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Large clean mesocosms and simulated dust deposition: a new methodology to investigate responses of marine oligotrophic ecosystems to atmospheric inputs

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Abstract

Intense Saharan dust deposition occurs over large oligotrophic areas in the Mediterranean Sea and the Tropical Atlantic and its impact on the biogeochemical functioning of such oligotrophic ecosystems needs to be understood. However, due to the logistical difficulties to investigate in-situ natural dust events and due to the inherent limitations of microcosm laboratory experiments, new experimental approaches need to be developed. In this paper, we present a new experimental set up based on large clean mesocoms deployed in the frame of the DUNE (a DUst experiment in a low-Nutrient, low-chlorophyll Ecosystem) project. We demonstrate that these tools are highly relevant and provide a powerful new strategy to in situ study the response of an oligotrophic ecosystem to chemical forcing by atmospheric deposition of African dust. First, we describe how to cope with the large amount of dust aerosol needed to conduct the seeding experiments, by producing an analogue from soil collection in a source area and performing subsequent appropriate physico-chemical treatment in the laboratory including an eventual processing by simulated cloud water. The comparison of physico-chemical characteristics of produced dust analogues with the literature confirms that our experimental simulations are representative of dust, ageing during atmospheric transport, and subsequent deposition to the Mediterranean. Second, we demonstrate the feasibility in coastal area to installing in situ, a series of large ($6 \times 52\,m^3$) mesocosms without perturbing the local ecosystem. All the setup, containing no metallic part and with as less as possible induced perturbation during the sampling sequence, allows working with the required conditions for biogeochemical studies in oligotrophic environments where nutrient and micronutrients are at nano- or subnano-molar levels. Two distinct "seeding experiments" were conducted by deploying mesocosms in triplicates: three mesocosms serving as controls (CONTROLS-Meso = no addition) and three mesocosms being seeded with the same amount of Saharan dust (DUST-Meso = $10\,g\,m^2$ of sprayed dust). A large panel of biogeochemical parameters was measured at 0.1 m, at 5 m and 10 m in all the mesocosms and at a selected site outside

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the mesocosms, before the seeding and at regular intervals after. Statistical analyses of the results show that data from triplicate mesocosms are highly reproducible (variability <30% among triplicates) and that there is no significant difference between data obtained from CONTROLS-Meso and from outside the mesocosms.

This paper demonstrates that the methodology developed in the DUNE project is suitable to quantify and parameterize the impact of atmospheric chemical forcing to a low-nutrient, low-chlorophyll (LNLC) ecosystem. Such large mesocosms can be considered as 1D ecosystem so that the parameterization obtained from those experiments can indeed be integrated into ecosystem models.

1 Introduction

The biogeochemical impacts of atmospheric dust-derived Fe and other nutrients on oligotrophic LNLC environments are still poorly understood. This issue has received little attention compared to the large number of investigations of the impact of iron supply on productivity of high nutrient-low chlorophyll (HNLC) oceanic regions using bioassay experiments (Martin et al., 1994), mesoscale artificial iron fertilization experiments (see synthesis by de Baar et al., 2005; Boyd et al., 2007) and natural fertilization studies (Pollard et al., 2007; Blain et al., 2008). However the LNLC oceanic regions represent 60% of the global ocean (Longhurst et al., 1995) and over 50% of the global oceanic carbon export (Emerson et al., 1997).

Only very recently, the biogeochemical effect of dust in LNLC waters has been explored through microcosm experiments where different combinations of nutrients and dust were added to a natural assemblage of plankton. In two LNLC environments receiving episodic and strong dust deposition (the tropical Atlantic, (Mills et al., 2004), and the Mediterranean Sea (see for example Herut et al., 2005; Pulido-Villena et al., 2008), dust additions in microcosms showed moderate but significant responses from both heterotrophic and autotrophic organisms. Although such microcosm approaches can yield valuable information on specific forcing to a given natural assemblage, the

results are difficult to extrapolate to large marine areas or to time scales exceeding the duration of the experiment. Moreover, by relying upon a fixed and homogeneously distributed concentration of particles, they can alter the dust dissolution kinetics and do not account for particle migration through the water column. This precludes any estimation of C export induced by atmospheric deposition. Consequently, the question of the in situ biological response of LNLC regions and, particularly, of the Mediterranean Sea to atmospheric inputs has not yet been fully answered. Using spaceborne chlorophyll and dust data, no clear link between dust deposition and chlorophyll increase could be determined from extensive use of ocean color data (Dulac et al., 2004; Volpe et al., 2009), despite a few possible cases of large-scale dust-induced blooms identified with CZCS or AVHRR data (Guerzoni et al., 1999).

To cover this gap, we have developed a novel approach to study the effect of atmospheric input on a typical LNLC ecosystem. The strategy is based on aerosol additions into large and trace metal clean mesocosms that are more representative of the processes taking place in situ compared to a microcosm approach. The objective was to test, on a relevant number of biogeochemical parameters, the impact of a desert dust event on the natural planktonic community of a large water body in perfectly controlled conditions. This was developed in the frame of the DUNE project (a DUst experiment in a low Nutrient, low chlorophyll Ecosystem; http://www.obs-vlfr.fr/LOV/DUNE). The aim of this paper is to describe our original methodology and to demonstrate that it is highly relevant to meet our objectives. The detailed results and discussions of the biogeochemical and ecosystem responses obtained are considered in other papers (see for ex. Pulido-Villena et al., 2010; Wagener et al., 2010; Lagdhass et al., 2010).

This paper gives a detailed description of the methodology developed and applied during the first DUNE experiment (DUNE-1) in June 2008 during which two seeding experiments were conducted onto six large (52 m^3) mesocosms. After a brief presentation of the chosen LNLC site in the Mediterranean Sea, the different aspects related to the Saharan particles that have been used for seeding the mesocosms are discussed. The setup that was designed for the experimental mesocosm platform and the

description of the sequence of the experiment is then presented. Finally, by considering selected results among the whole data set obtained, the last section demonstrates the ability of the methodology to provide robust quantification and parameterization of the impact of atmospheric chemical forcing on a LNLC ecosystem.

2 The Scandola: an oligotrophic coastal "pristine" area

The experiment was conducted in a remote coastal low-nutrient, low-chlorophyll (LNLC) area of the Mediterranean Sea: the Natural Preservation Area of Scandola (Fig. 1), a marine and terrestrial zone protected from human activities since its creation in 1975 (http://www.parc-naturel-corse.com/patrimoine/scandola.html). A preliminary field study took place in May 2006 during which a careful inspection of the best location to conduct the seeding experiment was done. The selected site (Elbo Bay, see Fig. 1) has a seafloor at ~30 m depth. There is no terrestrial access and several restrictions for boat activities are imposed (e.g. no mooring allowed during night-time). The closest town is Galéria, a small village located at 5.88 miles/11 km and there is no industrial activity in the region. The motor boat ride between the field laboratory in Galéria and anchor site mesocosms lasts for 20 min in good meteorological conditions. There is no river close by and the site can only be influenced by direct runoff from the land. The site has already been chosen for numerous researches to study the influence of global change on natural ecosystems (see for ex. the project MedChange: http://piccard.esil.univmed.fr/medchange/spip/spip.php?rubrique47). The dominant winds in the area are SW and the dominant currents in the Elbo Bay allow the waters to move fast to the north (Romano et al., 2006; personal communication, 2007). Besides its remoteness, the site was selected because this part of the Mediterranean is representative of very clear ("blue") waters (Fig. 1).

3 Producing the necessary amount of representative Saharan dust

The annual mean dust deposition flux in Corsica during the period 1984–1994 has been 12.5 g m^2 (Loÿe-Pilot and Martin, 1996). In Corsica, a few events per year yield a deposition flux larger than 1 g m^2 and more recently event fluxes of ∼22 g m^2 have been recorded: 21.9 g m^2 in Nov. 2001 (Guieu et al., 2009), 22.2 g m^2 in February 2004 (Bonnet and Guieu, 2006; Ternon et al., 2010). We chose to mimic a high, but still realistic Saharan dust deposition event of 10 g m^2. The surface of each mesocosm being 4.15 m^2 (see Sect. 4), an amount of 41.5 g of dust per mesocosm was needed which results in a total amount of dust of ∼125 g for the three replicates. Such a large amount of particles cannot be collected from airborne dust in the vicinity of the experimental area and can hardly be collected in a source region. Our strategy rather consisted in producing dust from the soil of an appropriate source area.

