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Patagonian Dust as a Source of Macronutrients in the Southwest Atlantic Ocean

ABSTRACT. The role of Patagonian wind-borne dust as a source of macronutrients to the surface waters of the Southwest Atlantic Ocean was evaluated for the first time. During spring 2016, a series of experiments with dust was conducted to evaluate the dynamics of macronutrient dissolution in seawater. The results showed a differential contribution of macronutrients to seawater depending on the dust source and the amount added. Addition of a conservative amount of Patagonian dust to the seawater contributed nitrate (NO_3^-) and silicic acid ($\text{Si}(\text{OH})_4$), but not phosphate (PO_4^{3-}). Additional dust input to the system resulted in higher macronutrient concentrations. Particles collected from a nearby burned field did not contribute any macronutrients to the seawater. Thus, each dust event may affect biological productivity differently, depending on the source of the particles. Dissolution experiments suggest that macronutrients from dust are available immediately after particle deposition on the sea surface. The study includes field measurements of macronutrient concentrations before and after a dust storm at three nearshore marine stations. The data are consistent with macronutrient increase after the storms. Dust storms could become a very important source of nutrients to the ocean in future global warming scenarios.

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INTRODUCTION

The effect of aeolian dust on ocean biogeochemical cycles depends on two major factors: the chemical composition of the material transported and the nutritive conditions of the region where it is deposited. Dust composition may vary temporally because it depends on the source region (Krueger et al., 2004; Mendez et al., 2010; Martino et al., 2014) and on the season (Carmichael et al., 1996; Ben-Ami et al., 2009). Dust composition can also be altered by episodic events such as volcanic eruptions and forest fires (Al-Taani et al., 2015; Bergh and Compton, 2015). When a dust particle reaches the sea surface, a process of nutrient solubilization begins. The effect of nutrient inputs depends on the composition of the sink area. In high nutrient, low chlorophyll (HNLC) areas of the ocean, micronutrients such as iron are key to regulating primary productivity (Jickells et al., 2005; Maher et al., 2010). In contrast, in oligotrophic coastal areas, primary productivity benefits from the input of macronutrients such as nitrate and phosphate (Herut et al., 1999; Pulido-Villena et al., 2010). Because aeolian dust can be transported thousands of kilometers before it is deposited, the plume of a particular event may simultaneously influence coastal and oceanic regions, leading to complex marine ecosystem interactions. Globally, several regions are considered to be dominant sources of dust. For instance, dust from the arid regions of North Africa and the Arabian Peninsula, known as the dust belt, is deposited over vast areas far from its source (Washington et al., 2003; Mahowald et al., 2005).

Patagonia, Argentina, displays particular environmental conditions that promote the transport of aeolian dust toward the Southwest Atlantic Ocean (Johnson et al., 2010; Gaiero, 2007; Crespi-Abril et al., 2016, 2018a). These conditions include frequent, strong westerly winds (average wind gusts of 36 m s^{-1} ; Labraga, 1994), a semi-arid climate (annual precipitation regime below 300 mm and relative humidity below 5%), and low

vegetation coverage (10%–60%; Bertiller and Bisigato, 1998). The transport of dust from Patagonia to the sea is constant but highly variable in intensity (Gaiero et al., 2003; Crespi-Abril et al., 2018b). Although wind drives dust events (i.e., short-duration episodes of increased wind-borne dust particles), factors related to the source of particle emission, such as soil moisture or vegetation coverage, determine whether a dust event will occur. In other words, strong winds are a necessary but not sufficient condition for inducing a dust transport event (i.e., not all windstorms produce dust events, but all dust events are driven by intense winds). During extreme dust storms and sporadic volcanic eruptions, dust plumes can cover large areas of the Southwest Atlantic Ocean (Simonella et al., 2015; Crespi-Abril et al., 2016). As Patagonian dust represents a major source of micronutrients (particularly iron) to the Southwest Atlantic Ocean (Jickells et al., 2005; Simonella et al., 2015), dust may intensify the biological pump there, increasing carbon sequestration, and potentially affecting global climate (Maher et al., 2010).

