

## Aerosol inputs enhance new production in the subtropical northeast Atlantic

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[1] Atmospheric deposition is an important source of limiting nutrients to the ocean, potentially stimulating oceanic biota. Atmospheric inputs can also deliver important amounts of organic matter, which may fuel heterotrophic activity in the ocean. The effect of atmospheric dry aerosol deposition on the metabolic balance and net production of planktonic communities remains unresolved. Here we report high inputs of aerosol-bound N, Si, P, Fe and organic C to the subtropical NE Atlantic and experimentally demonstrate these inputs to stimulate autotrophic abundance and metabolism far beyond the modest stimulation of heterotrophic processes, thereby enhancing new production. Aerosol dry deposition was threefold to tenfold higher in the coastal ocean than in the open ocean, and supplied high average ( $\pm$ SE) inputs of organic C ( $980 \pm 220 \mu\text{mol C m}^{-2} \text{d}^{-1}$ ), total N ( $280 \pm 70 \mu\text{mol N m}^{-2} \text{d}^{-1}$ ), Si ( $211 \pm 39 \mu\text{mol Si m}^{-2} \text{d}^{-1}$ ), and labile Fe ( $1.01 \pm 0.19 \mu\text{mol Fe m}^{-2} \text{d}^{-1}$ ), but low amounts of total P ( $8 \pm 1.6 \mu\text{mol P m}^{-2} \text{d}^{-1}$ ) to the region during the study. Experimental aerosol inputs to oceanic planktonic communities from the studied area resulted, at the highest doses applied, in a sharp increase in phytoplankton biomass (sevenfold) and production (tenfold) within 4 days, with the community shifting from a dominance of picocyanobacteria to one of diatoms. In contrast, bacterial abundance and production showed little response. Primary production showed a much greater increase in response to aerosol inputs than community respiration did, so that the P/R ratio increased from around 0.95 in the ambient waters, where communities were close to metabolic balance, to 3.3 at the highest nutrient inputs, indicative of a high excess production and a potential for substantial net CO<sub>2</sub> removal by the community in response to aerosol inputs. These results showed that aerosol inputs are major vectors of nutrient and carbon inputs, which can, during high depositional events, enhance new production in the NE subtropical Atlantic Ocean.

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### 1. Introduction

[2] Atmospheric inputs are known to be a major vector of nutrients to the open ocean [Graham and Duce, 1982; Duce et al., 1991; Baker et al., 2003; Mills et al., 2004; Jickells et al., 2005], where they are believed to stimulate primary production [Johnson et al., 2003; Mills et al., 2004; Zhang et al., 2004; Jickells et al., 2005]. Whereas discussions on the potential biological effects of these inputs have focused on autotrophic processes [Johnson et al., 2003; Mills et al.,

2004; Jickells et al., 2005], atmospheric inputs can also deliver important amounts of organic matter [Cornell et al., 1995; Scholes et al., 2003], which may fuel heterotrophic activity in the ocean [Seitzinger and Sanders, 1999; Durrieu de Madron et al., 2000; Dachs et al., 2005]. However, whereas there is considerable information on the input of inorganic nutrients to the ocean, the inputs of organic carbon delivered to the ocean with atmospheric deposition remain poorly resolved.

[3] The effects of inorganic nutrients and organic carbon delivered to the ocean with atmospheric dry aerosol deposition on the metabolic balance and net production of planktonic communities also remain unresolved. A recent report concluded that enhanced atmospheric dry aerosol deposition at the Canary Islands was not accompanied by enhanced sedimentary particulate organic carbon flux outside the mixed layer [Neuer et al., 2004], suggesting that any enhancement of gross primary production was too low to be resolved by rather crude assessment of production

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used in that study [Neuer *et al.*, 2004] or that the excess primary production was consumed within the mixed layer, with no net increase in community production. In contrast, recent studies showed increased primary production in response to experimental dust inputs [Mills *et al.*, 2004; Bonnet *et al.*, 2005]. Current understanding suggests that atmospheric dry aerosol deposition may increase primary production particularly in high-nutrient, low-chlorophyll areas, whereas its main effect elsewhere is believed to be increased nitrogen fixation [cf. Jickells *et al.*, 2005].

[4] Here we assessed depositional fluxes of aerosol-bound N, P, Si, Fe and organic C to the NE subtropical Atlantic and test experimentally their effects on phytoplankton and bacteria abundance and production, as well as on community metabolism (primary production and respiration) and net community production (primary production–community respiration). We do so through a combination of direct estimates of atmospheric dry aerosol deposition and experimental additions of this material to planktonic communities.

## 2. Methods

### 2.1. Sampling Area and Aerosol Collection

[5] The study was conducted during a cruise aboard the R/V *Hespérides* in May–June 2003 across a box delimited by the West African coast and 26°W along parallels 26°N and 21°N, an area subject to Saharan dust influence [Duce *et al.*, 1991; Viana *et al.*, 2002; Jickells *et al.*, 2005]. The cruise spanned from open ocean stations (three stations at each transect) to coastal waters affected by upwelling (two stations on the N transect and three on the S transect), as revealed by the examination of T-S cross sections. Aerosols were collected on quartz fiber filters (QFF, Whatmann) using a modified high volume collector that efficiently collects particles smaller than roughly 30 microns in diameter. Samples were taken in 20 transits between sampling stations. Aerosol mass concentrations ( $C_{TSP}$ ) were determined by gravimetry. Two aerosol samples were taken simultaneously: one for Fe analyses, and the second for total suspended particles (TSP), nitrogen phosphorus and organic carbon and silicate analyses.