3.1 Collection and production of the fine particles

The frequency of Saharan dust events over the western Mediterranean basin increases between March and October, with its maximum during the dry season (June to August) (Bergametti et al., 1989; Moulin et al., 1998). The northeastern Sahara (eastern Algeria, southern Tunisia and western Libya) appears to be the major source of dust collected in Corsica during springtime (Bergametti et al., 1989; Guieu et al., 2002). Indeed, seven out of eight of the dust events recorded in Corsica in March, April or May in 1985 and 1986 originated from this region (Fig. 2). Southern Tunisia was thus chosen as the source region to collect soil to produce dust for seeding. We selected as our sampling zone of superficial soils, the main dried affluent of Oued El Hallouf (33°25′38″ N, 9°02′08″ E) at the east of Chott ElDjerid (Fig. 3). This is an area where episodic rains drain fine alluvial material deposited in a succession of crust-like clay layers alternated with intermediate fine sand from Aeolian origin (Fig. 4). This type of soil has a maximum efficiency for Aeolian emissions (Marticorena et al., 1997).

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The size distribution of soil-derived aerosols is completely different from that of soils in arid areas, composed of sands and silts with modes between 100 and 700 µm in diameter (Chatenet et al., 1996). At a certain distance from its source, soil-derived dust constitutes a coarse aerosol mode with a mass-median diameter (MMD) of 2 to 7 microns (see e.g. Dulac et al., 1989; Maring et al., 2003; Smolik et al., 2003). Such fine particles are produced during Aeolian erosion by a sandblasting process of clay aggregates by saltating sand grains (Gomes et al., 1990) and the aerosol production efficiency increases with the fraction of clay in the soil (Marticorena et al., 1997). In order to reproduce fine long-range transported desert dust particles, we sampled a soil rich in clay minerals in an Aeolian aerosol source area and we reproduced the effects of sandblasting and sedimentation by grinding and dry-sieving clay aggregates from the soil. Only the fraction <20 µm was considered for the seeding experiments.

We collected several tens of kg of soil using cleaned plastic material for collection and storage, by selecting clay layers below the superficial sand voile or sand layer. Free sand was also collected separately. To avoid any metal contamination, all subsequent manipulations of the soil material were performed using clean plastic or plastic-coated material including Nylon meshes for sieving. We cleaned and rinsed thoroughly materials in direct contact of soil in 0.2 mol L^1 suprapure HCl acid baths and Milli-Q water.

After collection, we found that a first sieving step with a 3-mm mesh was effective in eliminating all free sand and keeping only crusted clay pieces for further processing. We then dried the soil in 1 L buckets at 105 °C during 24 h. The water content of samples was of the order of a few percent except for pure sand (0.6%). Once dried, the soil was crushed with an agate pestle. All small organic debris and small roots seen during grinding were discarded with plastic or PTFE-coated tools.

The size distribution of an aliquot of the free sand was determined with a 12-stage column of standard metal meshes (630, 500, 400, 315, 250, 160, 125, 100, 63, 50, 20, <20 µm) and fitted to a lognormal distribution with a χ^2 fitting procedure (Chatenet et al., 1996). The sand was found to be very fine and extremely sieved by Aeolian transport with a MMD of about 75 µm and a geometric standard deviation of about 1.2.

Following a compromise between the decrease with particle size of cohesive forces and the increase in size of gravity forces, this mode is in the range of the most easily mobilized particles by the wind (Marticorena and Bergametti, 1995). An interesting consequence of this size distribution is that a mesh at 40 µm would be able to retain more than 99.9% of the sand. The same procedure was applied to a sample of ground clay. It showed a bimodal distribution with the 2 modes accounting each for about half of the total: the narrow mode of the Aeolian sand and a broader mode of smaller particles with a MMD of about 40 µm and a geometric standard deviation of about 1.9, likely dominated by clayey aggregates.

We then produced the fine particles by an intense dry-sieving (at least one hour and up to one night on the vibrating column at the maximum energy allowed by the system) of the crushed clayey material using a column of 3 Nylon meshes of 100, 40 and 20 µm (Fig. 5). We kept the finest fraction of soil particles (<20 µm) since dust larger than 20 µm are rapidly removed during atmospheric transport (Maring et al., 2003). The basic hypothesis is that the laboratory mechanical action of crushing and sieving has an equivalent effect for breaking the aggregates than the mechanical action of saltation and sandlasting under the action of the wind. It was found necessary to clean the meshes with a brush or if necessary, water between samples to avoid clogging. The fine particle production efficiency ranged between 5 and 15% relative to the initial crushed material. This processing was performed at IRA in South Tunisia. It is worth noting that we tentatively performed the same processing at LISA near Paris, but it turned out that we obtained very small production efficiency. We have no clear explanation but speculate that differences in relative humidity might play an important role. The analysis by IRA of an aliquot of the fraction below <100 µm indicated a soil pH of 7.9 and an organic content of about 2%.

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3.2 Aging the dust

Due to the concomitance of dust and polluted air masses in the Mediterranean basin, the mixing between dust and anthropogenic pollution seems to be a usual process: direct observations by analytical electron microscopy of Mediterranean individual aerosol particles report, for example, the abundance of sulphate particles mixed with dust and their association to calcium in the form of gypsum ($CaSO_4$), attributed to in-cloud reaction (e.g. Levin et al., 2005; Kalderon-Asael et al., 2009). Many other studies conducted in the Mediterranean highlight this association, which is attributed to the heterogeneous reaction of gaseous H_2SO_4 onto the surface of mineral $CaCO_3$ particles (e.g., Formenti et al., 2001; Falkovich et al., 2001). A significant interaction between HNO_3 and dust is also observed in both the western and eastern Mediterranean basins (Putaud et al., 2004; Koçak et al., 2007). Laboratory studies on heterogeneous chemistry show that the Ca content of particles is a paramount parameter explaining their reactivity (e.g. Krueger et al., 2004), partly because their hygroscopicity is increased. From samples collected during episodes of transport of northern African mineral dust to Israel, Falkovich et al. (2001) indicate that organic material can be also internally mixed with mineral dust. Aymoz et al. (2004) detected also various organic acids (including oxalic acid) in the aerosol coarse mode over the Alps and suggested some uptake of organic acidic gases during transport. The dust uptake of secondary acids (H_2SO_4 or HNO_3) or organic compounds is likely to be the main factor for the enhancement of solubility and hence the bioavailability of nutrients in dust particles during atmospheric transport (Jickells et al., 2005; Anderson et al., 2010). Solmon et al. (2009) conclude, for example, that 30% to 70% of particulate soluble iron over the North Pacific Ocean basin can be attributed to atmospheric processing. In the same way, mineral dust mixed with nitrate is also an important vector for nitrogen fertilization of surface oceans (Baker et al., 2003).

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The South Tunisian source region is known to produce calcium-rich dust (Bergametti, 1987; Avila et al., 2007) due to carbonated lithology of soils in this region (Claquin et al., 1999). The calcium index of dust shows high calcite concentrations in the dust originated from Tunisia, northern and central Algeria, and Morocco, and low concentrations south of approximately 27° N (Kandler et al., 2007). Desboeufs and Cautenet (2005) emphasize that the Tunisian dust has a high potential for mixing with anthropogenic pollutant over the Mediterranean Sea due to their calcite content. Consequently, we chose to mimic this atmospheric uptake of inorganic and organic soluble species on dust during transport via in-cloud reaction. Our protocol to aging dust is based on previous works from Desboeufs et al. (2001) enabling the laboratory simulation of cloud evapocondensation cycling for small amounts of dust (~1 g), that reproduces the photochemistry and the gradients in pH and ionic strength during cloud processing of dust particles. The procedure was adapted to process the large amount of dust necessary for the DUNE seeding experiments, while working with dust loading corresponding to natural conditions. This simulation consists in mixing dust with synthetic cloud water (see next paragraph) in a bottle (condensation step), then spreading the suspension on a polystyrene tray (32.5×44.5 cm^2) and evaporating the aqueous phase under clean air flux (Fig. 6). This is performed inside a clean room and all the material used during the whole process has been cleaned using ultraclean protocols for trace metals (Losno et al., 1991).

To our knowledge, no information on the chemistry of cloud droplets in presence of dust is available in the Mediterranean. The choice of "cloud water" conditions for the condensation step has been based on the work of Meskhidze et al. (2003). They calculate from data in rainwater (East Asia) that during mixing in cloud process, the pH around dust could be very low (around 1) due to the large part of dissolved acid and the low water quantity, explaining the observed values of nitrate on dust. From this calculation and the actual concentration of sulphate and nitrate measured in rain collected in the western Mediterranean area (Löye-Pilot and Morelli, 1988; Quereda Sala et al., 1996; Balestrini et al., 2000; Muselli et al., 2002; Aiuppa et al., 2003; Loÿe-Pilot

et al., 2005; Avila et al., 2007), we estimated dust/water ratio content in Mediterranean evaporating cloud water around 10 000. We worked with a high dust loading in water of 100 g L^1, corresponding to 10 000 times more than a typical "desert" rain event (10 mg L^1; Ridame et al., 2002). As a consequence all the concentrations have been multiplied by a factor 10 000 in order to stay in the same ratio of concentrations as in natural rainwater. Besides the inorganic acid species, we have also considered in the aging simulation the presence of oxalic acid, which is the major organic acid found in the Mediterranean rain waters and aerosols (Peña et al., 2002; Bardouki et al., 2003; Aymoz et al., 2004) and is known to enhance the dissolution of iron (Cwiertny et al., 2009; Paris et al., 2010). Table 1 summarizes the average conditions of "desert" rain concentrations used as reference and the concentrations used for our simulation. Preliminary tests of dissolution of the Tunisian fine soil fraction showed that it was little influenced when simulated solar light was applied. Consequently, no added light has been used during the cloud cycling simulation. From this cloud cycling protocol summarized in Table 1, 250 g of the fine fraction of Tunisian soil has been processed and stored in a clean container. This processed dust is named hereafter as "evapocondensed dust" or "dust EC", and original dust as "dust nonEC".

