**Biogeosciences
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# Longitudinal variability of the biogeochemical role of Mediterranean aerosols in the Mediterranean Sea

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## Abstract

The Mediterranean Sea is a semi-enclosed basin characterized by a strong thermal stratification during summer during which the atmosphere is the main source of new nutrients to the nutrient-depleted surface layer. From aerosol sampling and micro-
cosm experiments performed during the TransMed BOUM cruise (June–July 2008) we showed that: (i) the Mediterranean atmosphere composition (Al, Fe, P) was homogeneous over ∼28° of longitude and was a mixture with a constant proportion of anthropogenic contribution and a variable but modest contribution of crustal aerosols. This quite stable composition over a one month period and a long transect (∼2500 km) allowed to define the Mediterranean atmospheric "background" that characterizes the summer season in the absence of major Saharan event and forest fires, (ii) primary production significantly increased at all tested stations after aerosols addition collected on-board and after Saharan dust analog addition, indicating that both additions relieved on-going (co)-limitations. Although both additions significantly increased the $N_2$ fixation rates at the western station, diazotrophic activity remained very low (∼0.2 nmol $N L^{-1} d^{-1}$), (iii) due to the presence of anthropogenic particles, the probable higher solubility of nutrients associated with mixed aerosols (crustal + anthropogenic contribution), conferred a higher fertilizing potential to on-board collected aerosol as compared to Saharan dust analog. Finally, those experiments showed that atmospheric inputs from a mixed atmospheric event ("summer rain" type) or from a high-intensity Saharan event would induce comparable response by the biota in the stratified Mediterranean SML, during summer.

## 1 Introduction

Marine oligotrophic regions are characterized by very low concentrations of chlorophyll-*a* in their surface waters (<0.1 mg m$^{-3}$; Carr et al., 2006). For the Low Nutrient Low Chlorophyll (LNLC) regions, the weak biological activity reported results from a strong

nutrient deficiency in surface waters. Atmospheric deposition is now well-known to constitute one of the major sources of new nutrients for surface waters in open oceans. However, the impact of this new nutrients input on the biological community still remains poorly understood.

5    The Mediterranean Sea is one of the most oligotrophic oceanic regions. Characterized by rapid dissolved inorganic phosphate turnover times, the Mediterranean Sea can be considered as a Low Phosphate Low Chlorophyll (LPLC) environment (Moutin et al., 2008). During summer, as the Mediterranean Sea is characterized by a strong stratification and a sharp thermocline (~10–20 m deep; D'Ortenzio et al., 2005), the
10   vertical diffusion of nutrients from below is extremely reduced and the surface mixed layer (SML) is severely nutrient depleted (Marty et al., 2002; Moutin et al., 2002; Pulido-Villena et al., 2010). During this period, the Mediterranean oligotrophy exhibits a longitudinal eastward gradient (Moutin and Raimbault, 2002; Bosc et al., 2004) reaching its highest intensity in the Eastern Mediterranean. The main external source of new
15   nutrients to the SML at that period is the atmosphere, which provides both natural (Saharan dust) and anthropogenic aerosols. Although recent satellite measurements suggest that natural Saharan deposition does not play a significant role in the sustainment of the phytoplanktonic dynamics in the Mediterranean Sea (Volpe et al., 2009), experimental evidence of fertilization by atmosphere has been shown from in vitro ex-
20   periments on both heterotrophic (see for ex Pulido-Villena et al., 2008) and autotrophic communities (Klein et al., 1997; Bonnet et al., 2005; Eker-Develi et al., 2006). Indeed, atmospheric deposition provides phosphorus (Bergametti et al., 1992; Migon and Sandroni, 1999; Ridame and Guieu, 2002; Markaki et al., 2003; Pulido-Villena et al., 2010; Guieu et al., 2010), nitrogen (Loÿe-Pilot et al., 1990; Herut et al., 1999; Kouvarakis et
25   al., 2001; Sandroni et al., 2007; Bonnet et al., 2005; Markaki et al., 2010) as well as iron (Bonnet and Guieu, 2006; Theodosi et al., 2010) to the SML in the Mediterranean Sea.

In this context, the aim of the present study was to investigate the spatial variability of the chemical composition of the Mediterranean aerosols and to evaluate the impact

of atmospheric deposition on the biological activity in the SML during summer, according to the longitudinal gradient of oligotrophy. In particular, we investigated (1) the aerosol chemical composition (P, Fe, Al), (2) the potential fertilizing effect of new nutrients from aerosols on biomass and production of autotrophic communities (including diazotrophs), (3) the influence of the nature of aerosols on their fertilizing potential, by comparing the effect of additions of both on-board collected aerosols and Saharan dust analog.

## 2   Material and methods

Aerosol sampling and microcosm experiments were performed during the trans-Mediterranean BOUM (Biogeochemistry of Oligotrophic to Ultra-Oligotrophic Mediterranean, http://www.com.univ-mrs.fr/BOUM/) campaign (16 June–20 July 2008) on board R/V *Atalante*. The main goal of the campaign was to improve the knowledge of the Mediterranean ecosystem functioning, following three main themes: (i) Longitudinal description of the biogeochemistry and the biological diversity, (ii) Biological production and organic matter fate in contrasted oligotrophic environments and, (iii) Biogeochemical fluxes and trophic web representations as a function of the intensity of the oligotrophy.

### 2.1   Sampling

All manipulations took place under laminar flow bench inside a clean container and all material was acid-cleaned following trace-metal protocols prior utilization.

### 2.1.1   Aerosol sampling

Aerosol samples were continuously collected during the BOUM cruise using a sampling device designed to avoid ship contamination (see description in Wagener et al., 2008).

Prior to filtration, filters (polycarbonate, 47 mm diameter, 0.45 µm porosity) were acid-cleaned with a 2% solution of supra-pure hydrochloric acid (Merck Suprapur grade) and thoroughly rinsed with ultra pure water then dried under a laminar flow bench and stored in acid-cleaned Petri dishes. On board, four aerosols samples were collected simultaneously at about $1 \, m^3 \, h^{-1}$ pumping rate. The total amount of air pumped on each filter was recorded using volumetric counters. A total of $9 \times 4$ samples were collected and labeled from Aero 2 to Aero 10 (from the Eastern to the Western Mediterranean, Fig. 1). After each sampling, one of the 4 collected filters was stored in the dark at ambient temperature ($\sim$25 °C) in its Petri dish for further chemical analysis in the laboratory (total concentrations of Al, Fe and P). Two filters were devoted to the on-board microcosm experiments.

