition, ashed CARAGA samples were digested using a digestion protocol adapted from Heimburger et al. (2013). About 20 mg of ashed samples were weighed and transferred to a Savillex[™] PFA digestion vessels with 0.5 mL of ultrapure water to avoid the loss of samples. The samples were then digested using 2.5 mL of mixture of Suprapur[®] acid (1 mL HCl 30 %, 1 mL HNO₃ 65 % and 0.5 mL HF 40 %) during 14 h in an air oven at 130 °C in closed vessels. When the digestion vessels were cooled, the acid was completely evaporated on a heater plate. Overall, 130 μL of suprapur[®] HNO₃ and then 13 mL of ultrapure water was added. Finally, the contents of each vessel were transferred into an acid-cleaned 15 mL tube for elemental analysis. The full analysis was carried out in a ISO class 5 clean room with material washed with Ultrapur then Suprapur[®] HCl. At least three blanks (ashed filters without particles) were produced for each set of acid digestion in order to estimate the potential contamination during the protocol.

Analyses were performed with a SPECTRO AR-COS (<http://www.spectro.com>) inductively coupled plasma-atomic emission spectrometer (ICP-AES) for markers of desert dust (Al, Ca, K, Mg, Na and Ti), nutrients (P and Fe) and trace metals (Cd, Co, Cr, Cu, Mn, Ni, V and Zn). Due to digestion with hydrofluoric acid and the high volatility of formed SiF₄, we could not obtain the contents of silicon.

2.3 Test of elemental mass loss during the CARAGA protocol

In order to estimate the change in elemental composition during the CARAGA sampling and treatment protocol, tests have been carried on analogues of typical Saharan dust or soot particles, which were subject to the collection protocol and then ignition in the laboratory.

Wet deposition being the major pathway to solubilize nutrients and trace metals, analogues of typical wet deposition CARAGA samples were made by simulating rainwater containing two kinds of particles: dust and soot, which are the

main insoluble aerosols (Ault et al., 2011). Desert dust samples were prepared from the fine fraction of soils ($< 20 \mu\text{m}$) collected in semi-arid areas of Douz (Tunisia) and Banizoumbou (Niger). The elemental solubility in desert dust varies depending on several factors, the mineralogical composition of the particles being one of the major ones (Journet et al., 2008). We selected these soils because their mineralogical and elemental compositions were well known (Guieu et al., 2010; Paris et al., 2011; Desboeufs et al., 2014a). In addition, they represent two extreme mineralogical and chemical characteristics observed in the dust emission zones of northern Africa, influencing the western Mediterranean atmosphere (Bergametti et al., 1989): the Douz soil is rich in calcium carbonate and clay ($\text{Ca} / \text{Al} = 4.16$ and $\text{Fe} / \text{Al} = 0.51$) and the Banizoumbou soil is rich in iron oxides and quartz ($\text{Ca} / \text{Al} = 0.06$ and $\text{Fe} / \text{Al} = 0.63$) (Formenti et al., 2014). Soot samples are traffic particles collected in a tunnel in Paris. Indeed, black carbon measured in the western Mediterranean is mainly anthropogenic carbon-containing particles from combustion emission (Mallet et al., 2016).

Simulations of rainwater were made by adding $50 \pm 0.2 \text{ mg}$ of particles (fine fractions of soils or soot) into $250 \pm 2 \text{ mL}$ of ultrapure water acidified at $\text{pH} = 4.7$ with Suprapur[®] sulfuric acid. This pH value and the sulfuric acid are characteristics of atmospheric conditions and are commonly used to mimic the release of trace metals from aerosol in rainwater (Desboeufs et al., 2001). After 30 min of contact time and automatic shaking, we reproduced the CARAGA sampling of wet deposition through filters and collected the filtrated solution. The time of 30 min corresponds to the most prevalent average time of rainfall in the western Mediterranean Basin (Rysman et al., 2013). A day (24 h) later, we rinsed the filter holder using $100 \pm 5 \text{ mL}$ of ultrapure water to simulate the rinsing step of the CARAGA protocol. We produced three replicates for each type of particle. The filtrated rinsing water was collected. Dissolved nutrients and trace-metal concentrations were determined in the filtrated simulated rainwater and rinsing water to estimate the loss associated with the soluble fraction during the collection of the insoluble fraction. The dissolved concentrations were analysed with a ICP-AES for major elements: Al, Ca, P, Fe and Ti, and with a Thermo Fisher Scientific[™] Element 2, high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) for trace metals Cd, Co, Cr, Cu, Mn, Ni, V and Zn. Blank values for rainwater corresponding to acidified ultrapure water without soils that passed through the collector ($n = 3$) were subtracted to the measured concentrations.

In order to assess the potential change of the sample elemental composition due to the calcination step, we simulated sampling of rainwater using the Douz and Banizoumbou soils with the above-described protocol but by adding 90 mg of soils. After filtration and rinsing, filters were dried in the oven at 40°C for 2 h and then weighed, about 20 mg of dry soil was collected in a clean Eppendorf tube, the rest

(with filter) was ashed based on the CARAGA protocol, then weighed, and about 20 mg was also collected in an Eppendorf tube. Both of them were digested for analysis by ICP-AES and compared. This test was carried out in triplicates for each soil.