3.3 Dust characterization

Both non-processed and evapocondensed dust types were used for the mesocosm experiments. In order to compare the responses obtained in both cases, an exhaustive physico-chemical characterization of both dust samples was carried out before seeding, including particle size distribution, chemical and mineralogical composition.

Size distribution Particle size analysis was performed from liquid suspension of Tunisian dust by employing a laser technique based on the laser obturation time of transition (TOT) theory (De Falco et al., 1996; Weiner et al., 1998; http://www.ankersmid.com/AF/Laser.Obscuration.Time.Technique/) using an Ankersmid EyeTech CIS1 multichannel particle size analyzer equipped with an ACM-101 magnetic stirring measurement cell. The measuring particle diameter (D) range is 0.04–2000 µm. Channels

have a constant size resolution in logarithmic scale ($\log_{10}(D) \approx 0.0405$). The water suspension was first ultrasonically and mechanically agitated to break up any aggregate. Sub-samples of 2 mL each, were then taken from the same agitated sample and transferred into sample cells. A small magnetic spin bar into the sample cell stirred the solution to prevent particles from settling. To ensure good data quality, we imposed a measurement confidence level of 95% in both number and volume size distribution. The confidence level is the probability that the measured mean size of the sample particles is within ± 2.5% of the true mean. Hence, the instrument continued scanning the sample until this confidence level was reached.

The volume size distribution of non-processed dust and evapocondensed dust are quasi-identical (Fig. 7a). The sieving mesh of 20 µm produces a clear cut-off of the particle size distribution but it looks that the cut-off efficiency of the 20- µm mesh of the sieve is rather maximum at 30 µm than at 20 µm. The spectra present a volume median diameter around 6.5 µm and a peak at ∼10 µm. A large body of observations of the column-integrated particle volume size distribution during dust outbreaks in the Mediterranean is available (Tomadin et al., 1984; Dulac et al., 1989; Kubilay et al., 2003; Masmoudi et al., 2003; Derimian et al., 2006; Tafuro et al., 2006). The presence of coarse particle modes in desert aerosols is clearly pointed out by these various authors with a particle diameter mass or volume peak value generally within the 2–8 µm range. This is also observed elsewhere (see for instance the compilation in Reid et al., 2003). Reid et al. (2003) conclude that larger modal diameters (∼9–13 µm) observed for coarse dust aerosol particles with optical particle counters result from methodological biases.

There are a few evidences from dry and wet deposition samples, however, that particles greater than ∼8–10 µm control both the dry (Dulac et al., 1989, 1992) and wet deposition fluxes (Pitty, 1968; Dulac, 1986; Guerzoni et al., 1993; De Falco et al., 1996). Consequently, the size distribution of our dust analogue appears shifted to large values when compared to dust transported over the Mediterranean, but looks better representative of the size distribution of deposited dust.

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We could adjust a sum a 3 lognormal modes to the volume size distribution up to 30 µm in diameter by minimizing a χ^2 using the Microsoft Excel solver (Fig. 7b). To remove the tail of the fitted distribution towards large particles, which caused an excess of particles larger than 20 µm in diameter in the fitting procedure, we accounted for a cut-off efficiency of the 20- µm sieving mesh linearly increasing from 0 at 20 µm to 1 at 30 µm. We end up with 3 modes of roughly the same total volume (30–36% each) and with the following respective volume-median diameters (VMD): VMD_1 ~1.6 µm, VMD_2 ~6.2 µm and VMD_3 ~12 µm (geometric standard deviations are ~2.6, ~1.8 and ~1.4, respectively). It is striking to note that these modal diameters roughly correspond to those of the three mineral aerosol modes that were observed to be produced by wind erosion of arid soils (mass-median diameters of 1.5, ~6.5 and 12–16 µm; Alfaro et al., 1998).

Figure 7a also presents the particle size distribution expressed in number concentration. The distribution peaks at 0.1 µm, and median and mean diameter values are 0.22 and 0.32 µm, respectively. This implies that about a half of the particles may pass through the 0.2- µm porosity filters used to separate soluble and particulate phases in seawater, so that associated chemical elements will be accounted for in the dissolved phase. Such small particles only carry less than 1% of the total dust mass but may impact the assessment of the soluble fraction in seawater for low-solubility elements such as iron. Finally, the number size distribution of our dust analogue shows that almost 99% of the particles are below 1 µm in diameter which means that they will have a very weak settling velocity in seawater if they are not self aggregating to form larger particles or if they are not embedded in or adsorbed on larger biogenic aggregates.

Mineralogical composition Step-scan X-ray powder-diffraction data for the samples were retrieved over a 2θ range of 3–80° with Co K-α radiation on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer equipped with a Fe monochromator foil, 0.6-mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a Vantec-1 strip detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. Mineral identification was done using the International Centre

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for Diffraction Database PDF-4 and Search-Match software by Siemens (Bruker). This analysis is semi-quantitative due to, notably, the low volume of supplied dust for the analysis.

The results showed the dominance of quartz (40%) and calcite (30%) followed by clays (25%). The clay fraction is composed mainly of illite and kaolinite and includes palygorskite at trace level, which is a typical mineral of Northern Sahara (Formenti et al., 2008). Dolomite was also detected.

Chemical composition The elemental composition of the particles was obtained by both Wavelength Dispersive X-ray fluorescence (WD-XRF) and high-resolution Inductively Coupled Plasma-Mass Spectrometry (HR-ICP-MS) after acid digestion. WD-XRF analyses were performed using a PW-2404 spectrometer by Panalytical. Excitation X-rays are produced by a Coolidge tube (Imax= 125 mA, Vmax= 60 kV) with a Rh anode; primary X-ray spectrum can be controlled by inserting filters (Al, at different thickness) between the anode and the sample. Each element was analysed three times, with specific conditions (voltage, tube filter, collimator, analyzing crystal and detector), lasting 8 to 10 s. Two types of analyses were carried out on the dust by WD-XRF, a first analysis using borate glass discs (Quisefit et al., 1994) and a second one by deposition on filter (Quisefit and Randrianarivony, 1998). The elemental analysis by ICP-MS was performed after the method by Pretorius et al. (2005). Dust were decomposed in high-pressure containers using HF-HNO_3-$HClO_4$, sample solutions were then subsequently dried and redissolved in 1% v/v HNO_3 for direct measurement with HR-ICP-MS. A double-focusing sector field Element2 ICP-MS (Thermo Finnigan, Bremen, Germany) associated to conventional PFA spray chamber, 100 µL. min^{-1} microflow PFA nebuliser and saphire injector were used. Finally, total concentration of carbon (TC) and nitrogen were measured in triplicate with a LECO900 elemental analyzer (CHN), on aliquots of the desiccated samples (3–4 mg).

The chemical composition (Table 2) is in agreement with the results obtained on the mineralogical composition. The dominant Ca content is directly related to the presence of calcite in the samples and agrees with literature data on chemistry of Tunisian dust

(e.g. Avila et al., 2007). Si/Al ratio is 3.75, this is higher than the average mass ratio classically measured in mineral dust (3, see e.g. Formenti et al., 2008), and indicates a small enrichment of the sample in quartz compared to typical African dust. Concerning Fe and P, their concentrations are comparable with available Saharan dust data (Guieu et al., 2002; Formenti et al., 2008).

The comparison between non-processed and evapocondensed dust shows a similar chemical composition except for S and N, and to a lesser extend for C. The good comparison for trace elements such as Cu and Co enables to conclude on the non contamination of dust during the experimental aging process. The S and N contents have been increased by a factor 130 and 10, respectively, by the simulated cloud water processing. This result is consistent with a mixing of dust and sulphate and nitrate observed over Mediterranean (as mentioned above) that we intended to mimic. The S and N enrichment is probably associated to the reactivity of calcite with the inorganic acid H_2SO_4 and HNO_3 added in the simulated cloud water. During the evaporation step, dissolved calcium reacts with sulphate and nitrate and forms $CaSO_4$ and $Ca(NO_3)_2$ to the detriment of the calcium carbonate which content should decrease in the sample (Gibson et al., 2006). These results display that in same proportion, sulphate seems to be more reactive with calcite than nitrate, contrary to the observations of Hwang and Ro (2006). Thus, the loss of 20% of C could result from a combination of the removal of carbonates species by reactivity with inorganic acids and enrichment by formation of oxalate salts in surface of dust.