### 2.1.2 Seawater sampling

Surface seawater was sampled at 4 stations (A, B, C and 17, Fig. 1) at 8 m depth (above the base of the surface mixed layer), following the same protocol as described in Blain et al. (2008) that allows direct pumping of the seawater inside the clean container. Non-filtered seawater was collected into acid-washed 4.5 L polycarbonate bottles at stations A, B, C and 17 to perform the microcosm experiments. In addition, filtered seawater ($<$0.2 µm – Sartobran cartridge filters) was collected for measurements of initial dissolved iron (DFe) concentration. DFe samples were acidified to pH 2 (Ultrapur – Merck HCL – 30%) and stored in the dark at 4 °C. Non-filtered seawater was collected for measurements of initial abundances of autotrophic organisms (prokaryotes, nano- and pico-eukaryotes) and heterotrophic bacteria. Samples were preserved with 2% formaldehyde according to Trousselier et al. (1995).

### 2.2 Aerosols addition experiment

Non-filtered seawater (4.5 L) was immediately amended with two types of aerosols: a whole aerosol filter sampled on board (Aero 2, 3, 4 and 5, see Fig. 1) and a "Saharan

dust analog" ($1\,mg\,L^{-1}$). It is noteworthy that due to on-board schedule pressure, aerosol filters used were not necessarily geographically representative of the area where the seawater was sampled (Fig. 1). At that point, it is important to mention that the discussion on the aerosol characteristics (see Sect. 5.1) shows that this geo-graphical difference does not constitute an issue in this experiment.

The protocol for preparing the Saharan dust analog is fully described in Guieu et al. (2010). Briefly, Saharan analog was produced from ($<20\,\mu m$) soil collected in Tunisia followed by an appropriate chemical treatment in the laboratory with the goal to mimic the aging during atmospheric transport. In particular N content was increased by a factor 10 by the simulated cloud water processing. That Saharan evapocondensed dust (named hereafter "Saharan dust analog") contains 2.31% of Fe, 1.15% of nitrogen and 0.05% of phosphorus (Guieu et al., 2010).

Each treatment (+Saharan dust analog and +collected aerosols) was performed in duplicate. For each experiment, two unamended bottles were kept as controls. The bottles were capped with septum caps to avoid the presence of air bubbles inside the bottle and sealed with polyvinyl chloride tape. All the bottles were incubated dur-ing 48 h in an on-deck incubator at appropriated irradiance ($\sim$50% ambient light level representing the light intensity encountered at 8 m). A running seawater system con-tinuously supplied sea surface waters to maintain a constant temperature. After 24 h, 2.5 mL of $H^{13}CO_3^-$ and 5 mL of $^{15}N_2$ gas (99%, EURISOTOP) were added in each bottle for primary production and $N_2$ fixation determinations (dual $^{13}C/^{15}N_2$ label tech-nique). Bottles were incubated for another 24 h in the on-deck incubators.

At the end of the experiment, aliquots were taken from all the experimental bottles in order to measure (i) autotrophic organisms and heterotrophic bacterial abundance, and (ii) primary production and $N_2$ fixation rate.

## 2.3 Sample treatment and chemical analysis

### 2.3.1 Acid digestion of aerosol filters

Acid digestion of aerosol samples, three reagent blanks, three filters blanks and two certified reference material (GBW07313: marine sediment from National Research Centre for Certified Reference Materials of China), was performed in the laboratory according protocol described by Ternon et al. (2010).

### 2.3.2 Aerosol metal analysis

Particulate aluminium and iron were analyzed by ICP-AES Jobin Yvon Horiba (JYH Ultima C) by H. Miche at the CEREGE laboratory, on the acid-digested samples. The detection limit of the apparatus (15 ppb for aluminium and 5 ppb for iron) was well below the lowest concentration of the digested aerosols samples. Digestion reagents blanks and filters blanks were under the detection limit for both aluminium (Al), and iron (Fe). Reference material recovery was $100 \pm 5\%$ for aluminium and $100 \pm 2\%$ for iron.

### 2.3.3 Aerosol phosphorus analysis

Phosphorus (P) was analysed in the laboratory from diluted (1/10) acid-digested samples by spectrophotometry (Murphy and Riley, 1962; Zhang and Chi, 2002) using a long waveguide capillary cell (LWCC) of 2-m long, following the same protocol and analytical parameters as Pulido-Villena et al. (2010). Detection limit, defined as three times the standard deviation of 4 measurements of the reagent blanks, was 2.7 nM. Digestion reagent blanks and filters blanks values were respectively $15 \pm 2$ nM ($n = 3$) and $2.0 \pm 0.2$ nmol P.filter$^{-1}$ ($n = 3$). Considering 3 times the standard deviation of the filter blanks and an averaged air volume of 45 m$^3$, these numbers lead to an "aerosol P detection limit" of 12 pmol m$^{-3}$.

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### 2.3.4 Dissolved iron (DFe) concentration in seawater

60 mL samples for DFe were filtered on 0.2 µm porosity polycarbonate membrane and analysed by flow injection with online pre concentration and chimiluminescence detection (FIA – CL) following the same protocol, analytical parameters and instrument as Bonnet and Guieu (2006) (in the present study, detection limit (DL) = $12 \pm 2$ pM and average of 4 measurements of the reagent blanks = $35 \pm 8$ pM).

### 2.3.5 Autotrophic eukaryotes (pico and nano), prokaryotes (*Synechoccocus* and *Prochloroccocus*), and heterotrophic bacteria abundances

4 mL of seawater samples were fixed with formaldehyde (2% final concentration). After at least 10 min on the bench at room temperature in the dark, samples were frozen in liquid nitrogen then stored at $-80\,°C$ until their analysis in the laboratory. Counts were performed with the FACSCalibur flow cytometer (Becton Dickinson at the LOBB, Banyuls-sur-mer, France) equipped with an air-cooled argon laser (488 nm, 15 mW), as described in Trousselier et al. (1995) and in Obernosterer et al. (2005). Due to a sampling problem, no abundance data are available at station C.

### 2.3.6 Primary production and $N_2$ fixation rate

Seawater (4.2 L) was filtered onto pre-combusted 25 mm GF/F filters, and stored at $-20\,°C$ until analysis. Concentrations of N and C in particulate matter as well as $^{15}$N-enrichment in PON and $^{13}$C-enrichment in POC were quantified with a mass spectrometer (Delta plus, ThermoFisher Scientific, Bremen, Germany) coupled with a C/N analyzer (Flash EA, ThermoFisher Scientific) via a type III-interface. Standard deviation (SD) was 0.004 and 0.009 µmol L$^{-1}$ for PON and POC, respectively, and 0.0001 atom% and 0.0002 atom% for $^{15}$N and $^{13}$C enrichments respectively. $N_2$ fixation rates were calculated by isotope mass balanced as described by Montoya et al. (1996), in parallel with primary production.

### 2.3.7 Statistical treatment

The microcosm experiments being performed in duplicates, numbers obtained for each parameter in the different treatments (control, +collected aerosol, +Saharan dust analog) were compared using a one-way ANOVA and a Fisher LSD means comparison test ($\alpha = 0.05$).