### 2.2. Aerosol Analysis

[6] Aerosol samples for Fe were collected on acid-washed, 0.2-mm polyethersulfone filter (Supor-200, Pall Gelman Sciences) extracted with 4.5 M quartz-distilled acetic acid to estimate labile Fe followed by strong acid digestion to estimate refractory Fe [Landing and Bruland, 1987]. Fe in the extracts was determined by graphite furnace atomic absorption spectrometry (GFAAS, Perkin-Elmer AAnalyst 800). Total N and P and Si concentrations were analyzed in an autoanalyzer, following persulfate digestion of the filters, according to standard procedures [Hansen and Koroleff, 1999]. Aerosol organic carbon was determined by the thermal-optical transmittance in a Sunset Laboratory Carbon Analyzer using the NIOSH temperature control [Birch and Cary, 1996]. We used clean filters as blanks for all of these determinations.

[7] Aerosol samples were collected during transects between stations. The ratio of aerosol organic carbon to aerosol elemental carbon averaged 10.1 and ranged from

3.6 to 18.5. These values are significantly higher than those found for primary emission, which are around 2 [Seinfeld and Pandis, 1998]. This result indicates a lack of contamination from the ship exhaust, which would result in a higher EC contribution. Furthermore, EC concentrations averaged  $0.82 \mu\text{g m}^{-3}$  and ranged from 0.05 to  $2.5 \mu\text{g m}^{-3}$ , characteristic of oceanic regions [Seinfeld and Pandis, 1998].

### 2.3. Dry Deposition Fluxes

[8] Atmospheric deposition of aerosols was measured with a modified water deposition sampler. The water deposition sampler for dry aerosol deposition has been described by T. Holsen and collaborators [Tasdemir and Losen, 2005, and references therein]. It measures the magnitude of aerosols deposited to a real water surface instead of a surrogate surface. Even though the use of surrogate surfaces and models has been quite common, it may lead, depending on wind speed, atmospheric stability and aerosol size distributions, to important errors, likely resulting in underestimation of the dry deposition fluxes. The water deposition sampler used here is basically a tray with water receiving the deposited particles. The aerosols collected were quantified by gravimetry after filtering the water. The measured deposition velocities ( $dv$ ) ranged from  $0.6 \text{ cm s}^{-1}$  to  $4.1 \text{ cm s}^{-1}$ . These values are comparable, for example, to those used ( $dv = 2 \text{ cm s}^{-1}$ ) for estimating deposition of aerosols larger than  $2 \mu\text{m}$  [Duce *et al.*, 1991; Baker *et al.*, 2003] and higher than those measured using surrogate surfaces instead of a water surface [Torres-Padrón *et al.*, 2002]. However, the settling velocities measured by us are even lower than those reported by Tasdemir and Losen [2005]. Large aerosols such as dust dominate dry aerosol depositional fluxes, which are also a complex function of wind speed, atmospheric turbulence, among other factors [Jurado *et al.*, 2004]. Therefore the settling velocities estimated here are representative of large aerosols (dust, nitrate, Fe) but may overestimate the fluxes of fine aerosols, such as those that contain ammonium. The average wind speed during the cruise was  $8 \text{ m s}^{-1}$ , with sampling periods with wind speeds higher than  $15 \text{ m s}^{-1}$ . These high wind speeds do result in high deposition velocities as measured here and predicted by models (see supplementary material of Jurado *et al.* [2004]).

### 2.4. Experimental Assessment of Aerosol Effects on Planktonic Communities

[9] The impact of aerosols on planktonic communities was assessed in two experiments using aerosols collected using high-volume collectors into QFF filters and extracted by sonication ( $2 \times 30 \text{ min}$ ) into 250 mL of surface seawater, (1) a pulse experiment to assess responses to a single input of  $405 \mu\text{g}$  aerosol TSP  $\text{L}^{-1}$  to four replicated 2-L units of surface seawater (collected at 25.99°N, 18.0°W), and (2) a dose-response experiment assessing the response to nine levels of aerosol pulses, increasing in geometric sequence from 0 (control) to  $811 \mu\text{g}$  TSP  $\text{L}^{-1}$ , to 2-L units of surface seawater (collected at 21.0°N, 23.0°W). Seawater nutrient concentrations were low at both these stations (phosphate  $< 0.2 \mu\text{mol P L}^{-1}$ , nitrate  $< 0.2 \mu\text{mol N L}^{-1}$ ). The experimental design involved uncertainties, as the aerosol input rates occurring along the cruise