Finally, we have shown that our strategy to produce a large amount of dust to be used for seeding in large mesocosms was appropriate as the physico-chemical composition of the obtained dust is comparable to actual aerosols collected in the Mediterranean environment. Evapocondensed dust is representative of Saharan dust mixing with airmasses influenced by anthropogenic activity. Non-processed and evapocondensed dust were used in two different seeding experiments during DUNE1.

4 The marine experimental platform

In LNLC waters, the concentrations of both nutrients and micronutrients are expected to be at nanomolar levels, therefore extreme caution was necessary in designing the different aspects of the mescoscosm experiment in order to avoid any type of contaminations at all steps (building, deployment, mooring, filling, seeding, sampling etc). The terms of reference were that all the parts have to be made of plastic, to be transportable to the site with a small boat and that the setup allows maximum light to reach seawater inside the mesocosms. The specificities of DUNE (fertilization by atmospheric input, studies of trace metals and low level nutrients) have been driving our choices concerning (1) the material and the shape of the bags, (2) the design of a holding structure and (3) the sampling system. Indeed, the know-how concerning mesocosm currently used by the scientific community had to be adapted for our specific objectives. We started from the existing design developed by J. Seppälä (see for ex. Olli and Seppälä, 2001).

4.1 The bags

The selected mesocosms consist in large bags made of two 500-µm thick films of polyethylene mixed with vinyl acetate (EVA, 19%) with nylon mesh in between to allow maximum resistance and light penetration (HAIKONENE KY, Finland). They are 2.3 m in diameter and 12.5 m in height for the cylindrical part plus 2.2 m for a conical part at the bottom (surface is 4.15 m^2 and total volume 52 m^3). The conical bottom ends with a 3″ adapter that allows the fastening of a small trap to collect the sinking material. This original design was modified as follows to meet our goal. The filling of the bags is a crucial step and in previous mesocosms studies, it was performed by large volume pumps as the bottom opening is small precluding a rapid filling (see for ex. Schulz et al., 2008). The two existing options (large volume pumps or slow natural filling from below) were not retained for our study because both may deeply modify the structure of the surface waters and also may contaminate the inside water. The solution was to build the bags in two parts (Fig. 8): (1) a main cylinder (2.3 m diameter) ending with a diameter reduced to 1.5 m and (2) the final cone. At the extremity of the main

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cylinder and at the top of the final cone, two PVC circles (8 cm width) were installed, sandwiching the plastic. They were hold tightly together by the mean of 8 nylon screws providing a very good cohesion between the two parts. One cannot exclude some water exchange between inside and outside of the mesocosm going through this junction even if the PVC circles were tightly screwed but if it occurred, this would have concern extremely small water volume as there is no pressure gradient between the inside and the outside.

Even if the site where the mesocosms were deployed is protected from the dominant winds (SW sector), the site is subject to frequent wind events from other sectors, and swell and currents can be important inside the Elbo Bay (Romano et al., 2006). Such conditions could possibly deform the bags or even tear up the plastic material in particular in the above part of the mesocosm that is subject to the strongest strain. In order to rigidify the system and maintain at best the cylinder shape during the whole experiment, large PE tubes (diameter = 40 mm) were installed at five different levels inside horizontal tunnels made with the same plastic material and thermo glued inside the main cylinder (Fig. 8). At three points of each of those five PE rings, the same PE tube was used to make radius attached to custom-designed PVC parts placed at the center of the bag (Fig. 8b). Such part had two functions: it made a wire wheel that maintains the round shape of the bag and it centered the sampling tubing (see section "Sampling system" below).

In order to exclude the possibility that a 'real' Saharan event occurring during the experiment could disturb the experiment, the mesocosms were covered. The cover was designed in order to let the maximum light reach the water body inside the mesocosm and transparent PVC material was used. Measurements of the absorption spectrum (J. Ras, personal communication, 2008) indicate that PVC absorbs in the UV domain but not in the visible domain. Those covers were elevated by 10 cm above the top of the mesocosms to allow air circulation in order to avoid a confinement effect in the trapped water.

4.2 The holding structure

For the purpose of our fertilization experiment, six mesocosms were needed. We decided to design and assemble two PE structures that would be able to hold three mesocosms each (Fig. 9). The bags were held inside the PE structure at three points thanks to PVC cylindrical structures at the level of the upper ring and at the level of the ring bellow the sea surface: this allowed having no tension applying directly to the bags. The structures were moored using only non-metallic material (except for the screw anchors installed at the sea floor 25–30 m deep). Two structures of three mesocosms were deployed, one structure of three mesocosms being used to triplicate the experiment and the other to triplicate the control. Each holding structure was moored thanks to three screw anchors installed at 120° and connected to sub-surface buoys, themselves linked to surface buoys. The complete setup was a solid mooring able to absorb the swell effect, holding a supple and strong structure, both allowing that no tension applied directly to the bags.

4.3 Operation platform

All the seeding and sampling operations in mesocosms were performed from two mobile plastic platforms that were moved thanks to several two-way ropes installed in between buoys. In between the two structures of three mesocosms, reference measurements were performed in free seawater. Equipment and people were transported from Galéria to the bay by small motor boats. The final approach of the plateform was made by rowing.

4.4 The sampling system

The protocol established to conduct the fertilization experiment aimed at minimizing the disturbance of the water column trapped inside the bags, and to ensure at best "simultaneity" for the deployment. An original sampling system was designed with the

goal that the sampling induced as less as possible perturbation inside the mesocosms. In each bag, three braided clear PVC tubing (Holzelock-Tricoflex, inside diameter = 9.5 mm) were permanently installed at the center of the bags with one extremity at three different depths: 10 m, 5 m and 0.1 m. The other extremities were fixed outside of the mesocosms. The sampling was done by pumping: a PFA pump (St-Gobain Performance Plastics) activated by the pressurized air from a diving tank was connected successively to the extremities of the three tubing coming out of the mesocosm, allowing to sample directly at the three selected depths without introducing any device inside: this system allows to sample directly water, either non filtered or filtered (using different types of cartridges according to the parameter to be measured).

4.5 Filling of the mesocosms

The filling of all control and seeded mesocosms was done with the aim to reduce at minimum the risk of contamination. The main cylindric part of the mesocosms was first deployed: the bags, maintained squeezed by three small elastic ropes, had four small ballasts temporary attached on the PVC circle. They were presented at the surface of the water, inside the holding structure. Once fixed at the structure on three places, the elastic ropes were released, allowing the main cylinder to gently but rapidly (~10 min) deployed vertically with the assistance of one diver who stayed outside of the bag, at the level of the PVC circle. The whole operation of successively deployed the six bags (presentation at the surface, fixation at the structure and filling) took less than two hours. The main cylinder being deployed, it was left open for 24 h in order to stabilize the water mass inside. This step was also a way to remove possible particles that may have stick onto the plastic since the beginning of the fabrication. After 24 h, divers placed the conical bottom of the cylinder by screwing together the two PVC sandwiches (see Fig. 8 and Sect. 4.1 on bags). During the whole installation, the divers worked following the instruction to stay outside of the bags in order to infer a minimum disturbance of the waters in particular from air bubbles.

Figure 10 shows pictures of the whole setup, above the seawater level and below.

5 Fertilization experiments

Two seeding experiments were conducted in June 2008. The first one (named hereafter experiment "DUNE-1-P"; duration 8 days, 11–18 June 2008) mimicked a wet deposition event using evapocondensed dust and the second one (named hereafter "DUNE-1-Q"; duration 8 days, 20–27 June 2008) mimicked a dry deposition event using non-evapocondensed dust. For both P and Q experiments, the group of three seeded mesocosms is referred as 'DUST-Meso' and the other group with no dust as "CONTROL-Meso".