### 2.4 Other data used

### Air mass back trajectories

Back trajectories are usually used as an approach to determine the origin of air masses carrying the sampled aerosol. In this study, the HYSPLIT (Hybrid Single Particle Lagrangian Integrated trajectory from the NOAA Air Resource Laboratory) model was used (http://ready.arl.noaa.gov/HYSPLIT.php) with reanalysed archive meteorological data (GDAS). 5-days back-trajectory were calculated (1) every day with a finishing point at the ship position at 12h UT and (2) at three altitudes (10, 500 and 1000 m) with a starting time beginning up to 120 h before the time at the finishing point. The trajectory at 10 m was representative of the vessel mast height where sampling was performed.

## 3 Results

### 3.1 Aerosols composition

During the campaign, sampled aerosols exhibited little variations in their total Fe (40–180 ng m$^{-3}$), Al (50–320 ng m$^{-3}$) and P (3–16 ng m$^{-3}$) concentrations (Table 1). Aerosol insoluble mass can be estimated using aluminium as a lithogenic tracer, since in the Mediterranean environment the aerosol insoluble mass is mainly due to lithogenic material from Saharan origin (Loÿe-Pilot and Martin, 1996). Considering that the Saharan aerosols contain on average 7.1% aluminium (Guieu et al., 2002), the insoluble mass

of the sampled aerosols ranged between 0.7–4.5 µg m$^{-3}$. (Fe/Al) and (P/Al) ratios respectively ranged between 0.56–0.80 and 0.03–0.16.

## 3.2 Initial features at 8-m depth at the 4 tested stations

The upper surface mixed layer (SML) remained strongly stratified during the whole
cruise (∼10 m depth, Moutin et al., 2010), typical of summer conditions (see D'Ortenzio et al., 2005). At sampled stations, nitrate, nitrite and phosphate concentrations in the SML were below the detection limit (20 nM for nitrate and nitrite and 10 nM for phosphate; Pujo-Pay et al., 2010). Dissolved iron concentrations were ranging from 1.2 to 2.9 nM. Chlorophyll-$a$ concentrations ranged from 0.03 µg L$^{-1}$ at station C to
0.08 µg L$^{-1}$ at station 17 (Ras, personal communication).

Initial conditions for primary production, N$_2$ fixation, bacterial abundance and autotrophic prokaryotic and eukaryotic abundances at the tested stations are presented on Fig. 2. Mean primary production was low from 0.70 to 2.81 mg C m$^{-3}$ d$^{-1}$ (Fig. 2a). Decreasing primary production from station A to station C confirmed the eastward gradient of oligotrophy usually observed at that period (Bosc et al., 2004). Consistently, abundance of small phototrophic organisms such as *Synechococcus*, well adapted to nutrient depleted environments, increased toward the eastern Mediterranean (Fig. 2c) whereas bigger cells less adapted to oligotrophic conditions (see autotrophic pico and nano eukaryotes abundance, Fig. 2d) decreased toward the eastern Mediterranean.
No *Prochlorococcus* were detected at that sampling depth (8 m) at any station, consistently with Marty et al. (2008) findings in the North-western Mediterranean during the stratified period. Heterotrophic bacterial abundance decreased with increasing oligotrophy (Fig. 2e). Initial N$_2$ fixation rates were low at the 4 tested stations (from 0.08 to 0.16 nmol N. L$^{-1}$.d$^{-1}$, Fig. 2b) and did not allow to depict any trend along
these stations. Station 17 appears to be less oligotrophic than the three others with the highest primary production (2.81 mg C m$^{-3}$ d$^{-1}$), N$_2$ fixation (0.16 nmol N L$^{-1}$ d$^{-1}$), bacterial abundance (3.8 × 10$^5$ cell mL$^{-1}$), *Synechococcus* abundance (5496 cell mL$^{-1}$)

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and autotrophic eukaryotes ($357 \, \text{cell mL}^{-1}$).

### 3.3 Biological response to aerosol addition

#### 3.3.1 Evolution of fluxes

24 h after enrichments, the primary production increased significantly at all tested stations (Fig. 3a, Table 2) in bottles amended by both collected aerosols (named hereafter CA) (from 95 to 145%) and Saharan dust analog (named hereafter SDA) (from 80 to 135%). The highest averaged primary production increase was noticed at station 17 with 135 to 145% for respectively SDA and CA additions. Despite significant increase after SDA and CA addition, primary production ($1.27$–$6.88 \, \text{mg C m}^{-3} \, \text{d}^{-1}$ depending on the experiments) remained typical of oligotrophic environments.

$N_2$ fixation was shown to significantly increase (Table 2) at station A in bottles amended by both CA (+157%) and SDA (+164%) and also at station B in bottles amended by CA (+151%). At the other stations, no significant increase of $N_2$ fixation rates followed the additions (Fig. 3b). Despite the significant increase at stations A and B after additions, $N_2$ fixation rates remained low ($< 0.3 \, \text{nmol N L}^{-1} \, \text{d}^{-1}$).

#### 3.3.2 Evolution of abundances

*Synechococcus* abundance was shown to significantly increase only at station A (Fig. 3c, Table 2), in bottles amended by both CA (+150%) and SDA (+124%). Although the highest increase was recorded at station 17 (+193% for collected aerosol addition), statistical test showed that this increase was not significantly different from the control in either treatment, probably because of variability between duplicates. No significant increase was found at station B.

Pico- and nanoeukaryote abundance increased significantly only at station A, in bottles amended by both CA and SDA (Fig. 3d). No significant increase of the bacterial abundance was observed at either station (Fig. 3e) which is consistent with other

studies based on dust addition (Ridame, 2001; Bonnet et al., 2005; Herut et al., 2005) but different from in situ observation after a natural Saharan event and in vitro dust addition experiments in Pulido-Villena et al. (2008).

## 4 Discussion

### 4.1 Stability of the Mediterranean Aerosol characteristics during 2008 summer

Phosphorus concentrations were very consistent with values reported for samples collected at coastal sites of Mediterranean islands (5–14 ng m$^{-3}$ in Corsica, Bergametti et al., 1989, and ~4–25 ng m$^{-3}$ in Crete, Markaki et al., 2003) and much lower than concentrations reported for coastal populated area (70–85 ng m$^{-3}$ in French Riviera, Migon et al., 2001). According to the (P/Al) obtained for BOUM collected aerosols, 2 groups of samples can be identified: group 1 with P/Al = ~0.03–0.04 and group 2 with P/Al = 0.11 (Fig. 4). The (P/Al) ratio of both groups was mostly consistent with results reported for coastal area in Corsica: from 0.03 (crustal source) to 0.07 (anthropogenic source) in Bergametti et al. (1992), but well higher than the Saharan crustal reference (for ex. 0.012 in Guieu et al., 2002). Taking into account that recycled P from marine sources is negligible (<2%, Bergametti et al., 1992) and that no biomass fires, important source of P (Mahowald et al., 2008; Baker et al., 2006), occurred at that time in the surrounding Mediterranean area, the P enrichment relative to the Saharan crustal reference observed in all samples is expected to be from anthropogenic origin (from incinerators, fertilizers, chemicals, detergents and pesticides). The contribution of the anthropogenic source to the particulate P on collected aerosols can be estimated from the Enrichment Factor (EF) and can be expressed in percentage of the anthropogenic component of the total P, as explained in the caption of Table 1. EF$_P$ (2 to 13, Table 1) observed in all samples was consistent with values reported for open sea Mediterranean Sea (1–18, Carbo et al., 2005, for samples collected during the CYCLOPS cruise) and coastal area in Corsica Island (2–9, Bergametti, 1989), but

slightly above the values reported in regions where aerosols are mostly influenced by Saharan dust, such as the tropical Atlantic (~1 according to Baker and Jickells, 2006). From Fig. 5, one can see that air-mass trajectories during the whole cruise originated mainly from Western and Eastern Europe. Field observations report a very short Saharan rain event during the AERO 8 sampling. However, we expect that only a very small fraction could have contributed to the sample composition since our sampling device is designed to sample aerosols: the filter-holders are facing the ground and in this configuration, only particles can be sampled, not rain drops.