could only be calculated a posteriori, and the experimental doses had, therefore, to be assessed using our best judgment. These uncertainties are unavoidable and are, no doubt, responsible for the fact that previous experimental assessments of the biological response to aerosol additions used much higher experimental aerosol doses [e.g., Mills *et al.*, 2004; Bonnet *et al.*, 2005]. The first pulse experiment was calculated to represent a high-dose situation, whereas the gradient-addition experiment involved a logarithmic increase in dosage designed to encompass a broad range of doses, from very low to very high doses relative to those occurring in the region studied. Calculations showed that the experimental doses of aerosol material used correspond to the average input received in the sampling transect over the 4-day experimental period distributed over a 4-m water layer for the single-dose experiment, and to these inputs distributed across a 2- to 200-m water column for the dose-response experiment. The presence of important variability in net community metabolism, total organic carbon and  $p\text{CO}_2$  over the top 5 m of the water column during the cruise [Calleja *et al.*, 2005], suggests that the layer actively mixing was shallow during the study. These estimations of relative importance of doses are drawn from the measured TSP fluxes at the location where the incubations were initiated. Depending on the dry deposition flux, which is highly variable across experiments, the experiments can be representative of different doses. The experimental inputs comprised, therefore, realistic dosages, with the highest treatments being comparable to observed concentrations in surface waters after strong Saharan depositional events [Ridame and Guieu, 2002]. Furthermore, wet deposition can also be an important input of nutrients due to aerosol scavenging. Inputs during raining events, which did not occur during the present sampling cruise, can account for an important input of aerosols, comparable to those simulated in the present simulation.

[10] The yield of dissolved organic carbon (DOC) and inorganic nutrient additions associated with the aerosol inputs were derived from the rate of increase in dissolved organic carbon, nitrate, phosphate, ammonium and silicate concentrations immediately after aerosol additions. Briefly, DOC concentrations were measured on 10-mL samples transferred to glass ampoules (previously burned at 450°C for 4.5 hours) and acidified to a pH of 1–2 by adding  $\text{H}_3\text{PO}_4$ . DOC concentrations were analyzed by high-temperature catalytic oxidation on a Shimadzu TOC-5000A [Qian and Mopper, 1996]. Standards provided by Dennis A. Hansell and Wenhao Chen (University of Miami) of 44–45  $\mu\text{mol C L}^{-1}$  and 2  $\mu\text{mol C L}^{-1}$  were used to assess the accuracy of the measurements. Dissolved inorganic nutrients were measured on an autoanalyzer using standard colorimetric methods [Hansen and Koroleff, 1999], except for ammonium concentrations, which were measured spectrofluorometrically [Kéruef and Aminot, 1997] within 1 hour of collection. Biological responses were assessed, after incubating the samples over 4 days placed in acid-washed transparent 2.5-L Nalgene bottles on deck in a tank covered with a mesh screen to simulate the light environment at 5 m depth and flushed with surface seawater to maintain in situ temperature, by the increase in chlorophyll *a* concentration (exp. 1 and 2), phytoplankton (pico, nano, and micro) biovolume and primary production,

bacterial abundance and production, and community respiration, measured using standard procedures [Agusti *et al.*, 2000]. Primary production was determined as the total (particulate + dissolved)  $^{14}\text{C}$  incorporation of duplicate samples and blanks [Moran and Estrada, 2002] incubated for 3.5 hours, yielding a precision of  $\pm 3.5\%$  about the mean. Bacterial production was determined as the rate of radioactive leucine incorporation by bacteria, using the method described by Kirchman [1993] but in Eppendorf vials as suggested by Smith and Azam [1992]. In each sample, we added 40 nM leucine to triplicate vials plus one TCA-killed control. Bacterial heterotrophic production (BP) was calculated from leucine incorporation (Leu) using a leucine to carbon CF of 1.55  $\text{kgC mol leucine}^{-1}$ . The abundance of *Trichodesmium* at the sampling station was evaluated using vertical hauls from 30 m depth to surface with a 50  $\mu\text{m}$  mesh-size 25-cm-diameter net, and evaluated as number of trichomes under the dissecting microscope.

### 3. Results and Discussion

#### 3.1. Atmospheric Deposition of C, N, P and Fe to the NE Subtropical Atlantic

[11] The study period was characterized by average atmospheric concentrations of total suspended particles ( $\text{C}_{\text{TSP}}$ ) of 80  $\mu\text{g m}^{-3}$ , comparable to the regional average during NE wind direction air masses (mean  $\text{C}_{\text{TSP}} \pm \text{SE}$ ,  $59 \pm 13 \mu\text{g m}^{-3}$ ), and lower than that observed during strong aerosol dust events [Viana *et al.*, 2002]. Aerosol deposition was high (mean  $\pm \text{SE}$ ,  $215 \pm 22 \text{ mg m}^{-2} \text{ d}^{-1}$ ), as expected for the NE Subtropical Atlantic, which receives the highest aerosol inputs in the world ocean [Duce *et al.*, 1991; Jickells *et al.*, 2005]. Atmospheric deposition was threefold to tenfold higher in the coastal ocean than in the open ocean, consistent with proximate sources of aerosols upwind from the NW African continent. The fluxes reported here are somewhat higher than previously reported values [Baker *et al.*, 2003], owing to the fact that we used depositional velocities measured in situ (see section 2) rather than assumed values, which may in some cases add important uncertainties [Baker *et al.*, 2003], or values derived from land-base stations as used in other studies [Neuer *et al.*, 2004]. The depositional velocities measured for TSP were used to estimate the carbon and nutrient dry depositional fluxes from N, P, and labile Fe concentrations in aerosols.