Despite its relevance to marine ecosystem productivity, the potential contributions of Patagonian dust to increasing macronutrient concentrations, and its biogeochemical pathways into the system, remain uncertain (Crespi-Abril et al., 2018a). The goal of this work is to evaluate the contribution of Patagonian dust to the concentrations of nitrate (NO_3^-), phosphate (PO_4^{3-}), and silicic acid ($\text{Si}(\text{OH})_4$) in seawater. We performed a series of laboratory experiments and collected in situ measurements before and after a dust storm. The working hypothesis is that dust emitted from Patagonia injects macronutrients into the marine ecosystem.

METHODS

Laboratory Experiments

Laboratory trials included a dissolution experiment to determine the variation of macronutrient concentration over time after the addition of field-collected dust

to seawater as well as a washing experiment to determine whether the composition of dust particles changes after contact with water.

DISSOLUTION EXPERIMENTS

Three different dust stocks and one control were tested. For the first two stocks, S1 and S2, dust was collected during two different storms by means of an active collector placed at the western margin of Nuevo Gulf, Patagonia, Argentina. For the third stock, S3, dust was collected from a nearby burned shrubland by means of a passive collector. For each experiment and one control, 12 L microcosms were filled with $1 \mu\text{m}$ filtered, UV-treated seawater. The dust-treated microcosms were placed on a rotating plate ($\sim 3 \text{ rpm}$) to prevent dust particles from settling, and incubated in a culture chamber at $15^\circ\text{C} \pm 1^\circ\text{C}$ for a 12:12 photoperiod ($\sim 600 \text{ Lux}$, measured with a digital luxometer UNI-T Ut382). An aliquot of dust of 0.05 mg L^{-1} was added to each microcosm. This amount of dust is a proxy of the minimum theoretical amount that could reach the sea, assuming a deposition rate of 1 g m^{-2} and a 20 m deep mixed layer (Mendez et al., 2010; Anderson et al., 2016). For macronutrient analysis, duplicate samples of seawater from each microcosm and the control were collected at 0, 24, 48, 72, and 96 hours.

Because the amount of dust used in the low concentration experiment was the minimum expected for a wind-storm, a second experiment was conducted following the same methodology but increasing the dust concentration to 5 mg L^{-1} , 50 mg L^{-1} , and 500 mg L^{-1} with S2 and S3 dust stocks.

WASHING EXPERIMENTS

Two treatments were considered using the S2 dust stock. Assays were made by washing the dust aliquot with distilled water (DW) or seawater (SW), and one control was made without washing (U). The washing procedure consisted of adding 0.5 mg of dust to 1 L of water (either distilled or seawater according

to the treatment) and shaking it for 10 minutes. Then, the solution was centrifuged, the supernatant was removed, and the remaining material was dried in an oven (60°C for 48 hours). Macronutrients were analyzed using the same techniques as used in the dissolution experiments. Dust particles were analyzed using an X-ray (EDX) spectrometer coupled to a scanning electron microscope (SEM) to determine changes in the elemental composition of particles before and after the washing treatment.

FIELD MEASUREMENTS

To evaluate the variation in macronutrient concentrations after dust storms, an in situ study was conducted in Nuevo Gulf (Figure 1), a semi-enclosed basin connected to the adjacent shelf by a narrow mouth. Two small urban centers (~100,000 habitants in total) are located in the margins of the gulf; however, the effects of the two cities on nutrient concentrations are negligible because they are equipped with sewage treatment plants that do not discharge wastewater into the gulf. Rainfall is low (~200 mm yr⁻¹; Paruelo et al., 1995), and no rivers flow into the gulf. Atmospheric dust is the main source of continental material into Nuevo Gulf, making it a good place to study the effect of dust as seawater fertilizer.

Three fixed stations were established in order to acquire seawater samples at the surface and at 20 m depth. Samples were obtained from an inflatable boat by means of a Niskin bottle. Each sample was stored in duplicate in ultra-cleaned 250 ml bottles for each nutrient. At the moment of seawater sample collection, temperature, conductivity, O₂, and pH were recorded using a YSI 556 probe. Seawater samples were taken after a calm period (wind speed <4 m s⁻¹ on October 22, 2016), and after a west wind-storm (wind speed ~8–16 m s⁻¹, November 5, 2016) (Figure 2a,b). On November 3, 2016, a large dust plume was observed from satellite imagery coincident with the maximum wind velocity measured (Figure 2c). The aeolian dust plume covered more than 320 km of marine coastal area, prevailing over San Jorge Gulf and reaching the Argentine continental shelf break.