5.1 Initial conditions

The chlorophyll *a* concentration was typical of oligotrophic system (of the order of 0.1 µg L^1 for both experiments), the dissolved inorganic phosphorus was close to detection limit (2 nM) or below, in agreement with observations for summer conditions in open waters (DYFAMED time series, Pulido-Villena et al., 2010) and the nitrate+nitrite concentrations were low but detectable (0.2 µM). Dissolved iron was of the order of 2.5 nM at the beginning of both experiments. This is higher than typical concentrations of open sea waters in the NW Mediterranean Sea in late summer (e.g. Guieu et al., 2002; Bonnet and Guieu 2006) and it likely reflects a coastal influence (Wagener et al., 2010) but could also be due to some extent to a dust deposition that occurred in late May with a deposition flux of the order of 0.4 g m^2 (Dulac et al., 2010). While the seawater temperature during the whole DUNE-P experiment were in the range 17–21.5 °C and the stratification of the column water inside the mesocosms was not marked, it significantly increased during the DUNE-Q experiment with a range 18.5–26 °C. As seen on Fig. 10, the air temperature during the day was stable during DUNE-P with an average value of 23 °C; the air temperature increased rapidly at the beginning of

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the DUNE-Q experiment to reach an average value during the day of 29 °C. This rapid increase of the air temperature led to the establishment of a thermal stratification of the surface waters. A shift from spring to summer conditions thus occurred between P and Q experiments.

5.2 Seeding the dust

The dust was spread at the surface of the mesocosms by the mean of all-plastic 4-L (HD polyethylene) sprays (only the spray extension was made of a carbon tube): these devices were acid-cleaned (HCl 5%) and rinsed thoroughly (Milli-Q water) before use on the field. On the field and just before the seeding, the evapocondensed dust was mixed to 2 L of ultra-pure water (wet deposition experiment: DUNE-P) and the non-processed dust was mixed to 2 L of seawater (dry deposition experiment: DUNE-Q) (Fig. 12). Overall, the time necessary to prepare the dust-solution and to seed the three mecocosms was 40 min.

5.3 Sampling of the water column

The sampling session took place every morning at the same hours. Sampling of the two groups of mesocosms was simultaneously performed thanks to two mobile plastic platforms that were moved momentarily close to the structure: the whole sampling session was 2.5 h (including spiking and in situ incubation for bottles dedicated to N_2 fixation and primary production measurements). Sampling was also performed every two days outside of the mesocosms (at −0.1 m, −5 m and −10 m using the same tubing device as in mesocosms). This allowed us controlling that the evolution of the biogeochemical conditions inside the CONTROL-Meso were in good agreement with outside conditions and that there was no contamination. The whole sequence for both experiments is detailed in Table S1 (supplementary info, http://www.biogeosciences-discuss.net/7/2681/2010/bgd-7-2681-2010-supplement.pdf).

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The first sampling session took place the day before the seeding in order to determine the initial conditions of the experiment. Zooplankton sampling was performed with a WP2 plankton net (200 µm mesh size) outside the mesocosm at the beginning of the experiment (to avoid any contamination from the device which structure is totally metallic) and inside the mesocosm at the end of the experiment. The sampling was done between −12 m and the surface.

The sampling of the exported material was performed by the mean of small sediment traps (500-mL high density polyethylene bottles) screwed at the base of the mesocosms and changed every 2 d by divers: each sample represent thus the amount of material that was exported below 15 m during 48 h. When replacing by the diver, the small opening at the base of the bag (diameter = 3.5 cm) was left open for few minutes: as there is no pressure gradient between the inside and the outside of the bag this could have lead to an exchange of at most a volume of few hundreds of milliliters.

5.4 End of the experiment

At the end of the first experiment, the bottom cones were unscrewed by divers leaving the base of the mesocosms open. Thanks to underwater open bottom lift bags installed at the base of the bags, the main cylinder uplifted to the surface. This resulted in the emptying of the whole volume of water trapped inside the cylinder with the top of the mesocosms still attached to the holding structure. The bags were then ballasted to fill them again and 24 h after this operation, the bottom cones were screwed-back underwater by divers. To eliminate any possibility of memory effect between DUNE-P and DUNE-Q, the groups of seeded mesocosms were alternated.

6 Demonstration of the accuracy of the strategy

Reproducibility of chemical and biological parameters was tested for initial conditions between samples collected in the three CONTROL-Meso, three DUST-Meso and OUTSIDE. The variation coefficients (CV, %) obtained for those seven independent data

sets (for all the variables presented below) ranged from 7% to 33% for the P-experiment and from 5% to 33% for the Q-experiment. The maximum CVs, observed for DIP, chlorophyll-*a* concentration and N2 fixation rate, were explained by the fact that for these parameters, values were often close to the detection limit. This comparison of the initial conditions indicates that the chemical and biological characteristics of the waters in each of the 6 mesocosms and OUTSIDE were not significantly different from each other at the beginning of the experiments.

Data obtained during the experiment were submitted to statistical analyses to (1) test the reproducibility among triplicates and (2) compare the results obtained in the CONTROL-Meso with the OUTSIDE; in this case, temperature data were also considered. The parameters measured are presented below.

6.1 Measured parameters

Stocks. Bacteria abundance was determined flow cytometry with a FACSCalibur (BD) as described in Obernosterer et al., (2005) (BA1) and by microscopy after dapi stained cells (BA2). Dissolved iron concentrations (DFe) were determined by flow injection analysis with online preconcentration and chemiluminescence detection following exactly the same protocol, instrument and analytical parameters as described in Bonnet and Guieu (2006). Phytoplankton biomass was determined by HPLC (chemotaxonomic pigments were used to assess the contribution of the different algal groups) in two size classes (<3 µm and >3 µm). Concentrations of chlorophyll *a* (Chl*a*) were determined by fluorimetry ("Trilogy Laboratory Fluorometer" - Turner Designs) after extraction in acetone. Dissolved inorganic phosphorus concentrations (DIP) were measured by spectrophotometry using a long waveguide capillary cell (LWCC) of 1-m long (Zhang and Chi, 2002).

Fluxes. Concentrations of N and C in particulate matter as well as ^{15}N-enrichment in PON and ^{13}C-enrichments 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. N_2 fixation rates (N2 fix) were

calculated by isotope mass balanced as described by Montoya et al. (1996), in parallel with primary production (PP). Bacterial respiration rates were measured in triplicate in 24-h dark incubations of 0.8 µm-filtered seawater in 60 ml BOD bottles. The respiration rate was calculated as the difference between initial and final concentrations of dissolved oxygen. The concentration of dissolved oxygen was determined spectrophotochemically at a wavelength of 460 nm after following the Winkler standard protocol (Labasque et al., 2004). The sediment traps were preserved after collection with a solution of 2% buffered formaldehyde in filtered seawater. After samples treatment (following exactly the same protocol as described in Ternon et al., 2010), the mass fluxes (dry weight of material collected in sediment trap) were obtained by weighing the freeze-dried sample five times.

6.2 Reproducibility among triplicates

Our strategy was to conduct the seeding experiments in large mesocosms representing large bodies of water (52 m^3). The consequences of atmospheric deposition have never been investigated with such an approach, in particular concerning the aspect of cleanness required for trace metal and low level nutrient studies. In order to have the maximum robustness for the data obtained, the same dust addition was reproduced in three different mesocosms and control was also performed in triplicates. To evaluate the reproducibility of the data obtained between triplicate mesocosms, the coefficient of variation (CV, %) between triplicates of each measured parameter was calculated for every sampling time and at each sampling depth (Fig. 13).

As shown on Fig. 13, bacterial abundance (measured using two different techniques, see Sect. 6.1), dissolved iron, phytoplankton biomass >3 µm and primary productivity are the parameters the most reproducible among the 2 groups of 3 mesocosms, having the lowest CV average (≤20%). A range of 10–30% difference in between measurements at the same depth and time in the 2 groups of three mesocosms was observed for Chl-*a*, DIP and phytoplankton biomass <3 µm, and for N_2fix in the group of CONTROL-mesocosms. Nitrogen fixation was not reproducible in the group of

DUST-mesocosms. Indeed for that parameter, a heterogeneous response of the diazotroph activity was observed and this discrepancy is attributed to heterogeneous spatial distribution of those organisms (Ridame et al., 2009). The high CV in between triplicate mesocosms seems thus not reflecting a technical issue but is rather due to small scale high spatial variability, as already been reported for those organisms from in situ measurements (Ridame et al., 2010).

Concerning the material collected in the traps, the difference between triplicates was the highest during the P experiment, with a difference between the three traps of at least 30% of the mass collected and an average difference of 65% in the CONTROL The difference between traps for the CONTROLS of the Q experiment was also high, with an average of 45% difference for triplicate traps. CVs were lower for triplicate traps in the DUST mesocosms (28–35%). This discrepancy could come at first from the design of the trap itself as the time the sample collector was unscrewed from the base of the bag, closed underwater and an empty bottle placed again at the base of the bag allowed the bag to stay open for several minutes: some material could have escaped from the bag during that interval. Also, the shape of the bottom allowed a small flat rim close to the screw thread where some exported material did accumulate during the experiment and could not reach the trap. An iron budget during the DUNE-1-P and DUNE-1-Q, showed that only a maximum of 60% of the iron stock lost from the mesocosms after the fertilization (estimated after 48, 120 and 168 h) was recovered within the traps (Wagener et al., 2010). This supports the idea that the trap design could lead to uncertainties in and underestimates of the amount of exported material.