[12] Aerosol deposition supplied high average ( $\pm \text{SE}$ ) inputs of organic C ( $980 \pm 220 \mu\text{mol C m}^{-2} \text{ d}^{-1}$ ), N ( $280 \pm 70 \mu\text{mol N m}^{-2} \text{ d}^{-1}$ ), Si ( $211 \pm 39 \mu\text{mol Si m}^{-2} \text{ d}^{-1}$ ), and labile Fe ( $1.01 \pm 0.19 \mu\text{mol Fe m}^{-2} \text{ d}^{-1}$ ), but low amounts of P ( $4.4 \pm 1.7 \mu\text{mol P m}^{-2} \text{ d}^{-1}$ ) to the region. However, there was an important spatial variability in depositional fluxes. These differences are evident when comparing the samples from the coastal ocean to those from the open ocean (Table 1). In addition there were also differences between samples taken during the north transect and those taken during the southern transect (see Table 1). The higher depositional fluxes to the coastal ocean are due to higher nutrient concentrations in aerosols in this region. In the case of N and Fe, the concentrations in the coastal ocean aerosols are significantly higher than those in the open ocean. Conversely, P concentrations and depositional fluxes are



**Table 1.** Average and Standard Deviation of Dry Deposition Fluxes of Aerosol Organic Carbon (OC), N, P, and Labile Fe to the NE Subtropical Atlantic

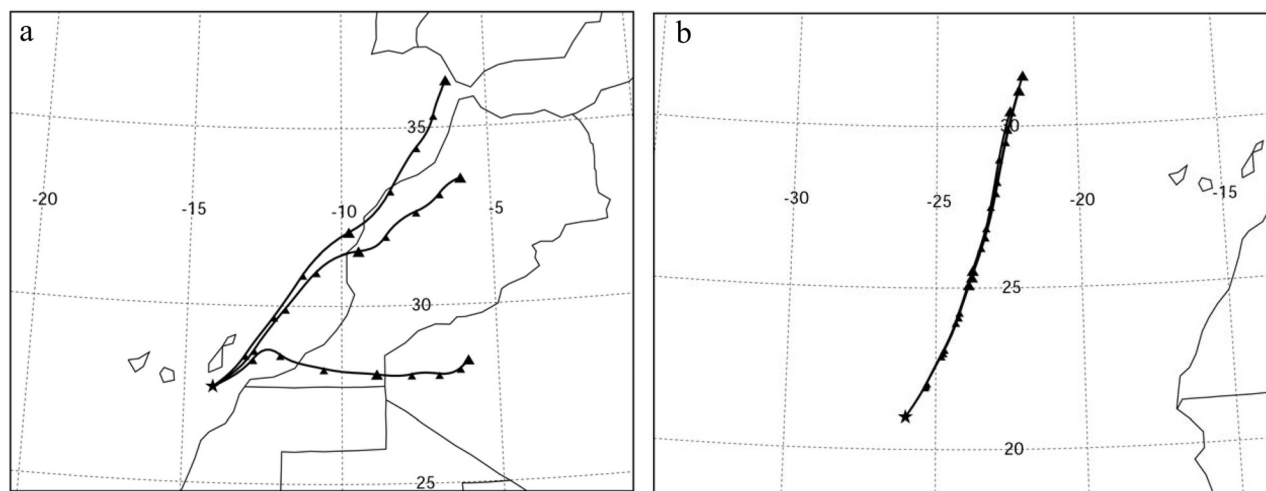
	Coastal Ocean	Open Ocean
<i>North Transect (26°N)</i>		
OC, $\text{mmol m}^{-2} \text{d}^{-1}$	$1.7 \pm 0.9$	$3.5 \pm 3.1$
N, $\mu\text{mol m}^{-2} \text{d}^{-1}$	$465 \pm 183$	$135 \pm 28$
P, $\mu\text{mol m}^{-2} \text{d}^{-1}$	$5.3 \pm 5.2$	$3.9 \pm 2.5$
Fe, $\mu\text{mol m}^{-2} \text{d}^{-1}$	$1.7 \pm 1.6$	$0.4 \pm 0.1$
N/P	$83 \pm 43$	$47 \pm 37$
N/Fe	$627 \pm 45$	$369 \pm 33$
P/Fe	$5.9 \pm 5$	$12 \pm 10$
<i>South Transect (21°N)</i>		
OC, $\text{mmol m}^{-2} \text{d}^{-1}$	$0.6 \pm 0.3$	$0.4 \pm 0.3$
N, $\mu\text{mol m}^{-2} \text{d}^{-1}$	$245 \pm 51$	$132 \pm 94$
P, $\mu\text{mol m}^{-2} \text{d}^{-1}$	$2.3 \pm 1.7$	$5.8 \pm 5.6$
Fe, $\mu\text{mol m}^{-2} \text{d}^{-1}$	$0.46 \pm 0.36$	$0.60 \pm 0.29$
N/P	$55 \pm 52$	$28 \pm 10$
N/Fe	$346 \pm 31$	$250 \pm 165$
P/Fe	$1.6 \pm 1.6$	$10.6 \pm 7.4$