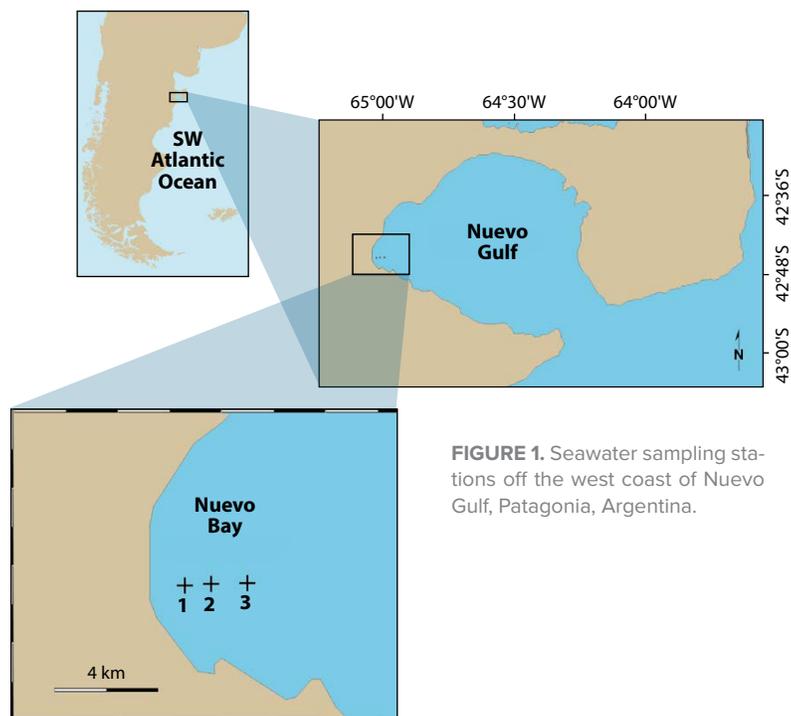


FIGURE 1. Seawater sampling stations off the west coast of Nuevo Gulf, Patagonia, Argentina.