Taking into account the design of the experiment and the field conditions, the reproducibility obtained from triplicate mesocosms is very good, except for N_2 fixation. Indeed, each bag was filled with 52 $m^3$and one cannot discard some small-scale spatial natural variability between the different water bodies enclosed but this could have been a minor effect as the initial conditions of measured stocks and fluxes in the 6 bags and OUTSIDE compare very well. Concerning the field conditions, bags were installed in situ where the swell, the influence of surrounding current and the light cannot be

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exactly the same in the 6 large mesocosms but we have evidence for light, a critical parameter for biology and chemistry, from pigments measurements (C. Brunet), that the photoprotective pigment ratio (the so called xanthophyll cycle) measured at 5 m depth were similar between the triplicates, revealing a non-significant difference of light perceived by cells at this depth.

This indicates that the evolution as a function of time and depth of both the CONTROL and the DUST mesocosms is well constrained by the numbers obtained. In fact, those CVs are closed to the precision of measurements themselves (for ex. replicate measurements of DFe concentrations on a same sample analyzed three times have a CV of ca. 3 to 8%; Wagener et al., 2010).

6.3 Comparison of parameters measured inside CONTROL-Meso and OUTSIDE

One major issue of the experiments presented in this paper concerns the representativeness of in situ biogeochemical conditions of the water body trapped in the mesocosms. To address this question, we performed t-tests between CONTROL-Meso and OUTSIDE for each measured parameter at every sampling depth and time. The prerequisite for this statistical analysis was the existence of a simultaneous measurement between CONTROL-meso and OUTSIDE. Thus the number of performed analyses varies among parameters depending on the frequency of sampling (Table 3) and on exceptional events such as the loss or contamination of a sample.

The full p-values data set computed from t-tests is reported in supplementary information (Table S2) and only a synthesis of those results is presented here. The computed p-values represent the probability of error involved in accepting the hypothesis of a difference and so, high p-values correspond to non significant differences between CONTROL-meso and OUTSIDE. Figure 14 represents, for all parameters, the cumulative distribution function of the computed p-values. This representation gives a synthetic view of the representativeness of water in the CONTROL-meso: if the difference between CONTROL and OUTSIDE is large, then, a large fraction of the computed analyses will give small p-values.

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For only DFe, more than 5% of all the t-tests performed indicate that data between CONTROL and OUTSIDE have a high probability (>0.98) to be different. For DFe, this number is 17%.

To complete the assessment of the representativeness of the water enclosed in the mesocosms, and in particular to control that there is no confinement effect due to the setup, seawater temperature was continuously recorded inside and outside one of the "CONTROL-meso" over the whole duration of both experiments. Temperature sensors equipped with autonomous data loger (Micrel S2T) were placed at 0.1 m, 5 m and 10 m. Those small sensors (10 cm in length×2 cm in diameter) are enclosed in PVC cover. In addition CTD profiles were performed during the whole duration of the experiment at different sites around the mesocosms platforms, in particular at the open waters "OUTSIDE" sampling site. The comparison (Fig. 15) shows a good agreement between temperature sensors measurements inside and outside the bags and indicate that CTD data compare well with the temperature recorded inside the mesocosm. Those data indicate that the temperature conditions inside the mesocosm well reflect the evolution of the in situ water temperature and that no confinement effect could be detected at any time for both experiments. These conclusions allowed us to construct the temperature evolution during both experiments (Fig. 11).

Statistical analyses performed gave robust evidence of the representativeness of the water trapped inside the mesocosms. This confirms the accuracy of the applied methodology and indicates that the presence of the bag does not modify the natural biogeochemical conditions, and that there was no chemical contamination. The direct consequence of this is that the CONTROL-meso can be used as a reference of the non perturbed ecosystem.

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7 Conclusions

To summarize, 1) the dust aerosol source soil collection, fine particle mechanical production and laboratory aging by a simulated cloud water was an appropriate strategy to get the necessary amount of representative dust to perform seeding experiments in large mesocosms simulating dry or wet atmospheric deposition of desert dust, 2) the experimental platform gave very satisfactory performance for the multidisciplinary studies undertaken during the DUNE-1 campaign; in particular, we have shown that the variation between triplicates are low for most of the parameters, that the deployment of the mesocosms did not induced a contamination of the enclosed water mass, and that the experimental setup did not inferred a confinement effect. Nevertheless, some improvements will have to be done concerning the experimental device for the collection of exported material.

The methodology developed in the DUNE project is suitable to quantify and parameterize the impact of atmospheric forcing to a LNLC ecosystem. Only this type of integrated in situ approach will allow us to eventually be able to parameterize the main processes, involved in the ecosystem functioning, in response to external forcing such as the atmospheric input. This will allow a realistic representation in biogeochemical models of the response to atmospheric chemical forcing because such large mesocosms can be considered as 1D ecosystems.

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Table 1. Chemical composition of (1) desert dust-loaded rains in the Mediterranean environment and (2) simulated Mediterranean cloud water.

	pH without buffering effect by carbonates	$[SO_4^{2-}]$ (M)	$[NO_3^-]$ (M)	$[C_2O_4^{2-}]$ (M)
Average of referenced Saharan rains*	4.7	10^{-5}	10^{-5}	6.10^{-6}
Simulated cloud water	0.7	10^{-1}	10^{-1}	$1.8\ 10^{-2}$

* Querada Sala et al. (1996), Löye-Pilot and Morelli (1988), Balestrini et al. (2000), Peña et al., 2002, Muselli et al. (2002), Aiuppa et al. (2003), Loÿe-Pilot et al. (2005), and Avila et al. (2007).

Table 2. Elemental composition of non-processed dust and evapocondensed dust

	Non processed Dust	(+/−)	Evapocondensed Dust	(+/−)
%Ca	18.62%	0.33%	17.95%	1.22%
%Si	15.16%	0.93%	13.59%	1.64%
%C	6.75%	0.01%	5.35%	0.06%
%Al	4.48%	0.12%	4.12%	0.39%
%Fe	2.28%	0.19%	2.31%	0.04%
%Mg	1.85%	0.17%	1.72%	0.28%
%K	1.19%	0.08%	1.15%	0.20%
%Ti	0.33%	0.03%	0.33%	0.03%
%N	0.11%	0.01%	1.15%	0.03%
%P	0.04%	0.01%	0.05%	0.01%
%Mn	0.035%	0.002%	0.035%	0.005%
%S	0.012%	0.001%	1.54%	0.01%
%Cu	0.0015%	0.0003%	0.0015%	0.0003%
%Co	0.0011%	0.0002%	0.0008%	0.0003%

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Table 3. Sampling planning. The corresponding sampling time/day are reported in Table S1 (http://www.biogeosciences-discuss.net/7/2681/2010/bgd-7-2681-2010-supplement.pdf)

P_experiment		depth	DFe	DIP	Chl*a*	BA1	BA2	N2Fix	PP	BR
		0		x	x			x	x	
P1	OUTSIDE	5		x	x	x		x	x	
		10		x			x			
		0	x	x	x		x	x	x	
P1	CONTROL	5	x	x	x	x	x	x	x	x
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P1	DUST	5	x	x	x	x	x	x	x	x
		10	x	x	x		x			
		0	x	x	x					
P2	CONTROL	5	x	x	x					
		10	x	x	x					
		0	x	x	x					
P2	DUST	5	x	x	x					
		10	x	x	x					
		0	x	x	x		x	x	x	
P3	CONTROL	5	x	x	x		x	x	x	
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P3	DUST	5	x	x	x		x	x	x	
		10	x	x	x		x			
		0	x	x	x		x			
P4	OUTSIDE	5	x	x	x	x	x			x
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P4	CONTROL	5	x	x	x	x	x	x	x	x
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P4	DUST	5	x	x	x	x	x	x	x	x
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P5	CONTROL	5	x	x	x		x	x	x	
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P5	DUST	5	x	x	x		x	x	x	
		10	x	x	x		x			
		0	x	x	x		x			
P6	OUTSIDE	5	x	x	x	x	x			x
		10	x	x	x		x			
		0	x	x	x		x			
P6	CONTROL	5	x	x	x	x	x			x
		10	x	x	x		x			
		0	x	x	x		x			
P6	DUST	5	x	x	x	x	x			x
		10	x	x	x		x			
		0	x	x	x		x			
P7	CONTROL	5	x	x	x		x			
		10	x	x	x		x			
		0	x	x	x		x			
P7	DUST	5	x	x	x		x			
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P8	OUTSIDE	5	x	x	x	x	x	x	x	x
		10	x	x	x		x			
		0	x	x	x		x	x	x	
	P8CONTROL	5	x	x	x	x	x	x	x	x
		10	x	x	x		x			
		0	x	x	x		x	x	x	
P8	DUST	5	x	x	x	x	x	x	x	x
		10	x	x	x		x			