The homogeneous (P/Al) of group 1 (~0.03–0.04) indicates that anthropogenic contribution to the total aerosol phosphorus (58–67%) is stable during most of the campaign over ~28° of longitude, with a non negligible and variable proportion of crustal contribution (from Al concentration, Fig. 4) in the absence of a dry Saharan event.

Phosphorus in samples group 2 (Aero 2, 9 and 10) had a stable and low Al content and higher and variable anthropogenic contribution ((P/Al) from 0.05 to 0.16, Fig. 4). (P/Al) ratios found for (i) Aero 2 was similar to the anthropogenic (P/Al) ratio = 0.07 defined by Bergametti et al. (1992), and (ii) Aero 9 and 10 were similar to the lowest (P/Al) ratios (~0.10–0.20) reported by Migon et al. (2001) in the French Riviera populated coastal area. Phosphorus in samples from group 2 had the highest enrichment factors (4 to 13) with an anthropogenic contribution to total aerosol phosphorus of up to 93 % (Aero 10, Table 1), consistent with Migon et al. (2001) findings (90–98%). Aero 9 and 10 were collected close to the coast in the north-western Mediterranean (Fig. 1), and were potentially the most influenced by European air masses (Fig. 5).

BOUM samples were representative of the Mediterranean atmospheric background in summer, formed by a homogeneous air mass at least over the eastern, the central and the south-western part of the Mediterranean open sea. According to phosphorus data, most of the transect was characterized by a significant and stable anthropogenic contribution and by a low but variable contribution of crustal origin, even in the absence of direct Saharan dry event.

## 4.2 Significant response of the primary production to aerosols additions

After the two types of aerosols additions, primary production significantly increased at all four tested stations (80 to 145%), with increases were similar between the collected aerosols (CA) and Saharan dust analog (SDA) treatments (Table 2). During the BOUM cruise, the Mediterranean SML was nutrient depleted (Pujo-Pay et al., 2010) and an external input of new nutrients, in particular nitrogen (N), phosphorus (P) and iron (Fe), induced by the introduction of both SDA and CA would have generated the observed enhancement of the biological activity. Biological activity during the spring bloom can decrease surface waters dissolved Fe (DFe) concentrations, to the point where subsequent algal growth is temporally Fe limited (Sarthou and Jeandel, 2001; Bonnet and Guieu, 2006). In summer, the situation is quite different as atmospheric iron accumulates in the surface mixed layer and high concentrations have been reported (Sarthou and Jeandel, 2001; Bonnet and Guieu, 2006; Theodesi et al., 2010). High DFe pool in the surface mixed layer over the whole cruise would have prevented phytoplanktonic activity from iron limitation (C. Ridame, personal communication).

### 4.2.1 Nutrient requirements

Increase in primary production after SDA and CA aerosols additions ranged between 0.57 to 3.73 mg C m$^{-3}$ d$^{-1}$ and 0.92 to 4.07 mg C m$^{-3}$ d$^{-1}$, respectively. Although the molecular ratio of carbon, nitrogen and phosphorus in phytoplankton is not well defined in the Mediterranean Sea, classical values of the Redfield ratio (C: N: P = 106: 16: 1) were used in this study in order to estimate the required P and N for the observed induced new carbon formed after the different aerosols additions. Following the Redfield ratio, P needs corresponding to the enhancement of the phytoplanktonic activity would thus respectively have ranged, for both SDA and CA treatments, from 0.6, 1 and 1.3 nmol P L$^{-1}$ at stations (C, B, A), and 3.1 nmol P L$^{-1}$ at station 17. The N-requirements to sustain the observed stimulation in both treatments would thus respectively have ranged from 9.4, 15.2 and 20.6 nmol N L$^{-1}$ at stations (C, B, A), and

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49.1 nmol N L$^{-1}$ at station 17. Those data have to be compared to the actual inputs provided by the aerosols additions.

### 4.2.2 Nutrients inputs

P total concentration in aerosols is known for both CA and SDA aerosols, while N total concentration was only measured in SDA (Table 3). Dissolution percentages of P and N in seawater determined in other studies for both SDA (35% for phosphorus with a similar particulate concentration, Pulido-Villena et al. (2008); ~100% for nitrogen in Dekaezemacker, 2009) and CA (45% for P in atmospheric particles derived from European air masses, Herut et al., 1999) aerosols were used to estimate the inputs of dissolved P and N induced in the experiments by the introduction of both types of aerosols. Respectively applied to the different aerosols additions, these percentages of dissolution would lead to an input of bioavailable P of 6 nmol P L$^{-1}$ in the SDA treatment and of 0.3 (AERO 2, 3 and 4) to 1.6 (AERO 5) nmol P L$^{-1}$ in the CA treatment (Table 3). In the same way, SDA addition would lead to an input of bioavailable nitrogen of ~800 nmol N L$^{-1}$ (Table 3). Total nitrogen was not measured in CA, precluding any direct estimation of bioavailable nitrogen from on board collected aerosols. However, N measurements in aerosols, performed in the Cretan Island (Finokalia) by Markaki et al. (2003), enabled to estimate that for the addition of a whole aerosol filter (corresponding to 57–86 m$^3$ air pumped) influenced by anthropogenic air masses (summer – N/NW and N/NE sectors) to 4.5 L of seawater (as performed in our experiments), the input of dissolved nitrogen would be of ~950 nmol N L$^{-1}$ (Table 3).

### 4.2.3 Comparison needs vs. inputs

Comparison between N needs (9.4 to 49.1 nmol N L$^{-1}$ according to Redfield ratio) and N inputs from aerosols (>800 nmol N L$^{-1}$), indicates that the both types of aerosols additions totally fulfilled the primary producers needs. The comparison between P needs (0.6 to 3.1 nmol P L$^{-1}$ according to Redfield ratio) and P inputs from aerosols (0.3

to 6 nmol P L$^{-1}$) is more complex since these numbers, based on rough calculations and literature data, are in the same range. However, slight differences can still be observed allowing hypothesis that must be considered carefully.