2.4 Estimation of contamination during CARAGA protocol

Using the proposed protocol 107 selected samples were digested and analysed for markers, nutrients and trace metals. In order to estimate the contamination and limit of detection (LoD) of the analytical protocol, nine blanks of CARAGA samples (filters exposed but not collected) were used and processed. Even if the protocol of chemical analysis was tested for 20 mg of ashed samples, the mass of several CARAGA samples was inferior to 20 mg, especially the less intense deposition samples. In this case, the totality of ashed samples was used for acid digestion. The minimum sample mass was 2 mg. The weighing uncertainty was $\pm 0.2 \text{ mg}$. It was not significant (1 %) for samples of 20 mg, but for samples of 2 mg, it could represent 10 % of uncertainty. However, these samples made a low contribution to total annual mass fluxes (Vincent et al., 2016). Therefore, we decided that the uncertainty in the weighing protocol was not significant for annual mass flux of nutrients and trace metals. We compared the lowest concentrations obtained for a 2 mg sample with blanks to check the reliability of measured concentrations (Table 1).

For P, Cr, Cu and Zn, concentrations of blank values were below the limit of detection, so we considered that contamination could be neglected. For elements except Cd, blank concentrations were quantifiable and presented low variability but remained largely inferior to minimum concentrations in 2 mg of CARAGA samples. Cd concentration was inferior to LoD, so we could not estimate Cd content in samples with low mass. For calculations of mass fluxes, we subtracted these blanks values to elemental concentrations obtained in the CARAGA samples. We did not take into account Cd in the following study because of the large uncertainty on its concentrations.

3 Results and discussion

3.1 Estimate of elemental mass loss during the CARAGA protocol

Averages of elemental mass loss and the standard deviation of three replicates for three types of particles (soils of Douz and Banizoumbou, and traffic soot) during the sampling of wet deposition are presented in Table 2. Loss by dissolution during collection and rinsing has been calculated as fractional solubility:

$$S = \frac{\text{Elemental mass in filtered and rinsed solution}}{\text{Elemental mass in initial particles}} \times 100\%. \quad (1)$$

Table 1. Limit of detection (LoD; calculated with three times the standard deviation for nine blanks) and elemental concentrations in blanks and CARAGA samples (in ppb).

Elements		LoD	Mean for blanks	Sample (2 mg)
Marker elements	Al	2.2	2.5 ± 0.7	1395.5
	Ti	0.16	0.11 ± 0.05	73.76
Nutrients	Fe	0.4	0.9 ± 0.1	773.6
	P	6.2	<LoD	157.3
Trace metals	Cd	0.29	0.63 ± 0.07	<LoD
	Co	0.57	0.64 ± 0.19	8.67
	Cr	0.6	<LoD	34.6
	Cu	1.0	<LoD	16.4
	Mn	0.4	0.8 ± 0.1	71.5
	Ni	0.9	1.2 ± 0.3	18.3
	V	0.7	1.1 ± 0.2	22.1
	Zn	0.9	<LoD	36.0

The largest mass losses were observed for major alkali and alkaline earth metals: Ca, K, Mg and Na. Al and Ti, which are the major tracers of dust, presented solubility lower than 1 % for the two dust analogues. The low solubility of Al and Ti makes it possible to use them as markers of sources in CARAGA samples, but it is not the case for the ratios K / Al and Ca / Al typically used to characterize the desert dust sources (Scheuven et al., 2013). For nutrients, the mass loss for Fe (0.11–0.68 %) was lower than 1 % for all types of aerosols analogues, whereas the maximum mass loss of P reached 13.3 ± 2.3 % in soils in Douz. The results on the fractional solubility were in agreement with the background on P and Fe solubility in mineral dust (Anderson et al., 2010) and in black carbon particles (Desboeufs et al., 2005). For trace metals, the mass loss was typically under 3 % except for Zn (4.8–8.8 %), Cu (1.7–6.6 %) and Mn (2.8–10.8 %) for which the solubility was lower than 10 %. In the literature, few data are available on the aerosol fractional solubility in rainwater and in particular for dusty rain, solubility values of Al (0.24 %), Fe (0.06 %), Cu (8.37 %) and Mn (5.62 %) in rainwater in Istanbul reported by Başak and Alagha (2004) are consistent with this study. The solubility values are variable from one aerosol analogue to another: Mn present in the Banizoumbou soil is more soluble than in traffic soot, whereas Cu, Co, Ni, Cd and Zn contained in traffic soot are more soluble than the ones in Banizoumbou soil. The ICP-AES analysis performed on samples before and after the ignition protocol point out that elemental mass loss during the calcination was not significant for tracer elements (Al and Ti), nutrients (P and Fe) and trace metals (Co, Cr, Cu, Mn, Ni, V and Zn).