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Table 3. Continued

Q_Experiment		depth	DFe	DIP	Chl*a*	BA1	BA2	N2Fix	PP	BR	b<3μm	b>3μm
		0	x	x	x		x	x	x			
Q1	OUTSIDE	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q1	CONTROL	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q1	DUST	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x							
Q2	CONTROL	5	x	x	x							
		10	x	x	x							
		0	x	x	x							
Q2	DUST	5	x	x	x							
		10	x	x	x							
		0	x	x	x		x	x	x			
Q3	CONTROL	5	x	x	x		x	x	x		x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q3	DUST	5	x	x	x		x	x	x		x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q4	OUTSIDE	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q4	CONTROL	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q4	DUST	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x		x	x
Q5	CONTROL	5	x	x	x		x	x	x			
		10	x	x	x		x					
		0	x	x	x		x	x	x		x	x
Q5	DUST	5	x	x	x		x	x	x			
		10	x	x	x		x					
		0										
Q6	OUTSIDE	5									x	x
		10										
		0	x	x	x		x					
Q6	CONTROL	5	x	x	x		x				x	x
		10	x	x	x		x					
		0	x	x	x		x					
Q6	DUST	5	x	x	x		x				x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q7	OUTSIDE	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q7	CONTROL	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q7	DUST	5	x	x	x	x	x	x	x	x	x	x
		10	x	x	x		x					
		0	x	x	x		x					
Q8	CONTROL	5	x	x	x		x					
		10	x	x	x		x					
		0	x	x	x		x					
Q8	DUST	5	x	x	x		x					
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q9	OUTSIDE	5	x	x	x	x	x	x	x	x		
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q9	CONTROL	5	x	x	x	x	x	x	x	x		
		10	x	x	x		x					
		0	x	x	x		x	x	x			
Q9	DUST	5	x	x	x	x	x	x	x	x		
		10	x	x	x		x					

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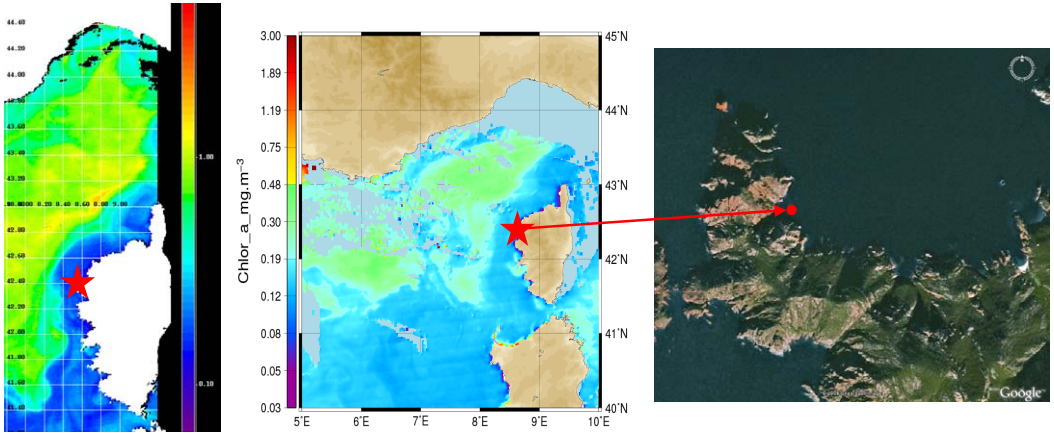

Fig. 1. MODIS satellite image showing the chlorophyll-*a* distribution in the Ligurian Sea during the spring bloom (left image, 1st May 2008) and during the DUNE-1 experiment (central image, 16 June 2008); the DUNE mesocosm site in Scandola reserve on the coast of Corsica is marked in red: the site is characterized by "blue" waters typical of oligotrophic systems (source: MODIS, Nasa, E. Bosc personal communication, 2008). The area chosen is a very "blue" area because of the uplift of the Ligurian Current along the Corsican coast that isolates the coastal area from more productive waters of the center of the Ligurian Sea: during both experiments, the waters were typical of oligotrophic conditions. The GoogleEarth satellite image on the right shows the local configuration of the bay, protected from dominant westerly winds and swell by a peninsula.

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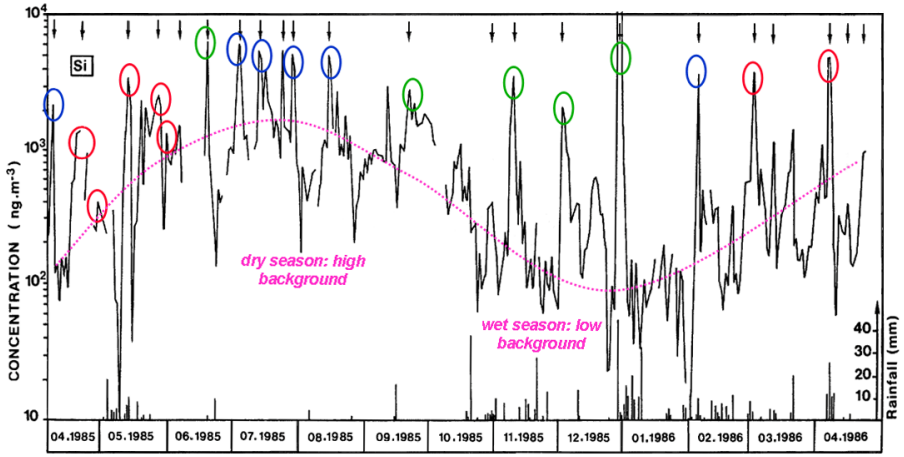

Fig. 2. Atmospheric concentration of particulate Si used as a tracer of African dust and rainfall as observed on a quasi daily basis in NW Corsica from April 1985 to April 1986. The pink dotted curve features the contrasted background between the dry and wet seasons in Corsica. Arrows indicate African dust outbreaks identified by air mass back-trajectories. When clearly identified, dust source regions are indicated by colored ovals: south of 30° N in red; Morocco-western Algeria in green; eastern Algeria-Tunisia-western Lybia in blue (after Bergametti et al., 1989).

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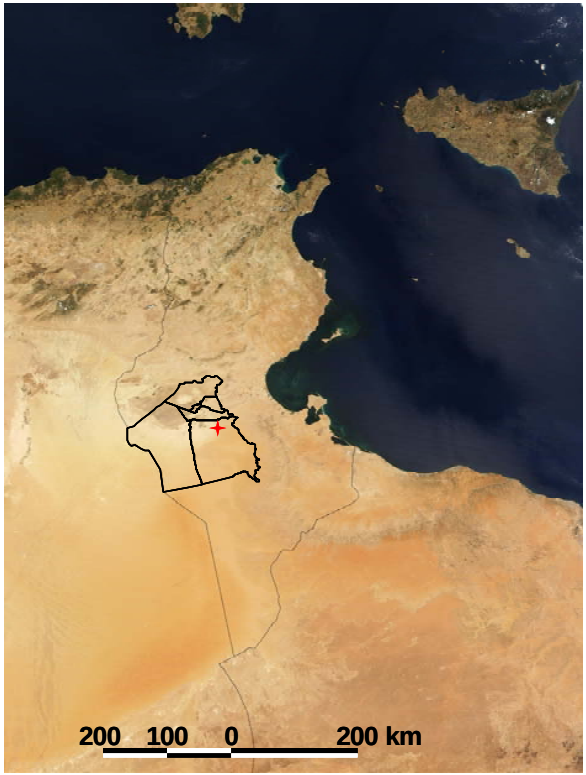

Fig. 3. MODIS satellite view of Tunisia with indication of national frontiers (credit: Jacques Decloitres, NASA/GSFC/Land Rapid Response Team) and districts of the Governorate of Kebili (bold line). The soil collection location (33°27.7′ N, 9°20.8′ E) is marked by the red star in the district of Douz, SW of the Chott El Djerid (darker area) and at the NE margin of the Great Eastern Erg.

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Fig. 4. Photo of the soil sampling area in the dry bed of Oued El Hallouf. In the centre of the front plan are visible clearer rests of clay deposits uncovered by the more orange sand (photo F. Dulac).