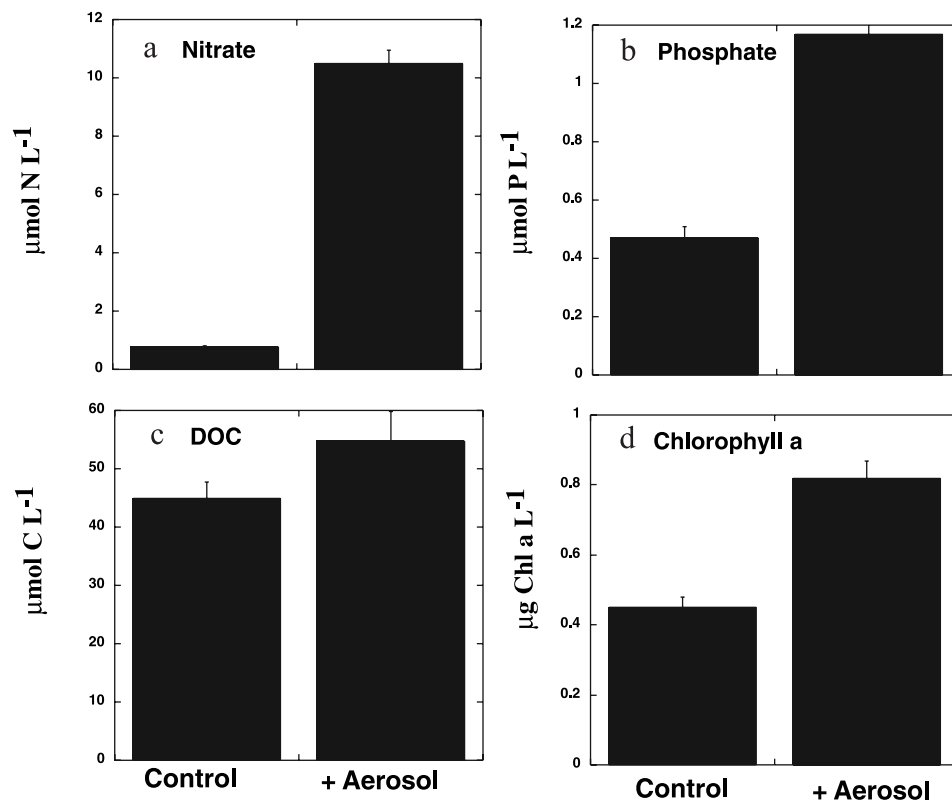
not significantly different in the coastal than in the open ocean (Table 1).

[13] The analysis of air mass back trajectories for each sampling period provides important information on the recent history of aerosols and potential sources. Figure 1 shows the 48-hour back trajectory (NOAA Air Resources Laboratory, HYSPLIT model, FNL data set) for two representative sampling periods, one in the coastal region (Figure 1a) and another in the open sea (Figure 1b). For the coastal sites, air masses came from the NW African continent and thus, presumably, with important anthropogenic influence. Conversely, in the open ocean, the air mass had been over the ocean for the previous 48 hours and only before that period could it receive anthropogenic inputs from SW Europe (Figure 1). Anthropogenic activities can provide important inputs of atmospheric N [de Leeuw *et al.*, 2003], for example from vehicle emissions [Schauer *et al.*, 2002], but with little influence on atmospheric levels of P. This could explain the spatial variability of N and P observed

here. Potential sources of P include biogenic aerosols (e.g., dead microorganisms, pollen), which have a small size and thus have longer atmospheric residence time [Mahowald *et al.*, 2005], and marine aerosols [Graham *et al.*, 1979]. Concerning Fe, the Fe/Al ratios observed here (0.1) are similar to those observed in desert dust [Tovar-Sánchez *et al.*, 2006] and lower than those from anthropogenic emissions [Schauer *et al.*, 2002].

[14] Aerosol deposition supported a substantial N input, consistent with the important contribution of N to aerosol mass [Jacob, 1999]. The depositional fluxes of N and P reported here for the open ocean were a factor of 2–3 higher than those reported in previous reports for the same region [Baker *et al.*, 2003]. The higher N and P fluxes reported here for the open ocean are due in part to the high deposition velocities measured here and presumably to higher concentrations than those measured elsewhere [Baker *et al.*, 2003]. Deposition rates are highly dependent on aerosol size and wind speed [Jurado *et al.*, 2004], so the presence of dust and high wind speeds during the sampling periods can explain the high deposition rates measured. However, in the case of N, the fluxes reported here may be somewhat overestimated as the ammonium fraction, which represented 23% of the N input, is associated to fine mode aerosol and thus is deposited with lower settling velocities than those measured for TSP here. There was a high variability of the total N/P values with higher values closer to the coast than in the open ocean, consistent with the anthropogenic sources as discussed above. In most of the stations, this ratio was higher than the Redfield value of 16, a trend that has been reported previously for this and other marine regions [Baker *et al.*, 2003; Guerzoni *et al.*, 1999]. Similarly, the high N/Fe and close to unity Fe/P ratios are equal to those reported for this region [Baker *et al.*, 2003]. The low abundance of P in atmospheric inputs indicates low inputs relative to N and probably is an additional factor driving the system toward the P limitation reported across large areas of the subtropical North Atlantic [Ammerman *et al.*, 2003; Cañellas *et al.*, 2000; Vidal *et al.*, 2003].

**Figure 1.** Back trajectories of air masses for representative sampling periods. (a) Forty-eight-hour back trajectory for a coastal site (27°N, 15°W) on 21 May 2003, and (b) 48-hour back trajectory for an open ocean site (21°N, 26°W) on 29 May 2003.