The tests emphasized that the main change in chemical composition between deposited aerosols and ashed CARAGA samples was due to the loss by dissolution during

wet deposition and by rinsing. The composition of nutrient and trace metals obtained from simulated CARAGA samples were representative of initial dust and soot analogues with a maximum of 13 % of underestimation for P, less than 10 % for Zn, Cu and Mn and less than 5 % for other elements. Tests were carried out for wet deposition. In the case of dry deposition, particles are rinsed and the contact time with water is less than for wet deposition. Thus, the underestimation due to dissolution would probably be lower in the case of dry deposition. The highest uncertainty of 13 % is inferior to the common discrepancy on the deposition fluxes estimated from different dry deposition samplers (Goosens and Rajot., 2008; López-García et al., 2013). To conclude, taking into account the underestimation of the soluble fraction, the CARAGA samples seem to be relevant for estimating the total deposition fluxes of Al, Fe, P, Co, Cr, Cu, Ni, Mn, Ti, V and Zn.

3.2 Chemical characterization of CARAGA samples

After sample analysis, weekly elemental mass fluxes for the 107 deposition samples were calculated from measured concentrations. These samples being associated with deposition of Saharan dust, we checked their chemical compositions with principal component analysis (PCA) and mass ratios X / Al, then compared them with Saharan dust composition in order to validate the use of the CARAGA samples to determine the origin of elemental deposition fluxes.

3.2.1 Principal component analysis (PCA) for 107 CARAGA samples

Principal component analysis was used to identify the possible sources of the deposition samples from the 107 intense events. Correlation between variables and factors for the elements Al, Fe, P, Ti, Co, Cr, Cu, Mn, Ni, V and Zn and commutative variance for five sampling sites were presented in Table 3. For each site, 2–4 possible sources were identified, and the first source always contributed much more than half the variance of data, and the two first factors were extracted as principal components that explained > 82 % of the variance of the sample data. The lower variances of the first factor explained 57.34 and 66.87 % at sites Lampedusa and Frioul respectively, showing more influence from other sources at these two sampling sites. In the studied 107 samples, all elements were globally issued from a similar source for each site, but other sources (especially of Zn, Cu, Cr, Co and P) influenced the sampling sites too, especially at sites Lampedusa and Frioul. In order to identify the outlier samples, individual observations located on plane factors of 1, 2 or 1, 3 are presented in Fig. 2, and the observations located higher (> 1 %) on axis Y (factor of 2 or 3) were considered outlier samples that were responsible for the low correlation between variables and the first factors for the studied elements.

Table 2. Elemental mass loss in soils of Douz and Banizoumbou, and traffic soot during the collection and ignition of wet deposition. Standard deviation (SD) results from triplicate experiments. Al, Ca, P, K, Na and Mg have been measured by ICP-AES and other elements by HR-ICP-MS.

Elements	Soil of Douz		Soil of Banizoumbou		Traffic soot		
	Mean (%)	SD (%)	Mean (%)	SD (%)	Mean (%)	SD (%)	
Markers	Ca	18.09	0.29	27.0	1.4	33.57	0.51
	Al	1.09	0.13	0.39	0.05	0.61	0.03
	Mg	3.43	0.03	30.40	0.51	8.81	0.18
	Na	10.09	0.56	4.60	1.27	95.5	2.2
	K	5.80	0.12	3.12	0.07	15.05	0.57
	Ti	0.57	0.09	0.12	0.02	8.55	2.89
Nutrients	P	13.3	2.3	*	*	10.3	1.0
	Fe	0.68	0.13	0.19	0.03	0.11	0.005
Trace metals	Cd	*	*	*	*	4.97	0.78
	Co	1.12	0.10	0.19	0.03	2.41	0.27
	Cr	1.01	0.11	0.11	0.02	0.38	0.01
	Cu	3.87	0.35	1.67	0.46	6.58	0.12
	Mn	2.78	0.06	10.77	0.20	7.52	0.08
	Ni	0.62	0.07	*	*	4.67	0.17
	V	3.47	0.12	0.38	0.06	2.00	0.09
	Zn	4.77	0.62	6.39	0.86	8.75	0.10

* Elemental concentrations were under the limit of quantitation (LoQ), so we could not calculate the elemental loss.

Table 3. PCA factor loadings for 10 elements and for 107 samples. F is factor. Only loads larger than 0.3 (in absolute values) are reported. Loads larger than 0.6 are in bold.

Sites	Le Casset				Corsica			Mallorca		Lampedusa			Frioul		
	F1	F2	F3	F4	F1	F2	F3	F1	F2	F1	F2	F3	F1	F2	F3
Al	0.97				0.97			0.99		0.70	−0.70		0.88		
Fe	0.97				0.99			0.99		0.90	0.41		0.98		
P	0.77			0.54	0.94			0.99				0.93	0.71	−0.31	−0.51
Ti	0.97				0.99			0.99		0.74	−0.65		0.95		
Co	0.35	0.93			0.82		0.54	0.86	0.51	0.81	−0.40		0.89	−0.33	
Cr	0.98				0.33	0.93		0.99		0.92			0.70	0.39	0.53
Cu	0.80		0.46		0.95			0.99		0.74	0.60			0.92	
Mn	0.91				0.96			0.99		0.94			0.96		
Ni	0.98				0.91			0.94		0.72	0.38	0.52	0.86		0.44
V	0.98				0.99			1.00		0.77	−0.62		0.97		
Zn	0.76		0.49		0.97			0.98		0.59	0.71		0.52	0.79	−0.30
Cumulative variances %	76.8	85.5	91.5	95.5	83.1	93.2	96.3	94.9	97.7	57.3	82.2	94.1	66.9	84.5	93.0