1. The dissolved P fraction from SDA (6 nmol P L$^{-1}$) is higher than the estimated uptake by primary producers ($\leq$3 nmol P L$^{-1}$). This could be explained by (i) a rapid and strong nutrient consumption by the bacterial community as already observed after analog additions (Pulido-Villena, 2009), or/and (ii) a significant nutrient consumption by primary producers during the first 24 h-incubation. Indeed, P and N needs estimations are for a new primary production induced between 24 h and 48 h. Very recent large mesocosm experiments testing biological response to the same SDA (Guieu et al., 2010), showed that primary production was highly stimulated 24 h after the seeding (DUNE experiment, Ridame et al., 2010), indicating a noticeable nutrients consumption between the first 24 h. Nutrients requirements estimations given here would thus correspond to a minimal need as they do not take into account the 0–24 h consumption.

2. The dissolved P fraction from CA (0.3–1.6 nmol P L$^{-1}$) is lower in some cases than the estimated uptake by primary producers (0.4–3.2 nmol P L$^{-1}$). It is important to mention that only inorganic forms of nutrients were considered here, other pool such as organic forms were not taken into account. Organic forms of nutrients are suspected to constitute an important part of anthropogenic particles and thus a non negligible proportion could be present in collected aerosols (Markaki et al., 2010).

During the BOUM cruise, Tanaka et al. (2010) have evidenced N limitation of the primary production at most of the long duration stations (A and B) and N-P co-limitation at station C. Dissolved N input from both types of aerosol would have probably fully relieved this N limitation. By contrast, the CA addition inducing the lowest P inputs would have only lead to a partial relieve of the P-limitation at station C.

## 4.3 Comparison of the fertilization effect from the two types of aerosols

SDA addition ($\sim$1 mg L$^{-1}$) was representative of a realistic dust deposition of 8 g m$^{-2}$ (Loÿe-Pilot and Martin, 1996; Guieu et al., 2010; Ternon et al., 2010), diluted over a whole 8 m deep surface mixed layer. Based on Al concentrations, introduction in seawater of CA would have lead to a particulate concentration of 0.01–0.03 mg L$^{-1}$ (Table 3). Such particulate concentration is representative of a typical "Mediterranean summer rain" event characterized by a strong scavenging of all the mixed aerosols accumulated in the air column before the event (Loÿe-Pilot et al., 1990).

In term of mass, SDA was introduced in higher proportion than CA (by a factor 100), resulting in higher inputs of both total nitrogen and total phosphorus. However, at all four tested stations, the induced primary production in the SDA treatments was not statistically different from that in the CA treatments (Table 2). Despite the mass difference, SDA and CA additions would have provided a similar amount of bioavailable nutrients to the biota which is in good agreement with estimates of dissolved N and P inputs from aerosols (Table 3). The higher ratio [% of PP increase/particles mass] (Fig. 6) found for CA (1.09–2.51) compared to SDA (0.02–0.03) indicates that the proportion of soluble bio-available nutrients released by CA is indeed much higher compared to the one from SDA.

Collected aerosols are composed by a mixture of crustal and anthropogenic particles. Due to lower pH environment anthropogenic particles were shown to present higher solubility than crustal particles; also, anthropogenic carbonaceous species increase the solubility of species associated to aerosols, such as metals (Desboeufs et al., 2005). Furthermore, the smaller size of anthropogenic particles in regard to crustal particles increases their ratio surface/volume (Baker and Jickells, 2006) which consequently increase their solubility. Thus, it is most probable that the mixed character as well as the low size of BOUM CA would have resulted in more "atmospheric labile nutrients".

Finally, those experiments show that atmospheric inputs from a mixed atmospheric event ("summer rain" type) or from a high-intensity Saharan event would induce comparable response by the biota in the stratified Mediterranean SML.

## 4.4 Effect on community structure

Biological community evolution after enrichments did not allow determining which biological community beneficiated from atmospheric inputs. Indeed, unless at station A, no significant increase in abundance in neither autotrophic organisms nor heterotrophic bacteria was observed (Fig. 3c, d and e). It is most probable that while phytoplankton activity was enhanced, the high grazing pressure from heterotrophic nanoflagellates (Caron et al., 1999) prevented the increase in picophytoplankton abundance at stations C, B and 17.

## 4.5 Atmospheric fertilization benefited to $N_2$ fixation

Nitrogen fixation was suspected to be a key process in the Mediterranean Sea to explain the high N/P ratio in the deep layers (Béthoux and Copin-Montégut, 1986). Recent measurements performed in the open Mediterranean Sea showed low $N_2$ fixation rates during summer (in both Western and Eastern basins: $0.05 \, \text{nmol} \, \text{N} \, \text{L}^{-1} \, \text{d}^{-1}$, May–June 2007, in Ibello et al., 2010; in the north-western part: $\sim$4–7.5 $\text{nmol} \, \text{N} \, \text{l}^{-1} \, \text{d}^{-1}$ in July–August 2004 in Garcia et al. (2007); and 0.5 to 2 $\text{nmol} \, \text{N} \, \text{l}^{-1} \, 12 \, \text{h}^{-1}$ in late summer 2004 in Marty et al., 2008). The weak $N_2$ fixation rates (0.08–0.16 $\text{nmol} \, \text{N} \, \text{L}^{-1} \, \text{d}^{-1}$) measured at all tested stations are in the same order of magnitude with those measured during the BOUM transect by Bonnet et al. (2010) and Ridame et al. (2010) and are in good agreement with the scarce literature data (Krom et al., 2010, and references therein). The diazotrophic activity was significantly increased after additions of both SDA and CA at station A and of CA at station B. Nevertheless, these rates remained low after the additions ($<0.30 \, \text{nmol} \, \text{N} \, \text{L}^{-1} \, \text{d}^{-1}$), and could only sustain 0.07–1.5% of the induced primary production (based on a C: N of 8.6 measured by Tuit et al. (2004) for the

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unicellular $N_2$-fixing cyanobacteria *Crocosphaera*). Introduction of chemical elements from both SDA and CA additions would have benefited to nitrogen fixers, as already observed by Mills et al. (2004) in the tropical Atlantic: the relief of nutrient (co)-limitations (in particular P and/or Fe) by an atmospheric Saharan input, benefited to $N_2$ fixers activity. The identity of limiting elements during the BOUM cruise was explored by the complementary study of Ridame et al. (2010). It appeared that addition of iron had no impact on the diazotrophic activity. By contrast, in the western and eastern basins, $N_2$ fixation was limited by the phosphorus availability.

## 5 Conclusion

Conducted during the oligotrophic season, this study provides an aerosol data set along a ~2500 km transect in the Mediterranean open sea. The Transmed BOUM campaign (June–July 2008) was characterized by stable and homogeneous air masses, with the north-western part of the transect being more influenced by regional European aerosols. During that period, aerosols were from mixed (crustal/anthropogenic) origins (according to P and Al concentrations, and seemed to represent well the Mediterranean atmospheric background with a constant proportion of anthropogenic contribution and a variable but modest contribution of crustal aerosols.