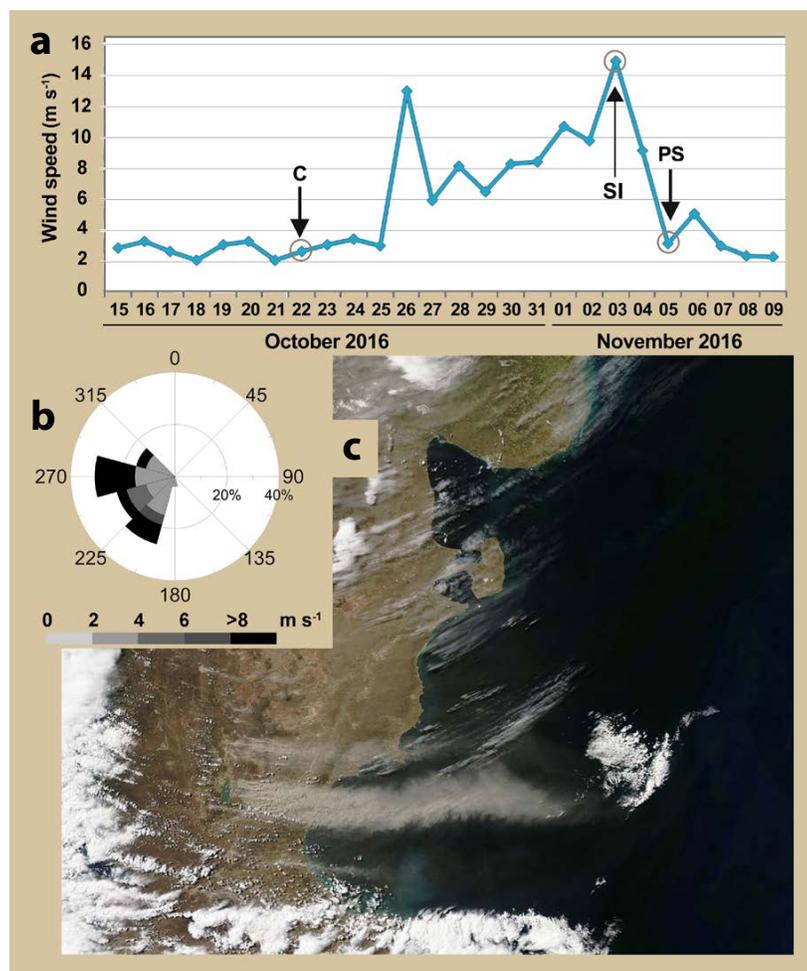


FIGURE 2. (a) Wind intensity during the study period. C = Calm period sampling. PS = Post-storm sampling. SI = Satellite imagery shown in (c). (b) Wind direction during the sampled windstorm. (c) Satellite image from November 3, 2016, showing the dust plume over the Argentine Sea (<https://earthdata.nasa.gov/earth-observation-data/near-real-time/rapid-response/modis-subsets>).

Dust Collection

Dust was collected following two methodologies: (1) passive collection and manual recovery from 20 l PVC cylindrical containers with 300 cm² collecting mouths, and (2) active collection using a high-volume active collector (air filtering capacity up to 60 m³ h⁻¹) with a high-purity quartz microfiber filter (Merck Millipore AQFA) over a 24-hour period. Microfiber filters were previously weighed using an analytical balance (Sartorius CPA124S) before and after the sampling period.

Chemical Analyses

Analytical determinations of NO₃⁻, PO₄³⁻, and Si(OH)₄ concentrations were carried out using a Skalar San Plus autoanalyzer

(Skalar Analytical® V.B., 2005). All seawater samples were stored in 250 ml ultra-cleaned bottles at -20°C until laboratory analysis.

RESULTS

Laboratory Experiments

DISSOLUTION EXPERIMENTS

The results obtained in dissolution experiments using 0.05 mg dust per liter of filtered, UV-treated seawater varied according to the type of dust used. Using the S1 dust stock, an immediate increase in NO₃⁻ (~1.25 μM) and Si(OH)₄ (~3.10 μM) over the control samples was observed (Figure 3a). For S2 and S3 stocks, no macronutrient contributions were observed (Figure 3b,c).

Based on these results, dust from the

stocks S2 and S3 were used in higher concentrations to determine the amount of dust necessary to produce increases in nutrient concentrations. In the case of S2, nutrient addition was detected in dust concentrations higher than 50 mg L⁻¹, while S3 dust did not release nutrients at any of the concentrations used (Table 1).

WASHING EXPERIMENT

Our analysis indicated that all the dust particles used in this experiment had the same elemental composition (Figure 4). However, in the washing experiment, washed (with distilled water or seawater) dust particles did not release macronutrients, while in contrast, the unwashed particles (control) contributed a large amount of macronutrients (Table 2).

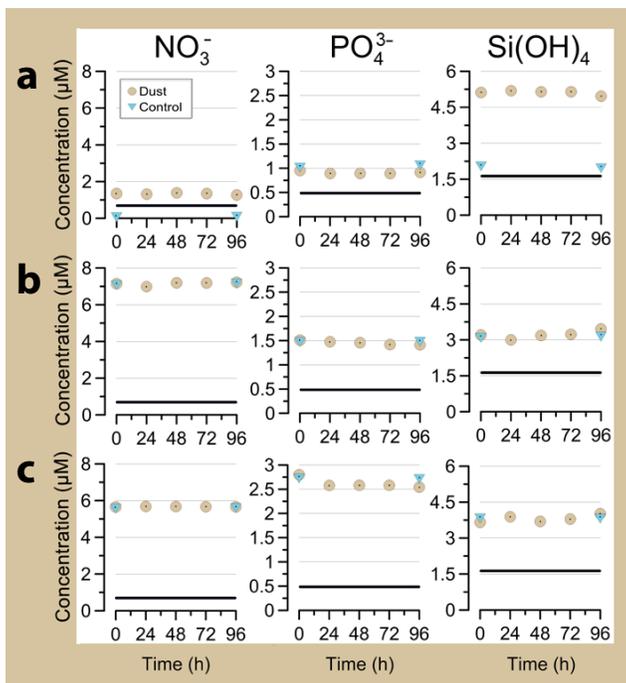


FIGURE 3. Nutrient concentrations measured during the dissolution experiments after adding 0.05 mg L⁻¹ of dust to seawater. Dust stocks from different storms provide different concentrations of macronutrients. (a) First experiment, S1 dust storm stock. (b) Second experiment, S2 dust storm stock. (c) Third experiment, S3 stock collected after a large shrubland fire. Brown circles indicate nutrient concentrations after dust was added. Light blue triangles indicate no dust added (control). The black lines indicate the minimum nutrient concentration necessary for the normal development of primary producers (Millero, 2013).