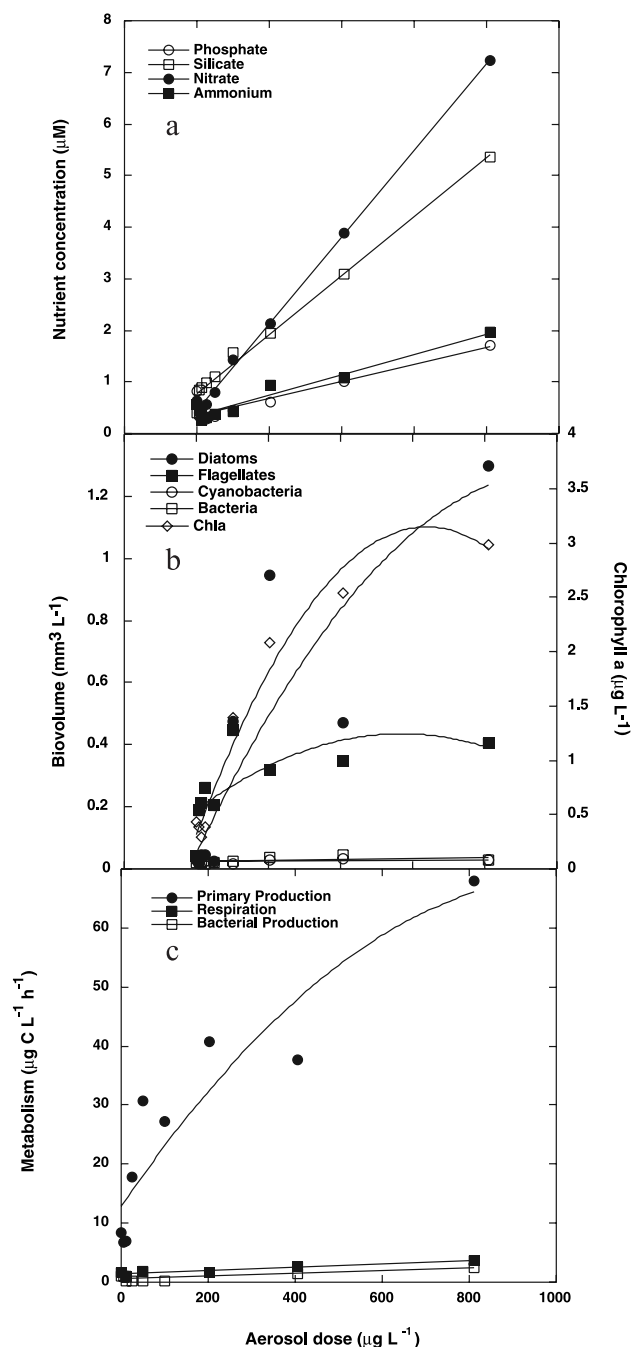
**Figure 2.** Effect of aerosol additions ( $405 \mu\text{g}$  aerosol TSP  $\text{L}^{-1}$ ) on (a, b) the average nutrient and (c) organic carbon concentrations, and (d) the average chlorophyll *a* concentrations developed 4 days after the aerosol addition, compared to values in unamended controls. Error bars represent  $\pm 1$  SE.

[15] The results presented refer to dry depositional fluxes whereas wet deposition can be an important vector for inorganic and organic nutrient and carbon inputs to the ocean [Duce *et al.*, 1991; Cornell *et al.*, 1995; Willey *et al.*, 2000; Kouvarakis and Mihalopoulos, 2001] and have indeed been shown in the past to stimulate primary [e.g., Owens *et al.*, 1992; Michaels *et al.*, 1993; Herut *et al.*, 1999; de Leeuw *et al.*, 2003; Zhang *et al.*, 2004] and bacterial [e.g., Klein *et al.*, 1997; Seitzinger and Sanders, 1999] production. However, there was no rainfall during the cruise when the study was completed, such that wet deposition, although an important vector for nutrients, could not be addressed in our study. However, wet deposition is probably not a dominant component of the atmospheric inputs in the semiarid region investigated.

### 3.2. Aerosol Effects on Planktonic Communities

[16] A pulse addition of aerosol material ( $405 \mu\text{g}$  TSP  $\text{L}^{-1}$ ), equivalent to that resulting from mixing of the measured average deposition over the 4-day duration of the experiment into a 4-m-thick water column, led to a significant (t-test,  $P < 0.05$ ) increase in nutrient concentrations and dissolved organic carbon (Figures 2a–2c). Nitrate and phosphate concentrations increased by, on average,  $9.7 \mu\text{mol N L}^{-1}$  and  $0.7 \mu\text{mol P L}^{-1}$  as a result of pulse aerosol additions. Phytoplankton biomass, as chlorophyll *a* concentration, doubled (mean  $\pm$ SE relative increase =  $1.86 \pm 0.23$  fold) 4 days following aerosol additions (Figure 2d). Inorganic nutrient concentrations increased linearly following aerosol additions with increasing