3.2.2 Characterization of CARAGA samples by mass ratios

In order to identify the main source at each site, Al contents and mass ratios X/Al were assessed because Al is a typical marker of dust particles. The mean Al contents in the CARAGA samples for the different sites were estimated by plotting total mass fluxes as a function of Al mass fluxes. The average of Al content, standard deviation and the determina-

tion coefficient (R^2) for every site are presented in Table 4. For the four stations of Corsica, Lampedusa, Le Casset and Mallorca, $R^2 \geq 0.80$ and Al contents were typical of Saharan dust particles (Formenti et al., 2014). These values are also in agreement with the results of Guieu et al. (2002) on Al concentration in wet dust deposition ranging between 6.0 and 8.3%. This indicates that African dust is the main contributor to the mass deposition fluxes, consistent with the conclusion by Vincent et al. (2016) that validated sampling and analyti-

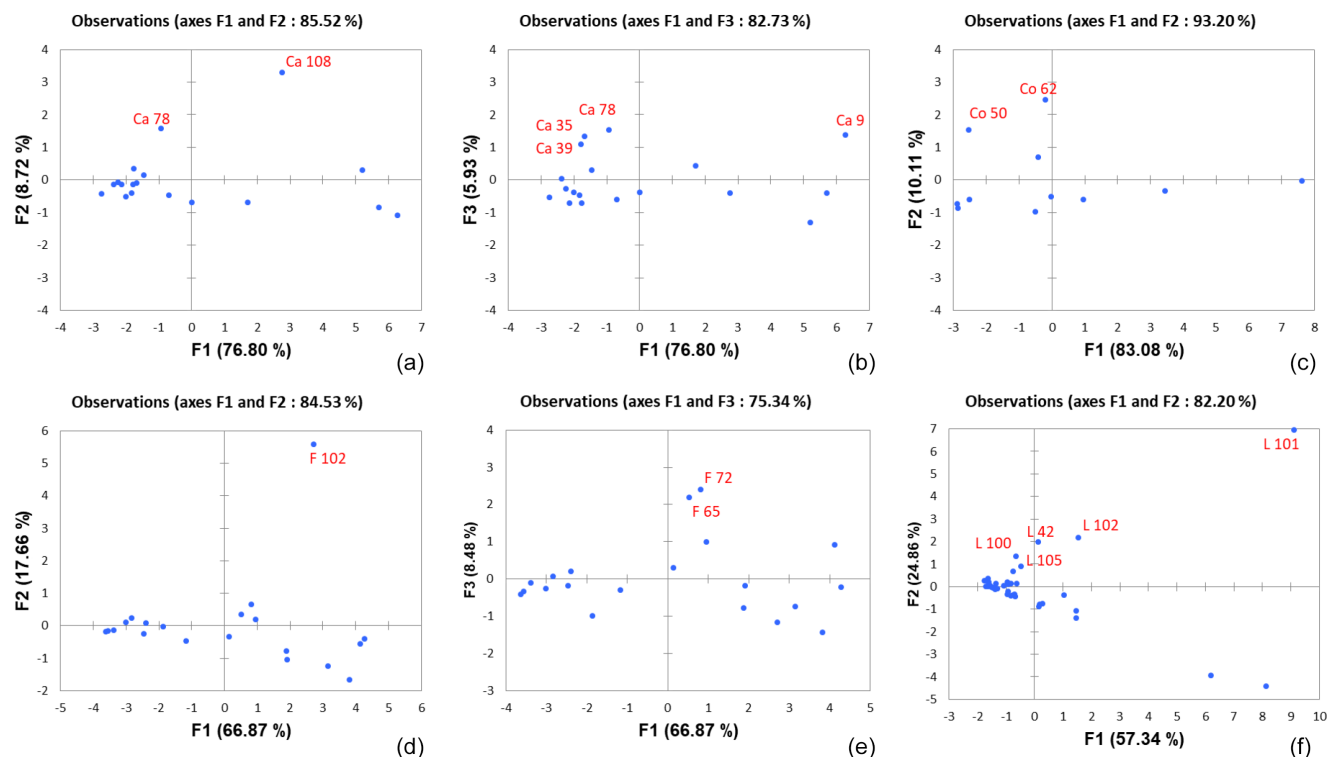


Figure 2. Outlier samples identified by PCA for four sampling sites: Le Casset, Corsica, Frioul and Lampedusa. (a) Outlier samples of Co at Le Casset. (b) Outlier samples of Zn and Cu at Le Casset. (c) Outlier samples of Cr at Corsica. (d) Outlier sample of Zn and Cu (and partially of Cr) at Frioul. (e) Outlier samples of Cr at Frioul. (f) Outlier samples of Zn, Cu and Fe at Lampedusa.

Table 4. Al contents in deposition samples for five sites: Le Casset, Corsica, Mallorca, Lampedusa and Frioul.