TABLE 1. Nutrients supplied by S2 and S3 dust stocks in filtered, UV-treated seawater.

S2 Stock	NO ₃ ⁻ (μM)	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)
5 mg L ⁻¹	0.20 ± 0.01	0.25 ± 0.01	0.00
50 mg L ⁻¹	1.15 ± 0.04	0.33 ± 0.01	0.19 ± 0.01
500 mg L ⁻¹	11.70 ± 0.04	1.12 ± 0.11	1.61 ± 0.23
S3 Stock	NO ₃ ⁻ (μM)	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)
5 mg L ⁻¹	0.02 ± 0.01	0.07 ± 0.04	0.00
50 mg L ⁻¹	0.00	0.12 ± 0.01	0.00
500 mg L ⁻¹	0.22 ± 0.01	0.28 ± 0.09	0.33 ± 0.03

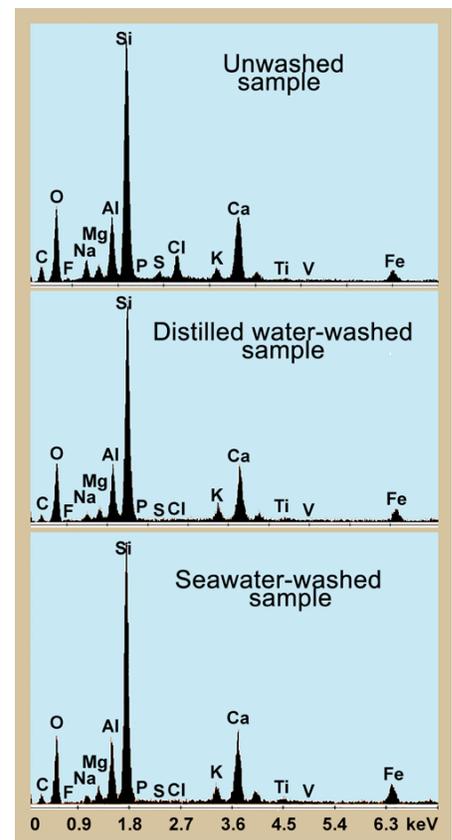


FIGURE 4. Elemental composition of dust particles obtained by energy-dispersive X-ray spectroscopy. No differences were observed despite the different treatments that were used to modify the contributions of macronutrients to seawater.

Field Measurements

After the calm period, seawater showed small differences between stations (Table 3). On average, down to 20 m water depth, conditions were homogeneous (O_2 close to saturation, salinity 34 psu, and pH 8.1). Temperature was between 12° and 13°C at 20 m depth, and two degrees higher on surface. The NO_3^- concentration was low at the surface (<0.5 μM) and higher at 20 m depth (~1.4 μM). The PO_4^{3-} concentration was ~1.0 μM , with higher values at 20 m depth. $Si(OH)_4$ was ~2.5 μM (Figure 5). The stoichiometric conditions during this period showed a $PO_4^{3-}:NO_3^-:Si(OH)_4$ ratio of 1.0:0.6:2.2.

After the windstorm, oxygen, salinity, and pH did not vary compared to the calm period; however, the temperature dropped 1°C at almost all the stations (Table 3). Compared with the calm period, the concentration of macronutrients during the windstorm was higher in all cases. The NO_3^- concentration was double that of the calm period. PO_4^{3-} and $Si(OH)_4$ concentrations mainly increased at 20 m depth, reaching a concentration ~2.0 μM and ~4.5 μM , respectively, and maintaining their proportions. The post-storm $PO_4^{3-}:NO_3^-:Si(OH)_4$ ratio was 1.0:1.2:2.2.