By providing new nutrients able to partly relieve the on-going limitations, atmospheric inputs stimulated primary production at all tested stations. From this data set, there is no way to determine which community sustained the new primary production induced by the atmospheric new nutrients. Nitrogen fixation was also shown to be enhanced by atmospheric deposition but remained very low during summer 2008. Limiting factors are investigated in a companion paper (Ridame et al., 2010).

The comparison of the potential fertilizing effect of Saharan dust analog and natural collected aerosol emphasis on the fact that mixed aerosols contain more labile nutrient fraction as compared to Saharan dust.

Increasing anthropogenic activities in Europe and North Africa would result in an increase of the anthropogenic contribution to the Mediterranean atmosphere chemical composition, implying that mixed aerosols have to be more considered in future research concerning potential fertilization of the ocean surface by atmospheric inputs. According to IPCC 2009, annual mean temperatures in the Mediterranean area are likely to increase more than the global mean. Such warmer atmosphere could influence the intensity and the length of the water column stratification, increasing the oligotrophic nature of the Mediterranean surface water. It is most probable that more oligotrophy would enhance the impact of external input of new nutrients by the atmosphere, and in particular mixed events such as summer rain.

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**Table 1.** Characteristics and elemental concentrations of aerosol samples collected during the BOUM cruise. The contribution of anthropogenic sources to atmospheric particulate phosphorus (P) can be calculated in percentage from the enrichment factor (EF), as follows:

$$EF_P = \frac{\left[ (P)/(Al) \right]_{aerosol}}{\left[ (P)/(Al) \right]_{crustal}}$$

Assuming $Al_{aerosol} \sim Al_{crustal}$, this expression gives $\left( \frac{P_{anthro}}{P_{aerosol}} \right) = 1 - \frac{1}{EF_P}$. This ratio, expressed in percentage, gives the anthropogenic contribution to the total P in the atmospheric aerosols.

| Sample label | Latitude | | Longitude | | Volume pumped | Al | Fe | P | Aerosol mass | P/Al | $EF_P$ | Anthropogenic P |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Beginning | End | Beginning | End | $m^3$ | $ng\,m^{-3}$ | $ng\,m^{-3}$ | $ng\,m^{-3}$ | $\mu g\,m^{-3}$ | | | % |
| AERO 2 | 35°54 N | 33°41 N | 17°22 E | 30°09 E | 46 | 81 | 61 | 4 | 1.14 | 0.05 | 4 | 78 |
| AERO 3 | 33°41 N | 33°38 N | 30°09 E | 32°38 E | 48 | 118 | 90 | 3 | 1.66 | 0.03 | 2 | 58 |
| AERO 4 | 33°38 N | 33°43 N | 32°38 E | 32°18 E | 42 | 142 | 102 | 4 | 2.00 | 0.03 | 2 | 59 |
| AERO 5 | 33°43 N | 33°59 N | 32°18 E | 18°06 E | 60 | 166 | 115 | 6 | 2.34 | 0.04 | 3 | 67 |
| AERO 6 | 33°58 N | 33°58 N | 18°03 E | 18°32 E | 44 | 321 | 179 | 11 | 4.53 | 0.03 | 3 | 64 |
| AERO 7 | 33°58 N | 36°45 N | 18°32 E | 12°17 E | 41 | 262 | 173 | 9 | 3.69 | 0.04 | 3 | 66 |
| AERO 8 | 36°45 N | 39°19 N | 12°17 E | 05°20 E | 45 | 207 | 120 | 7 | 2.91 | 0.04 | 3 | 66 |
| AERO 9 | 39°19 N | 40°09 N | 05°20 E | 05°06 E | 58 | 49 | 40 | 5 | 0.69 | 0.11 | 9 | 89 |
| AERO 10 | 40°09 N | 43°17 N | 05°06 E | 05°22 E | 18 | 97 | 78 | 16 | 1.37 | 0.16 | 13 | 93 |

**Table 2.** Results of the statistical comparison (ANOVA-FISHER test) between the control vs each treatment and the Saharan dust analog treatment (SDA) vs. the collected aerosol treatment (CA), at the end of the experiment for: primary production, $N_2$ fixation, *Synehcococcus* abundance and autrotrophic pico and nano eukaryotes abundance. No data are available for abundances at station C due to sampling problem. NS: the difference between the two treatments is not statistically different; S: the difference between the two treatments is statistically different.

| | Stations | | | |
|---|---|---|---|---|
| | A | B | C | 17 |
| **Primary production** | | | | |
| SDA vs. Control | S | S | S | S |
| CA vs. Control | S | S | S | S |
| SDA vs. CA | NS | NS | NS | NS |
| **$N_2$ fixation** | | | | |
| SDA vs. Control | S | NS | NS | NS |
| CA vs. Control | S | S | NS | NS |
| SDA vs. CA | NS | NS | NS | NS |
| **Synechococcus abundance** | | | | |
| SDA vs. Control | S | NS | no data | NS |
| CA vs. Control | S | NS | no data | NS |
| SDA vs. CA | NS | NS | no data | NS |
| **Eukaryotes abundance** | | | | |
| SDA vs. Control | S | NS | no data | NS |
| CA vs. Control | S | NS | no data | NS |
| SDA vs. CA | NS | NS | no data | NS |

**Table 3.** Total and soluble P and N (nM) from SDA (Saharan Dust Analog) and from CA (Collected Aerosol).

| | Composition % | Total concentration nM | Estimated dissolution % | Estimated dissolved concentration nM |
|---|---|---|---|---|
| Saharan Dust Analog (SDA). Particle mass = 1 mg l$^{-1}$ | | | | |
| N | 1.15 | 821 | 100[a] | 821 |
| P | 0.05 | 16 | 35[b] | 6 |
| Collected Aerosol (CA). Particle mass = 0.01–0.03 mg l$^{-1}$ | | | | |
| N | no data | no data | 100 | ~ 950[d] |
| P | 0.2–0.38 | 0.6–3.7 | 45[c] | 0.3–1.6 |

[a] Dekaezemacker (2009); [b] Pulido-Villena et al. (2010); [c] Herut et al. (1999); [d] Markaki et al. (2003)

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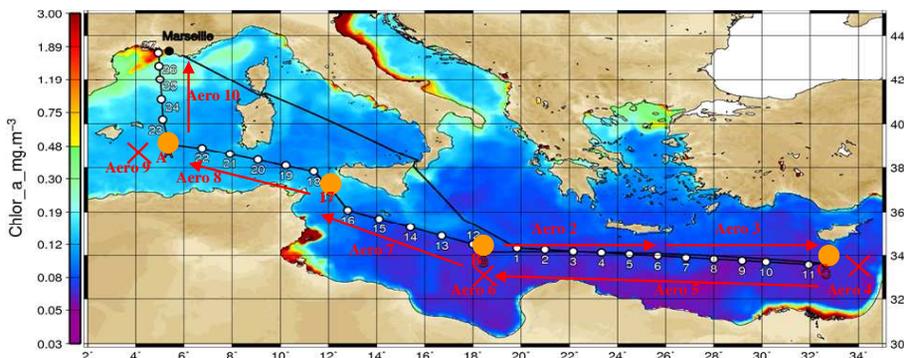
| Fertilisation experiment label | Seawater sampling | Aerosol samples used |
|---|---|---|
| 1 (+ SDA, + CA) | Station C | Aero 2 |
| 2 (+ SDA, + CA) | Station B | Aero 4 |
| 3 (+ SDA, + CA) | Station 17 | Aero 5 |
| 4 (+ SDA, + CA) | Station A | Aero 3 |