aerosol inputs (Figure 3), with the rate of increase indicative of yields equivalent to  $1.9 \pm 0.01 \mu\text{mol}$  total dissolved P,  $1.6 \pm 0.2 \mu\text{mol}$  phosphate,  $5.7 \pm 0.22 \mu\text{mol}$  silicate,  $12.3 \pm 0.4 \mu\text{mol}$  total dissolved N,  $8.4 \pm 0.14 \mu\text{mol}$  nitrate, and  $1.9 \pm 0.18 \mu\text{mol}$  ammonium per mg of aerosol. The resulting N/P ratio of 6.5 in the dissolved nutrient yield is rather low, well below that of the total aerosol deposition, indicating that a significant fraction of the aerosol N did not come into solution with the procedure followed. Dissolved organic carbon concentrations also increased linearly with aerosol inputs, with a yield of  $18.6 \pm 3.2 \mu\text{mol DOC mg TSP}^{-1}$  ( $R^2 = 0.79$ ,  $P = 0.0008$ ), with the yield of DOP and DON being relatively low ( $0.11 \pm 0.03 \mu\text{mol P mg TSP}^{-1}$ ,  $R^2 = 0.54$ ,  $P < 0.05$ ; and  $1.8 \pm 0.6 \mu\text{mol N mg TSP}^{-1}$ ,  $R^2 = 0.59$ ,  $P < 0.05$ ; respectively), implying aerosol-bound DOM to be have a stoichiometric ratio of 169 C: 10.3 N: 1 P. The yield of organic nutrients was, therefore, an order of magnitude below that of inorganic nutrients. Phytoplankton biomass, as chlorophyll *a* concentrations, increased asymptotically after 4 days of exposure to increasing aerosol inputs, with the sevenfold increase in phytoplankton biomass being primarily supported by an increase in diatom biomass, which were minor contributors to the communities initially present in the low-silicate (mean  $\pm$ SE surface concentration =  $0.44 \pm 0.2 \mu\text{mol Si L}^{-1}$ ) waters sampled, as well as an increase in the biomass of autotrophic flagellates with moderate aerosol inputs (Figure 3). Cyanobacteria, the dominant autotrophs in the region [Agusti *et al.*, 2000], and heterotrophic bacteria did not show any increase in response to aerosol inputs (Figure 3). Bacterial



**Figure 3.** (a) Increase in nutrient concentration, (b) microplankton biovolume and (c) metabolism in response to a gradient of aerosol additions. The nutrient concentrations represent those following aerosol additions (time 0), whereas microplankton biovolume and metabolism were measured 4 days following additions. Solid lines represent the fitted linear (phosphate,  $R^2 = 0.84$ ; silicate,  $R^2 = 0.98$ ; nitrate,  $R^2 = 0.99$ ; ammonium,  $R^2 = 0.94$ ; cyanobacteria,  $R^2 = 0.15$ , and heterotrophic bacteria  $R^2 = 0.15$  biovolume; respiration,  $R^2 = 0.89$ ; and bacterial production,  $R^2 = 0.18$ ) and second-order polynomial (Diatom,  $R^2 = 0.77$ , and flagellate,  $R^2 = 0.49$ , biovolume; chlorophyll *a* concentration,  $R^2 = 0.96$ ; and primary production,  $R^2 = 0.84$ ) regression equations. All regression equations are statistically significant (F-test,  $P < 0.05$ ), except those for cyanobacteria and heterotrophic bacteria biovolume (F-test,  $P > 0.05$ ).

production showed a very modest, albeit statistically significant (F-test,  $P = 0.005$ ) increase (2.7-fold) across the range of aerosol inputs examined, similar to that of community respiration (twofold; F-test,  $P = 0.003$ ). In contrast, total phytoplankton production increased by 1 order of magnitude ( $6.7$  to  $68.0 \mu\text{g C L}^{-1} \text{h}^{-1}$ ; F-test,  $P = 0.0006$ ) across the range of aerosol inputs examined (Figure 3). Primary production was highly reactive to aerosol inputs, as it doubled after 4 days following an input of only  $25 \mu\text{g TSP L}^{-1}$  (Figure 3). This aerosol input, distributed over the 4-day incubation, is comparable to that resulting from mixing the average input observed along the cruise across a 35-m layer.

### 3.3. Aerosol Inputs of Nutrients and New Production

[17] The results obtained confirm that aerosol deposition is an important source of nutrients, including N, Si, Fe, and, to a lesser extent P, to the NE subtropical Atlantic Ocean [e.g., Duce *et al.*, 1991; Sarthou *et al.*, 2003; Baker *et al.*, 2003], in a stoichiometric balance similar to global average values [Duce *et al.*, 1991]. The high N/P ratio (see Table 1) of aerosol inputs, a common feature of aerosol inputs [Baker *et al.*, 2003], is consistent with the high average total N/P ratio in the water column of the region studied (average N/P ratio = 23.5) and the observation of P limitation in the subtropical Atlantic [e.g., Cañellas *et al.*, 2000; Vidal *et al.*, 2003]. However, the N/P ratio in the soluble fraction (6.5) was much lower than that in the aerosol deposition, indicating much of the N fraction in the deposition to be insoluble material. The range of atmospheric N supply from aerosol deposition obtained here ( $50$ – $1100 \mu\text{mol N m}^{-2} \text{d}^{-1}$ ) closely matches the range of atmospheric N inputs inferred from mass balance calculations in the region ( $50$ – $1900 \mu\text{mol N m}^{-2} \text{d}^{-1}$  [Planas *et al.*, 1999]), explaining the observation of nitrate uptake rates consistently in excess of those possible from the internal vertical supply in the region studied [Planas *et al.*, 1999].