DISCUSSION

The results of the dissolution experiments indicate for the first time that Patagonian dust can be considered a significant source of NO_3^- and $Si(OH)_4$, but not of PO_4^{3-} , to surface waters in the Southwest Atlantic Ocean. These results imply that, in the Argentine Sea, if PO_4^{3-} is deficient in atmospheric dust particles, increases in primary productivity result from the atmospheric supply of NO_3^- and $Si(OH)_4$ (and possibly iron; Simonella et al., 2015) as well as some residual excess PO_4^{3-} available in the surface waters (Martino et al., 2014). Given that in the Argentine Sea the limiting nutrient is NO_3^- ($N/P < 1$ is frequently observed; Paparazzo et al., 2010, 2017), fertilization by dust would complement the region's other nutritional sources. In fact, the experiment with S1 shows that such a contribution can quickly restore NO_3^- availability to a system limited by that nutrient.

In a global context, compared to dust studies from other geographical areas, this nutritional release (NO_3^- and $Si(OH)_4$ without PO_4^{3-}) is a common feature in the fertilization of the sea by means of dust (Baker et al., 2003; Martino et al., 2014). In the Mediterranean Sea, dust storms contribute considerable amounts of PO_4^{3-} to surface waters (Özsoy, 2003), but concentrations are possibly mediated by acid processing of P in the atmosphere (Stockdale et al., 2016), which occurs frequently

TABLE 2. Washing treatments of S2 dust stock and their effect on nutrient supply. U = Unwashed sample. DW = Distilled water-washed sample. SW = Seawater-washed sample.

Dust Treatment	NO_3^- (μM)	PO_4^{3-} (μM)	$Si(OH)_4$ (μM)
U	11.65 ± 0.06	1.63 ± 0.09	2.19 ± 0.22
DW	0.24 ± 0.08	0.77 ± 0.06	0.00
SW	0.16 ± 0.04	0.72 ± 0.01	0.00

TABLE 3. In situ data collected during calm period and post dust storm period on surface and subsurface layers.

Calm Oct. 22, 2016	Station 1		Station 2		Station 3	
	0 m	20 m	0 m	20 m	0 m	20 m
Temp. (°C)	14.7	13.1	14.4	12.1	14.2	12.0
Salinity (psu)	34.0	33.8	34.0	34.0	34.0	34.0
O_2 (%)	97	101	105	105	105	100
O_2 (mg L ⁻¹)	7.97	8.52	8.70	9.13	8.76	8.54
pH	8.16	8.05	8.21	8.17	8.19	8.15

Post Storm Nov. 5, 2016	Station 1		Station 2		Station 3	
	0 m	20 m	0 m	20 m	0 m	20 m
Temp. (°C)	13.1	12.1	13.1	12.8	13.2	12.9
Salinity (psu)	34.1	34.1	34.1	34.1	34.1	34.1
O_2 (%)	98	91	104	99	118	108
O_2 (mg L ⁻¹)	8.34	7.88	8.86	8.49	10.00	9.25
pH	8.14	8.10	8.15	8.13	8.18	8.14