Sites	Le Casset	Corsica	Mallorca	Lampedusa	Frioul
Mean (%)	10.7	8.9	7.7	6.1	5.0
± 1 SD (%)	4.1	1.5	3.4	2.1	2.4
R^2	0.86	0.91	0.99	0.80	0.35

cal protocols. No clear correlation between Al concentrations and mass fluxes can be found in Frioul ($R^2 = 0.35$), pointing out that the deposited mass could be influenced both by African dust and other aerosols particles, in agreement with PCA results.

It is also interesting to note that Al contents increased with a south to north gradient, i.e. with the lowest values at Lampedusa, the closest site to Saharan dust sources, and the highest values at Le Casset, the most distant site from Sahara (Table 4). Vincent et al. (2016) emphasized that most of the time the origin of the deposited dust changed from one sampling site to the other: dust samples collected at Le Casset were mainly transported from the western part of the Sahara, whereas dust arriving to Lampedusa generally came from Tunisia and Libya. Nevertheless, the values of the Al content were probably not only related to the provenance of

dust, since the emission sources providing dust deposition in Corsica and in Mallorca were generally the same (Western Sahara/southern Morocco and Tunisia/eastern Algeria) (Vincent et al., 2016) and yet the Al content was different. Desboeufs et al. (2014b) observed an increase in the Al content in dust during its settling in the water column after deposition to the ocean. This increase was explained by the fact that the mass loss due to dissolution of the highest soluble species during settling modifies the mass percentage of the less soluble elements. The same effect could be observed in our samples due to the dissolution of soluble species during wet deposition as Ca, whose solubility can be increased by conversion of calcite to Ca sulfate or Ca nitrate during long-range transport (Scheuven et al., 2013). Vincent et al. (2016) showed that 80, 63, 60 and 53% of studied samples corresponded to wet deposition events at Le Casset, Corsica, Lampedusa and Mallorca respectively. The increasing contribution of wet deposition with distance to the dust source is consistent with the obtained Al contents, since the farther from source the site is, the more important the number of wet deposition samples and the higher the Al content. The consistency of Al content values with the dust references confirms the Saharan origin of deposition and supports the reliability of CARAGA data. However, the variability of the soluble part with distance makes it difficult to use CARAGA samples

to estimate the elemental content of deposition samples and hence to directly compare the composition of the deposition at the different sites. In the literature, inter-elemental mass ratios X / Al are often used to characterize the dust chemical composition and source (e.g. Formenti et al., 2008). Furthermore, Al has a low solubility in water, and trace-metal solubility is also relatively low in dust (< 5 % in Soil of Douz and < 11 % in soil of Banizoumbou), so that such ratios should not be strongly affected by dissolution and hence can be used to validate the use of CARAGA samples to estimate the origin of atmospheric elemental fluxes.

The average of inter-elemental mass ratios X / Al , standard deviation (SD) and the determination coefficient (R^2) for every site, and some references values are presented in Table 5. A correlation of $R^2 > 0.65$ was obtained between trace metals and Al contents regardless of the sampling site, and the X / Al ratio were close to values found in the literature for Saharan dust, except for Co, Cr, Cu or Zn at Lampedusa, Frioul and to a lesser extent at Le Casset.

At Lampedusa, the correlation are relatively low ($R^2 < 0.6$) for Fe, Cr, Cu, Mn and Zn. Excluding the five outlier samples (identified by PCA in Fig. 2f) (column Lampedusa* in the Table 5), we obtained better correlations with $R^2 > 0.7$ and a high consistency with reference dust values, except for Zn. The average mass ratio (35.08×10^{-3}) was two times larger than references values ($1.50\text{--}1.70 \times 10^{-3}$), which means that there was a very strong and frequent Zn anthropogenic source affecting deposition in Lampedusa during the sampling period. As a consequence, the atmospheric fluxes of Zn in Lampedusa could not be considered representative of dust deposition at this site. For the other trace metals, we can conclude that the main contribution of fluxes could be attributed to dust deposition during intense dust deposition event.

At Frioul, we already observed the low correlation of Al mass with total mass, showing a contribution of other sources of particles to the deposited mass. Indeed, Frioul is a rock/sand island in front of the industrialized city Marseille, which could be affected by resuspended mineral particles or by local anthropogenic sources. This conclusion is confirmed by the values of correlation found between Al and trace metals, as Cr, Cu or Zn (R^2 between 0.01 and 0.24), which were in general linked to one outlier sample (Fig. 2d) for Zn and Cu (31.3 and 64.5 % in mass respectively), and four outlier samples (three points in Fig. 2d, e identified by PCA and another one identified by mass ratio Cr / Al) for Cr (46.6 % in mass). However, even after removing the outlier points, the median mass ratios Cr / Al (2.34×10^{-3}), Cu / Al (1.24×10^{-3}) and Zn / Al (11.29×10^{-3}) are larger than dust reference values (Table 5). The Zn / Al values were in agreement with the previous values obtained in the north-western Mediterranean ($3\text{--}48 \times 10^{-3}$) where a very high anthropogenic component was found for Zn (Guieu et al., 2010), and according to Table 3, Zn and Cu had same origin. For this site, the interpretation of the chemical results is tricky, since even during intense dust events we suspect

a mixing with other anthropogenic atmospheric compounds that may not be important in terms of mass but impact the chemical dust signature.