**Fig. 1.** BOUM cruise track (black) indicating all BOUM sampling stations (white and red circles) reported on a map compilation of the sea surface chlorophyll-*a* concentration of June and July 2008 months (MODIS data, E. Bosc, personal communication). Aerosol sampling and the stations at which addition experiments were performed are respectively represented by the white arrows and the red circles. The table indicates the aerosols filters and seawater used for each fertilisation experiment.
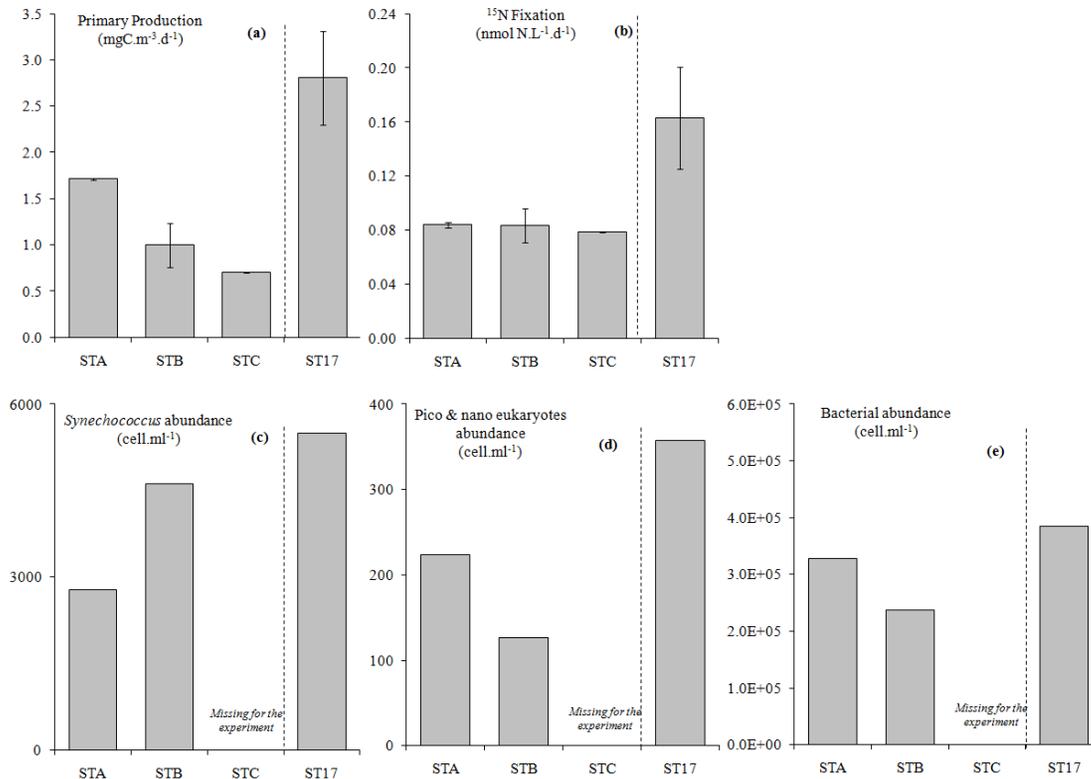
**Fig. 2.** Initial biological conditions in control bottles (**a** Primary Production and **b** Nitrogen Fixation) and for the $T_0$ sampling (**c** Autotrophic prokaryotes, **d** pico and nano eukaryotes organisms and **e** bacterial abundance) for each station before the addition experiment. Due to sampling problem, initial abundances of bacteria, autotrophic pico- and nano-eukaryotic organisms as well as *Synechococcus* are missing for the experiment performed at station C. Primary production and nitrogen fixation error bars represent the standard deviation from duplicate incubations (1 and 2) of the control.