[18] The results also show that aerosols inputs are important sources of organic carbon to the NE subtropical Atlantic Ocean, consistent with reports that aerosols may contain a significant load of organic carbon [Hetintzenberg *et al.*, 2003; Eglinton *et al.*, 2002; Scholes *et al.*, 2003]. The estimated average input of  $980 \pm 220 \mu\text{mol C m}^{-2} \text{d}^{-1}$  did not differ significantly (t-test,  $P > 0.05$ ) from the reported downward export flux of POC in the region of  $600 \pm 52 \mu\text{mol C m}^{-2} \text{d}^{-1}$  [Neuer *et al.*, 2002]. DOC released by aerosols may also contribute to the downward DOC export flux reported for the region [Vidal *et al.*, 1999] as there was no evidence of significant use of the DOC released by the aerosols, since no consistent (t-test,  $P > 0.05$ ) decline in DOC concentration along the 4-day experiment was observed, and the very modest increase in community respiration could be largely accounted for by the respiratory demands of the growing algal community. These observations suggest that the organic carbon associated with terrestrial aerosols may be semirefractory at best, consistent with observations that 60% of DOC derived from marine rain was used by bacteria in several days [Willey *et al.*, 2000]. In fact because of dynamic gas-particle partitioning of organic compounds, aerosol tend to be enriched in the high-molecular weight, semi-volatile organic compounds [Dachs and Eisenreich, 2000], which may not be easily



degraded. Furthermore, old refractory soil organic matter, which has long degradation times [Hansell *et al.*, 2004], is also abundant in aerosols [Eglinton *et al.*, 2002]. Furthermore, the low bacterial response to aerosol inputs could be associated with potential toxic effects of aerosol due to the multiple of organic and inorganic pollutants that enter with atmospheric deposition [Dachs and Eisenreich, 2000; Jurado *et al.*, 2004]. These could preferentially affect bacteria and picoautotrophs over phytoplankton due to their higher surface/volume ratio thus favoring their uptake [Del Vento and Dachs, 2002]. However, these effects cannot be elucidated with the present experimental design.

[19] The combined supply of nitrogen, silicate, iron and phosphorus with aerosol inputs led to a major stimulation of the autotrophic components, particularly diatoms, which are known to be the main agents of new production in the ocean and are stimulated by Si inputs [Dugdale and Wilkerson, 1998]. These observations are consistent with recent reports of increased primary production, largely through an stimulation of microphytoplankton growth, in response to dust additions [Bonnet *et al.*, 2005]. Indeed, primary production showed a much greater increase in response to aerosol inputs than community respiration did, so that the P/R ratio increased from around 0.95 in the ambient waters, where communities were close to metabolic balance, to 3.3 at the highest nutrient inputs, indicative of a high excess production and a potential for substantial net CO<sub>2</sub> removal by the community in response to aerosol inputs. Total primary production increased in response to aerosol additions at a rate of  $67.6 \pm 11.4 \mu\text{g C mg TSP}^{-1} \text{ h}^{-1}$  ( $R^2 = 0.83$ ,  $P < 0.001$ ) compared to the DOC yield of  $18.6 \pm 3.2 \mu\text{mol DOC mg TSP}^{-1}$ , so that the primary production by the community in only one hour exceeded the organic carbon associated with the aerosol input by 3 times. Accordingly, aerosol inputs drive the community to net autotrophic metabolism (i.e., primary production > respiration), and it would continue to do so even if the DOC supplied was highly labile, which was not the case.

[20] Further evidence of the important role of atmospheric deposition in enhancing net community production is provided by the regional assessment of simultaneously measured dry deposition fluxes and community metabolism. A concurrent maximum in net community production (NCP) of  $259.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$  across the photic layer [Calleja *et al.*, 2005] and high dry atmospheric nutrient deposition of  $230 \mu\text{mol N m}^{-2} \text{ d}^{-1}$  and  $6 \mu\text{mol P m}^{-2} \text{ d}^{-1}$ , respectively, were observed in our study at an oceanic station located at  $21.03^\circ\text{N}$ ,  $21.04^\circ\text{E}$ . These values exceed those in adjacent oceanic waters by fivefold for NCP [Calleja *et al.*, 2005] and 3- and 20-fold for N and P deposition. A dominance of diatoms in the community and a sizable bloom of the diazotroph N-fixing cyanobacteria *Trichodesmium* ( $5.4 \cdot 10^7$  trichomes  $\text{m}^{-2}$ ) was observed at this station, compared with low abundances ( $10^4$ – $10^5$  trichomes  $\text{m}^{-2}$ ) in adjacent oceanic waters, consistent with recent reports that experimental dust inputs promote nitrogen fixation [Mills *et al.*, 2004]. Although it is not possible to assert that the enhanced NCP and diatom-based community were due to enhanced atmospheric aerosol inputs, these observations are consistent with the experimental results.

[21] Our results add to recent demonstrations of enhanced nitrogen fixation in response to aerosol inputs [Mills *et al.*,

2004], to show that aerosol inputs, which are highest in the NE subtropical Atlantic, are major drivers of nutrient and carbon fluxes, as well as new production, in this region of the ocean. However, dust inputs from the Sahara, which are highly episodic, extend as far as the Sargasso Sea [Jickells, 1999], and aerosol depositional inputs within the range required to double primary production in the NE subtropical Atlantic surface waters (i.e.,  $25 \mu\text{g TSP L}^{-1}$ ) may sporadically occur over vast areas of the ocean, including the North and West Pacific and North Indian Ocean. Aerosol inputs may also be significant in oligotrophic areas where atmospheric deposition contributes significantly to total nutrient inputs [e.g., Jickells, 1999; Jickells *et al.*, 2005], and may support a pulse behavior of new primary production [Karl *et al.*, 2003]. The results presented suggest a dual role of aerosol inputs in increasing oceanic C uptake, by driving planktonic communities away from metabolic equilibrium to generate episodic new production and by directly contributing to the export of refractory DOC toward the ocean interior.

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