At Le Casset, Cu and Zn present correlations with Al with $R^2 = 0.26$ and 0.49. This correlation is due to four outlier samples (identified in Fig. 2b). After excluding these samples influenced by anthropogenic sources, which present a low proportion in mass (14.9 and 10.7 % for Cu and Zn respectively), the correlation coefficients are higher than 0.65 and the obtained ratios are consistent with reference values for Saharan dust (Cu: 0.43×10^{-3} ($0.38\text{--}0.50 \times 10^{-3}$) and Zn: 1.60×10^{-3} ($1.01\text{--}1.70 \times 10^{-3}$) in Table 5). According to Table 3, a P source (factor of 4) influenced the site Le Casset, because of the agricultural contribution in this rural location, and two outlier samples were responsible for the low correlation of Co according to Fig. 2a. Thus, at Le Casset, the contribution of outlier samples lower than 15 % for elemental mass fluxes and the good agreement between measured and referenced ratio confirm the main dust origin of Co, Cr, Cu, Fe, Ti, Mn, Ni, V and Zn in deposition samples. In Corsica, the lowest correlation with Al obtained for Cr is due two outlier samples (in Fig. 2c), presenting 36.9 % in Cr-deposited mass. Thus, at this site, the Cr fluxes correspond to a mix of dust and other sources. Finally, at Mallorca, the correlations higher than 0.6 (and even 0.9 excluding Co) show that the metal fluxes are typically associated with dust deposition.

A high correlation of P and Al is obtained at Mallorca ($R^2 = 0.97$) and Corsica ($R^2 = 0.84$) with a P / Al ratio (0.010–0.012) in agreement with typical dust composition (Table 5). We conclude that dust deposition was the main provider of P during intense dust event deposition at these sites. On the contrary, the non-linear trend obtained between P and Al fluxes at Le Frioul, Casset and Lampedusa shows that the P fluxes measured at these sites cannot be used for estimating P fluxes associated with dust deposition. The main parameters affecting P contents in atmospheric deposition are its fractional solubility (precipitation and duration of rain) or anthropogenic sources. To check the effect of dissolution, these ratios were calculated for dry and wet deposition separately, but no linear trend was obtained for dry nor for wet deposition samples. Concerning the anthropogenic influence, the non-linear trend is mainly due to a large repartition of data. It is therefore difficult to distinguish the fraction of P from Saharan dust and anthropogenic or other sources at these three sites.

To conclude on the validation of CARAGA samples to estimate origin of atmospheric deposition, the results showed that the atmospheric deposition of trace metals at Le Casset, Corsica, Mallorca and Lampedusa is mainly associated with dust fluxes during intense dust event, except Zn in Lampedusa and Cr in Corsica. The outlier samples at these sites represented less than 10 % of the deposited elemental mass. Thus the CARAGA samples can be used to estimate the atmospheric fluxes of these elements issued from dust deposition. On the contrary, the trace-metal composition of

Table 5. Inter-elemental ratio in samples collected at the different CARAGA sites and reference values. Rf1: reference values in soils of Banizoumbou and Douz. Rf2: reference values in wet deposition of dust near emitting area (Desboeufs et al., 2010) or in total deposition with dust signature in the western Mediterranean Basin (Ridame et al., 1999; Guieu et al., 2010). Rf3: reference values in transported Saharan dust (Formenti et al., 2003, 2008, 2011 and 2014) for the Saharan-emitting sources (PSA 1 to 3: northern Algeria/southern Tunisia, Mauritania/Morocco and northern Mali/southern Algeria respectively), corresponding with the identified provenance of our samples (Vincent et al., 2016).