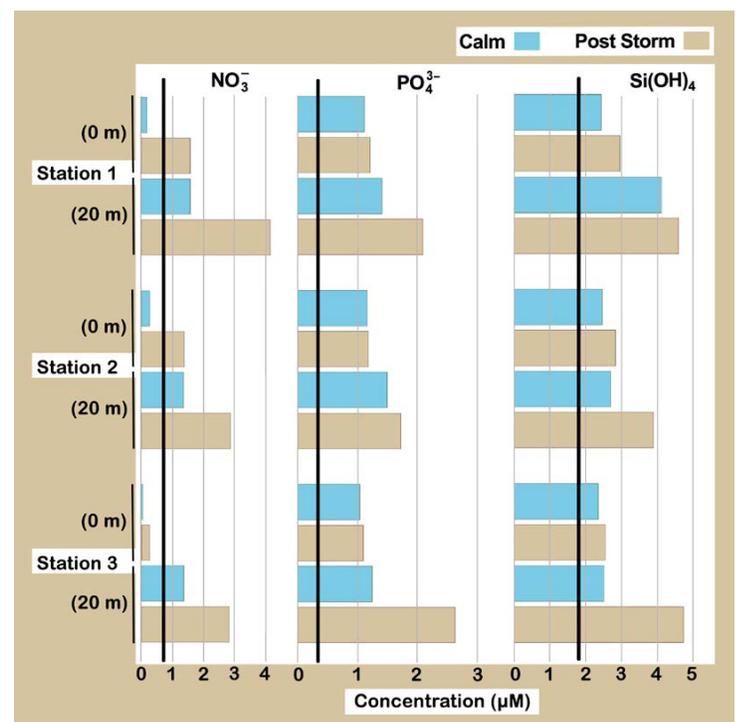


FIGURE 5. Nutrient concentrations at 0 m and 20 m depth under calm and post-storm wind conditions. All macronutrients increased after the dust storm. The black line indicates the minimum nutrient concentration necessary for the normal development of primary producers (Millero, 2013).

in that region. More studies are needed in the Patagonian region to determine whether this is the case or whether dust settling there simply lacks PO_4^{3-} due to its origin.

Our experiments also demonstrate the great variability in the contribution of nutrients from different dust stocks. This variability could be due to the different chemical composition of the stocks (which likely results from varying contributions of several emission sources) associated mainly with climatic and environmental events before deposition on the sea surface. The results obtained with dust from the S2 stock show that the concentration required to release a significant amount of nutrients is at least 1,000 times the concentration of S1 stock. This large amount of dust is often observed during intense windstorms in the study area (Crespi-Abril et al., 2018b). On the other hand, the experiment with S3 did not result in release of nutrients. Because that dust was collected from a burned field, it is very likely that the particles were mostly ash, which lacks macronutrients (Christensen, 1994).

The results of the washing experiments suggest that in terms of macronutrients, dust particles remain insoluble (or dissolve very slowly) even after releasing nutrients to the water. This assumption is reinforced by the fact that washed dust particles do not provide macronutrients to the water despite having the same elemental composition as unwashed particles. Similar to what was observed in Saharan dust (Ridame et al., 2014), our results show that dust contributes macronutrients to the ocean immediately and completely upon contact with water. This would indicate that dust particles act as carriers of macronutrients from land to the sea.

Washing experiments are also relevant from a methodological point of view. We recommend avoiding the frequently used technique of extracting dust from filters by washing with ultrapure water (e.g., Guo et al., 2014). This practice modifies the external layer of dust by

removing nutrients and thus affecting the results of the analysis.

Field measurements in Nuevo Gulf show that the magnitude of a windstorm can modify seawater macronutrient concentrations in this region. During the calm period, the surface concentration of NO_3^- ($< 0.5 \mu\text{M}$) was limiting, based on minimum environmental requirements ($0.7 \mu\text{M}$ for NO_3^- , $0.3 \mu\text{M}$ for PO_4^{3-} , and $1.8 \mu\text{M}$ for $\text{Si}(\text{OH})_4$) for the development of primary producers (Millero, 2013). After the storm, the concentration of NO_3^- ($\sim 1.5 \mu\text{M}$) was no longer limiting for primary producers. Two processes, dust deposition and water column mixing, could mainly explain this event. However, what could be the dominant process, if there is one, that governs the increase in macronutrient concentrations? To address this question, further studies are needed. Regardless, the present work suggests that dust input must be considered as a relevant factor in Atlantic Patagonia.

CONCLUSION

Patagonian dust deposition can increase macronutrient concentration in seawater after events involving intense westerly winds. The magnitude of this fertilization depends on the composition of the dust, which is mainly associated with emission sources and climatic and environmental events that act upon the dust particles before they reach the sea. Each dust event may contribute different concentrations and proportions of macronutrients that may in turn affect stoichiometry and biological processes in the upper mixed layer. Due to the instantaneous dissolution of macronutrients in seawater, fertilization would occur in the uppermost thin layer of the sea surface, and thus, dust particles would act as carriers that transport continental chemical compounds to the sea.

Due to global warming, the prevailing winds in Patagonia are intensifying (e.g., Thompson et al., 2011), and ocean stratification is expected to strengthen (e.g., Russell et al., 2006). If

these conditions translate into larger dust storms and greater nutrient limitation at the sea surface, in a future scenario, dust storms could have a great impact on ocean fertilization and primary production. 

SUPPLEMENTARY MATERIALS

Supplementary materials are available online at <https://doi.org/10.5670/oceanog.2018.408>.

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