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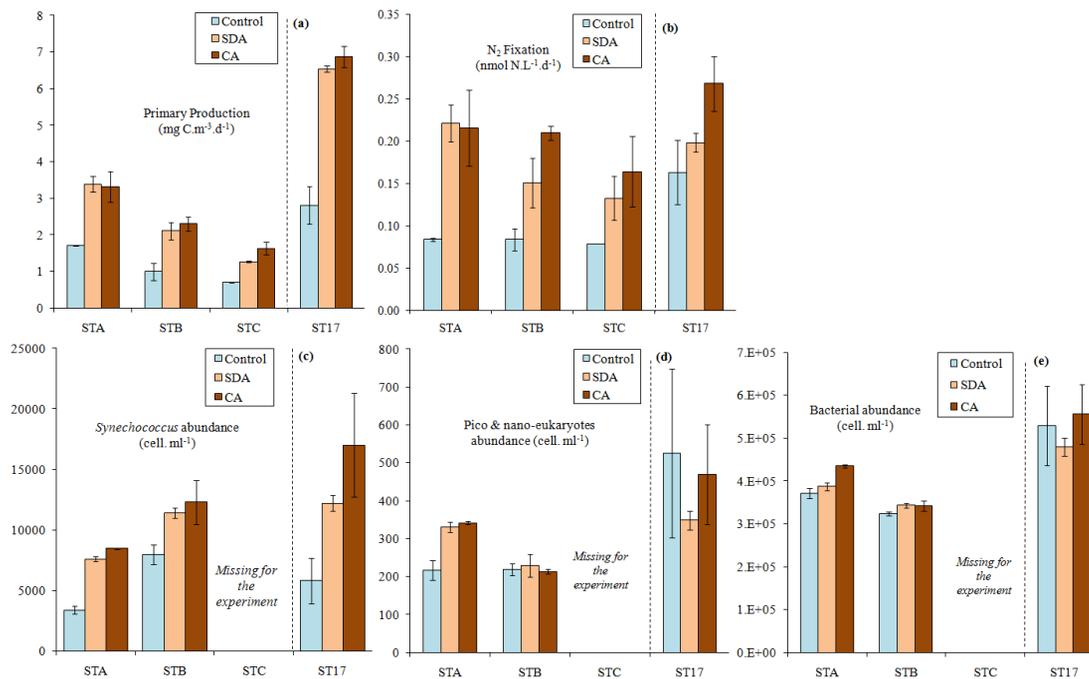
**Fig. 3.** Evolution in both treatments (+SDA and +CA aerosols) compared to the control at each tested stations for **(a)** primary production integrated over 24 h, **(b)** nitrogen fixation integrated over 24 h, **(c)** *Synechococcus* abundance, **(d)** autotrophic eukaryotes abundance, and **(e)** bacterial abundance. No data is available at station C for the *Synechococcus* community, the pico and nano eukaryotes and the bacterial community (see text). The error bars represent the standard deviation from duplicate incubations.
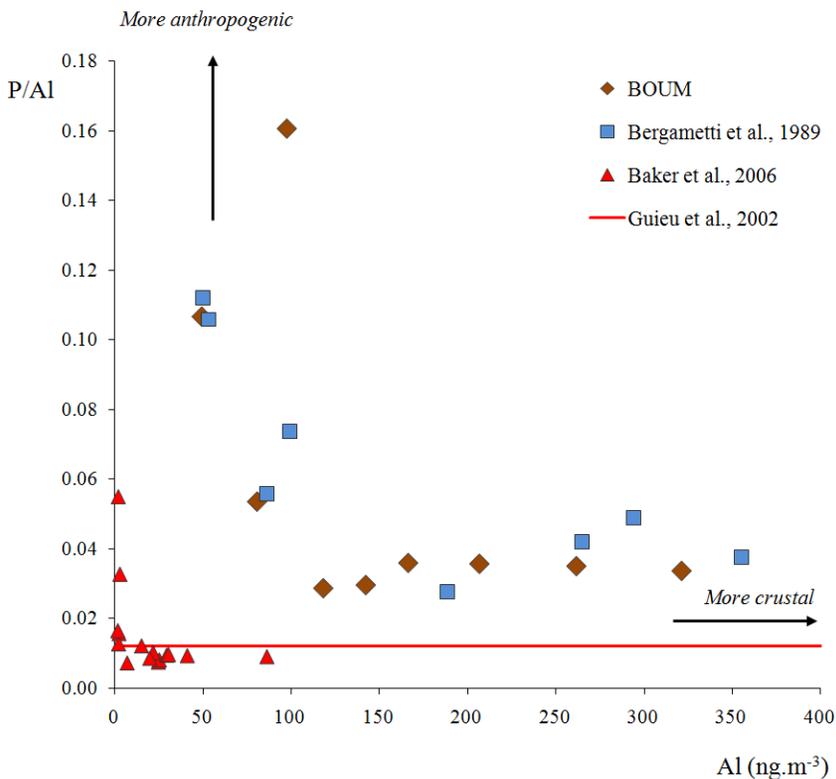
**Fig. 4.** P/Al ratio versus Al concentration in aerosols collected during the BOUM cruise and in other studies (aerosols collected in Corsica (Bergametti et al., 1992) and tropical Atlantic (Baker and Jickells, 2006)). Assuming $Al_{aerosol} \sim Al_{crustal}$, an increasing Al concentration for a constant (P/Al) ratio would indicate an increasing crustal content whereas an increasing (P/Al) ratio for a constant Al concentration would indicate an increasing anthropogenic content. (P/Al) = 0.012 represents the Saharan end-member in the Western Mediterranean (Guieu et al., 2002).

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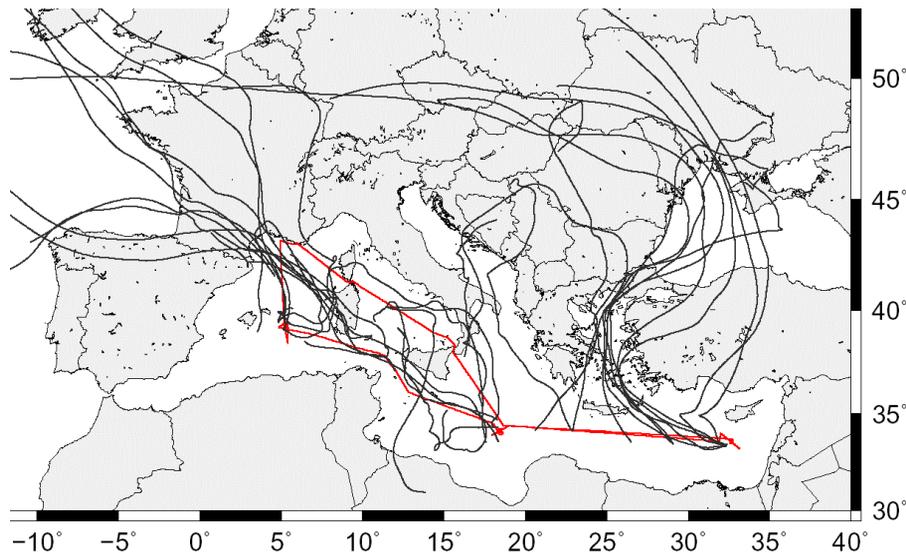
**Fig. 5.** 5-days air mass back trajectories (HYSPLIT) at 10 m computed for the whole duration of the cruise.
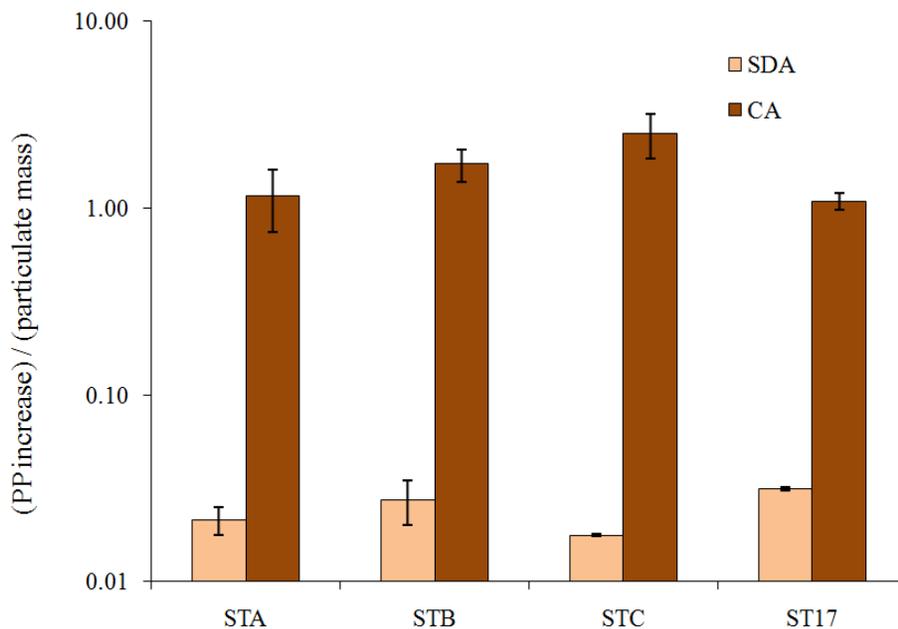
**Fig. 6.** Percentage of the increase of primary production (PP in %) normalized to the mass (µg) of particles added at the beginning of the experiment, for both SDA and CA at each tested station (x-axis). Y-axis is in log scale to amplify the results from SDA addition. The error bars represent the standard deviation from duplicate incubations.