Sites		Le Casset	Corsica	Mallorca	Lampedusa	Lampedusa*	Frioul	Rf1	Rf2	Rf3
Samples number		17	11	21	37	32	21			
Fe / Al	Mean	0.54	0.64	0.57	1.09	0.66	0.55	0.56–0.65	0.50–0.78	0.40–1.69
	±1 SD	0.03	0.09	0.18	10.24	0.79	0.21			
	R ²	0.99	0.95	1.00	0.12	0.98	0.73			
Ti / Al	Mean	0.06	0.07	0.06	0.08	0.07	0.06	0.06–0.21	0.07–0.13	0.06–0.11
	±1 SD	0.01	0.01	0.02	0.03	0.01	0.03			
	R ²	0.98	0.96	0.99	0.99	1.00	0.61			
P / Al	Mean	0.03	0.01	0.01	0.05	0.03	0.14	0.010–0.018	0.01–0.02	0.007–0.012
	±1 SD	0.02	0.01	0.03	0.32	0.08	0.14			
	R ²	0.52	0.84	0.97	0.01	0.45	0.33			
Co / Al 10 ⁻³	Mean	0.65	0.74	0.70	0.69	0.64	0.22	0.48–0.82		
	±1 SD	0.66	0.28	1.15	1.51	0.64	0.09			
	R ²	0.07	0.64	0.64	0.63	0.71	0.73			
Cr / Al 10 ⁻³	Mean	1.17	1.85	1.05	1.77	1.47	3.46	1.44–1.54		
	±1 SD	0.26	3.14	1.03	7.67	2.05	2.59			
	R ²	0.94	0.20	0.95	0.37	0.67	0.24			
Cu / Al 10 ⁻³	Mean	0.87	0.65	0.47	1.15	0.61	5.66	0.43–0.50		0.38
	±1 SD	0.57	0.30	1.31	18.21	1.22	13.18			
	R ²	0.49	0.86	0.92	0.01	0.70	0.01			
Mn / Al 10 ⁻³	Mean	6.34	6.17	5.47	10.70	7.23	6.21	10.81–13.54		5.9
	±1 SD	2.83	1.11	4.91	94.20	8.42	2.27			
	R ²	0.67	0.90	0.99	0.26	0.94	0.70			
Ni / Al 10 ⁻³	Mean	0.57	0.78	0.62	1.13	0.63	0.90	0.46–0.68		0.48
	±1 SD	0.18	0.51	1.24	9.42	0.58	0.40			
	R ²	0.89	0.75	0.85	0.07	0.86	0.51			
V / Al 10 ⁻³	Mean	1.55	1.68	1.25	1.53	1.47	1.34	2.15–2.84		1.40
	±1 SD	0.26	0.32	0.66	2.95	0.37	0.42			
	R ²	0.96	0.94	0.99	0.98	0.99	0.82			
Zn / Al 10 ⁻³	Mean	2.64	2.09	1.55	122.63	14.52	15.86	1.13–1.50	1.01	1.70
	±1 SD	1.56	0.91	2.85	1765.23	59.53	18.43			
	R ²	0.44	0.89	0.91	0.01	0.001	0.12			

* Mean, standard deviation and correlation coefficient obtained after discarding four outlier samples for Lampedusa.

the CARAGA samples on Frioul was influenced by anthropogenic sources and the atmospheric fluxes are not representative of dust deposition even during intense dust events. This is also the case for P fluxes at the sites Le Casset, Frioul and Lampedusa, whereas P fluxes in Mallorca and Corsica can be used to estimate the dust-derived P deposition fluxes.

3.3 Weekly mass fluxes of nutrients and trace metals

The weekly mass fluxes of P and trace metals and percentage of wet deposition (wet only and mixed deposition according Vincent et al., 2016), estimated for 107 samples covering the 2011–2013 sampling period, are presented in Table 6. The trace-metal fluxes in Table 6 are presented in two categories: the fluxes mainly associated with dust deposition (sites of Le Casset, Corsica (except Cr), Mallorca and Lampedusa*), and the fluxes associated with deposition from a mixing of dust

Table 6. Mean weekly mass fluxes of nutrients and trace metals for 107 intense events samples, standard deviation (SD) and contribution of wet deposition on total fluxes for five studied sites.

Sites		Dust deposition				Mixed deposition		
		Le Casset	Corsica	Mallorca	Lampedusa*	Lampedusa	Frioul	
$\text{mg m}^{-2} \text{wk}^{-1}$	Al	Mean	7.76	14.92	37.40	27.44	25.01	7.23
		± 1 SD	5.12	10.86	74.40	41.91	40.14	3.99
		Wet (%)	71	88	86	57	55	71
	Fe	Mean	4.16	9.48	21.46	17.93	27.30	3.97
		± 1 SD	2.65	7.21	41.15	23.10	47.08	2.77
		Wet (%)	72	89	80	60	36	68
	P	Mean	0.24	0.19	0.37	0.99	1.16	0.99
		± 1 SD	0.16	0.13	0.54	1.41	1.64	1.16
		Wet (%)	79	91	80	67	51	60
$\mu\text{g m}^{-2} \text{wk}^{-1}$	Co	Mean	5.04	11.46	26.10	17.48	17.27	1.57
		± 1 SD	5.77	6.33	26.48	16.34	16.31	1.27
		Wet (%)	80	90	69	49	44	75
	Cr	Mean	9.05	33.03	39.11	39.80	44.23	25.02
		± 1 SD	4.25	20.84	54.76	41.16	48.19	20.22
		Wet (%)	69	87	79	57	46	77
	Cu	Mean	6.73	10.14	17.43	16.84	28.88	40.94
		± 1 SD	2.50	4.50	19.02	12.84	51.70	115.52
		Wet (%)	65	84	76	64	34	82
	Mn	Mean	49.21	91.24	204.68	194.93	261.70	44.92
		± 1 SD	31.68	79.30	349.24	273.03	421.64	26.65
		Wet (%)	69	91	81	65	43	67
	Ni	Mean	4.40	12.05	23.14	19.59	28.23	6.48
		± 1 SD	2.14	5.79	28.49	21.15	38.19	3.90
		Wet (%)	68	84	83	66	41	73
	V	Mean	12.01	25.16	46.72	40.20	38.30	9.68
		± 1 SD	6.56	17.26	75.20	58.24	55.39	6.62
		Wet (%)	70	88	81	59	55	70
	Zn	Mean	20.47	32.15	58.00	345.48	3067.19	114.69
		± 1 SD	11.24	16.05	59.51	576.11	13063.10	153.65
		Wet (%)	70	85	76	61	7	72

* Not including five outlier samples enriched in trace metals (especially Fe) in Lampedusa.

and other sources, as local or anthropogenic sources (sites of Lampedusa and Frioul). As observed by Vincent et al. (2016) on total dust mass fluxes, a north to south increasing gradient on Al and trace-metal inputs linked to dust deposition is observed with the lowest mean weekly mass fluxes on Le Casset and the highest for Mallorca. Even if the island of Lampedusa is the closest site to African sources, and the annual mass fluxes in Lampedusa are more important than in Mallorca (Vincent et al., 2016), the recorded weekly metal-bearing dust fluxes on this site (Lampedusa* in Table 6) remains inferior to those recorded at Mallorca. Mass fluxes of P and trace metals linked to wet deposition are predominant at Le Casset, Corsica, Mallorca and Frioul (Table 6).

In Lampedusa, it appears that wet deposition predominates for dust deposition events (Lampedusa*), whereas the metal fluxes including anthropogenic sources are mainly from dry deposition. The lower dust metal fluxes found in Lampedusa* in comparison to Mallorca can be explained by the higher contribution of wet deposition in Mallorca. Inversely, the P fluxes found in Lampedusa* are the highest observed in the western basin, since P loss by dissolution induces a decrease of fluxes with the contribution of wet deposition. These results show that the fluxes of metals and P associated with wet deposition predominate in the western Mediterranean Sea environment. It has to be noted that, firstly, the mass fluxes estimated in this paper are averaged weekly mass fluxes for the

most intense dust events that account for 50–84 % in mass of the total deposition, as studied by Vincent et al. (2016), so we could not compare them with references values in the literature which are typically annual. Secondly, due to the effect of dissolution during the CARAGA sampling protocol, these fluxes are underestimated in the worst case by 13 % for P and 10 % for Zn, Cu and Mn, and 5 % for other trace metals.

4 Conclusion

The estimation of atmospheric deposition mass fluxes of nutrients and trace metals in the western Mediterranean Sea is critical to understand the role of dust deposition on phytoplankton activity. Few deposition measurements are available to document nutrient inputs for several years in the western Mediterranean Sea. To estimate these nutrients and mass fluxes of trace metals, we validated the possibility of using samples of mass measurements of atmospheric deposition performed under the same conditions with CARAGA collectors at five sites in the western part of the Mediterranean. A first step was to estimate elemental mass loss during the in situ collection and ignition protocol used for weighing samples. According to these tests with dust analogues and traffic soot, solubility larger than 15 % was observed for major metals, such as Ca, Mg and K, excluding the possibility to use the common Ca / Fe ratio to estimate source areas of deposited dust. However, the relative mass loss by dissolution of three aerosol analogues was lower than 3 % for dust tracers like Ti, Al, Fe and trace metals such as Cd, Co, Cr, Ni and V. The relative mass loss by dissolution was up to 10 % for Zn, Cu and Mn. For the major nutrient P, this loss by dissolution ranged from 10 to 13 %. During the ignition, the elemental mass loss for tracer elements, nutrients and trace metals was not significant. These results point out that there is no bias due to the sampling method and the lab protocols used to estimate elemental fluxes from CARAGA atmospheric deposition samples.

Chemical analyses of 107 CARAGA samples corresponding to the most intense dust deposition events observed between 2011 and 2013 in the western basin were performed to validate using CARAGA samples in order to estimate the elemental mass deposition flux of nutrients and trace metals. After checking the chemical composition of samples using PCA, Al content and inter-elemental mass ratios X / Al, the chemical composition of samples from all stations excluding Frioul have the typical chemical signature of Saharan dust, except for Zn in Lampedusa, Cr in Corsica and P in Le Casset and Lampedusa. These CARAGA samples were chemically exploitable and have been used to estimate P and trace-metal mass fluxes associated with dust deposition, keeping in mind the underestimation of soluble fraction. The deposition sampled at Frioul could be affected by other sources, even during an intense dust event, and hence elemental atmospheric

fluxes measured at this site are linked to a mixing of dust and other relatively local sources.

The atmospheric elemental fluxes estimated from CARAGA samples constitute the first regional assessment of a mean weekly mass fluxes of trace metals and P linked to intense dust deposition over the western Mediterranean Basin. The mean mass fluxes were dependent on the distance to the source and on the contribution of wet deposition. High averages and strong standard deviations of Al (dust marker) mass fluxes were observed at Lampedusa and Mallorca due to several intense dust events. Extreme Zn mass fluxes ($122.63 \pm 1765.23 \mu\text{g m}^{-2} \text{wk}^{-1}$) were observed at Lampedusa, which need to be thoroughly investigated, but were likely due to the large use of non-ferrous metal manufacturing in this environment strongly impacted by sea spray. Knowing that a good representation of these intense fluxes is critical to estimate the role of atmospheric deposition on marine biosphere in modelling (Guieu et al., 2014), the parameterization of wet deposition of nutrients and trace metals needs to be improved.

Data availability. To obtain the data from the CARAGA network, contact Gilles Bergametti or Benoit Laurent at LISA (<http://mistrals.sedoo.fr/Database-Content/?project=ChArMEX>).

Competing interests. The authors declare that they have no conflict of interest.

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