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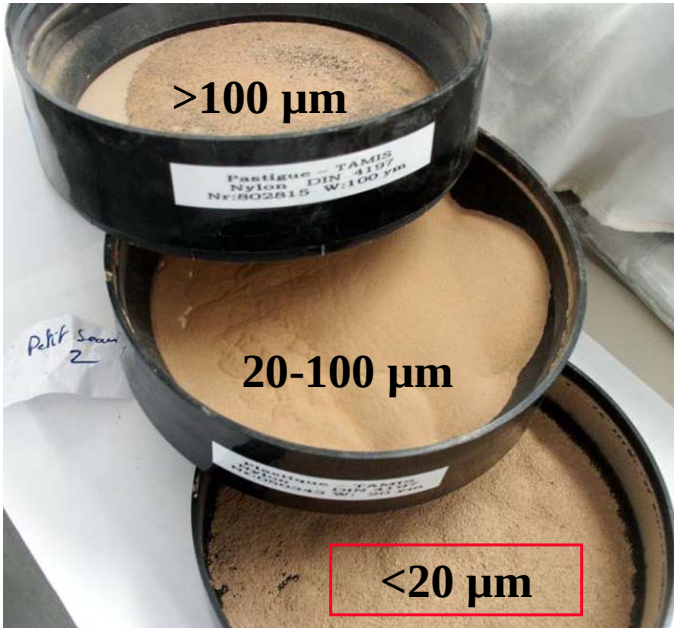

Fig. 5. Soil collected on the three stages of the dry sieving column at the end of the fine particle production process. The relative colors are indicative of the respective content: the upper stage (100- µm mesh) retains small organic debris (black grains), the largest sand grains and possibly clay aggregates; the intermediate stage (20- µm mesh) which contains about 3/4 of the total mass contains mostly the fine, orange-yellowish colored, sand mode and a fraction of aggregated clay; the bottom stage contains the light brown-yellowish, finest fraction of disaggregated particles, dominated by clay (photo F. Dulac).

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Fig. 6. Artificial aging of the atmospheric particles. The principle is to quickly evaporate a water-aerosol mixing in the typical proportions of a cloud drop that is deposited on ultraclean polypropylene plates under clean air within a laminar flow bench. Water is amended with substances normally observed in Mediterranean marine atmosphere. The added aerosols are the fine fraction of the dust collected in Tunisia. The evaporation leads to a pH gradient in the system induced by proton concentration related to decrease in water volume, exactly as it occurs inside a cloud. (photo S. Tran).

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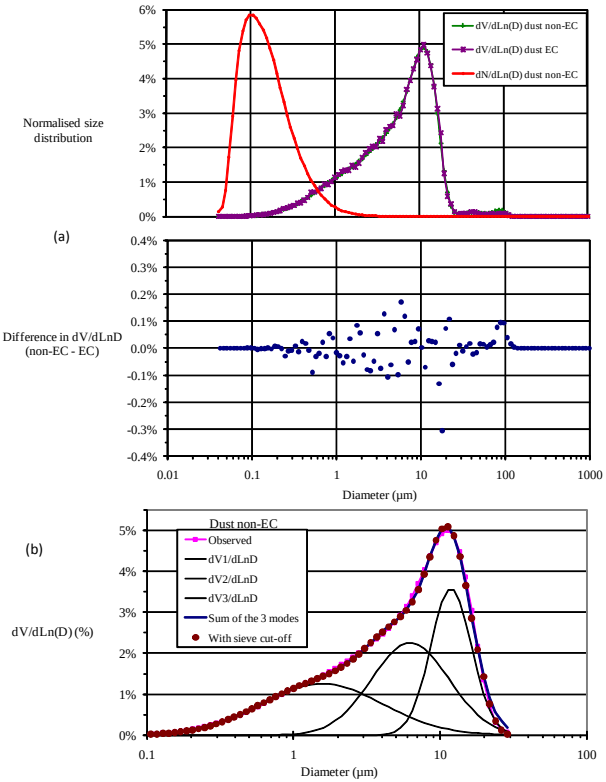

Fig. 7. (a) (top): normalised particle volume size distributions of non-processed and evapocondensed dust and absolute difference between the two distributions (below); **(b)** (bottom): fit of the size distribution with a sum of 3 lognormal modes and assuming a cut-off of the 20-µm mesh (see text).

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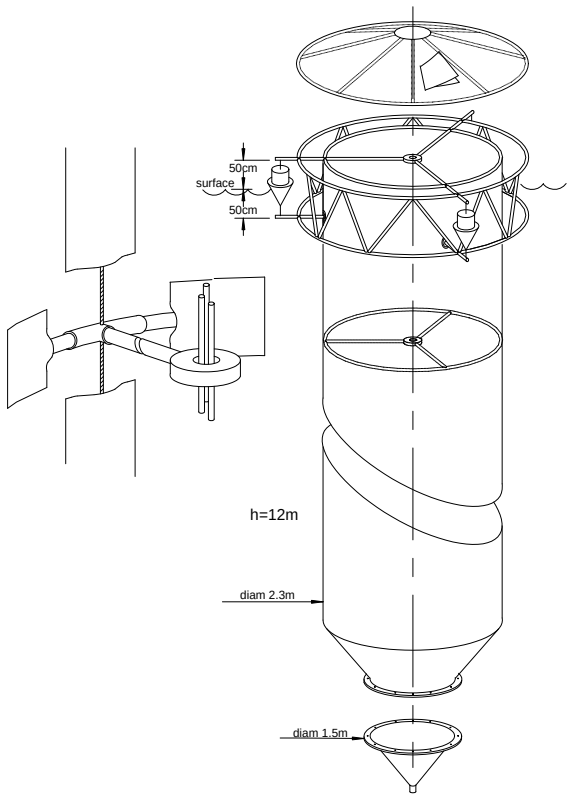

Fig. 8. Drawing representing the main features of the large-clean mesocosm device. The cone at the bottom is installed under water by 2 divers 24 h after the above part has been deployed from the surface: the 2 PVC sandwiches are joined with plastic screws.

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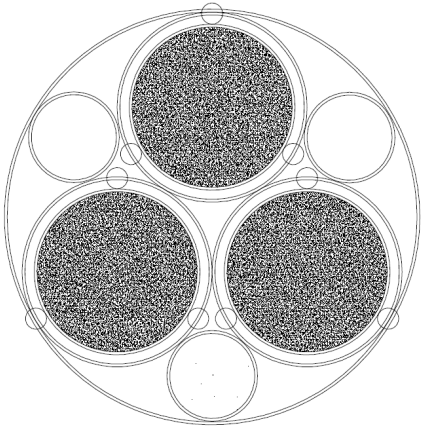

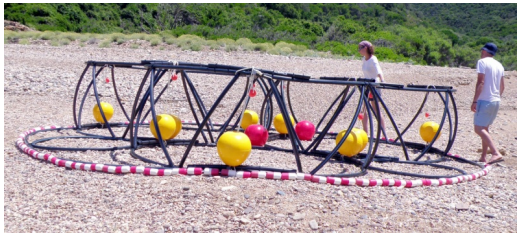

Fig. 9. Design of each PE structure holding 3 mesocosms (photo C. Ridame).

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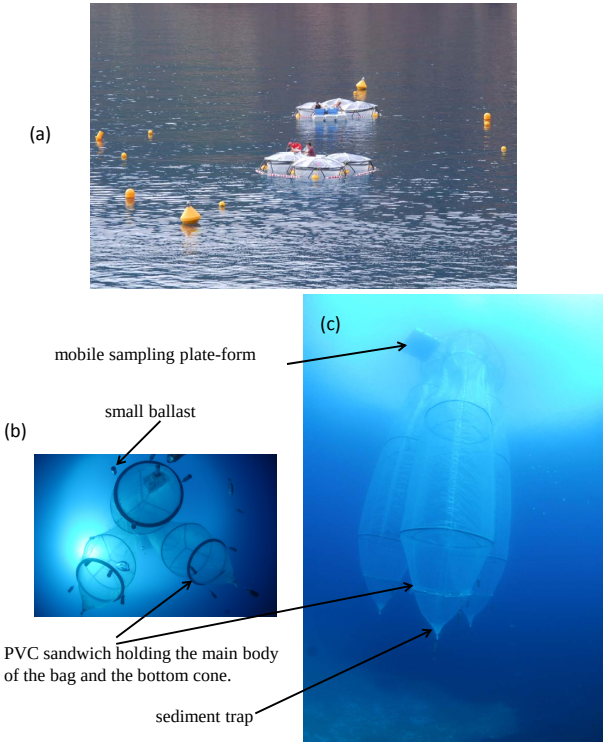

Fig. 10. (a) a view of the experiment from above: the two platforms in open waters separated from few meters. At mid distance between the two platforms is the position where the "OUTSIDE" sampling was performed. **(b)** a view from below, (from the side), of a group of three mesocosms; the seafloor is 10 m below the base of the mesocosms. At the surface, the plastic mobile platform moved temporally close to the structure for sampling every day. At the base of the bags: the small sediment traps. **(c)** a view from the seafloor showing the bases of three mesoscosms, in particular one can see the junction between the main body of the bag and the bottom cone thanks to the PVC sandwiches. (photo: David Luquet, OOV).

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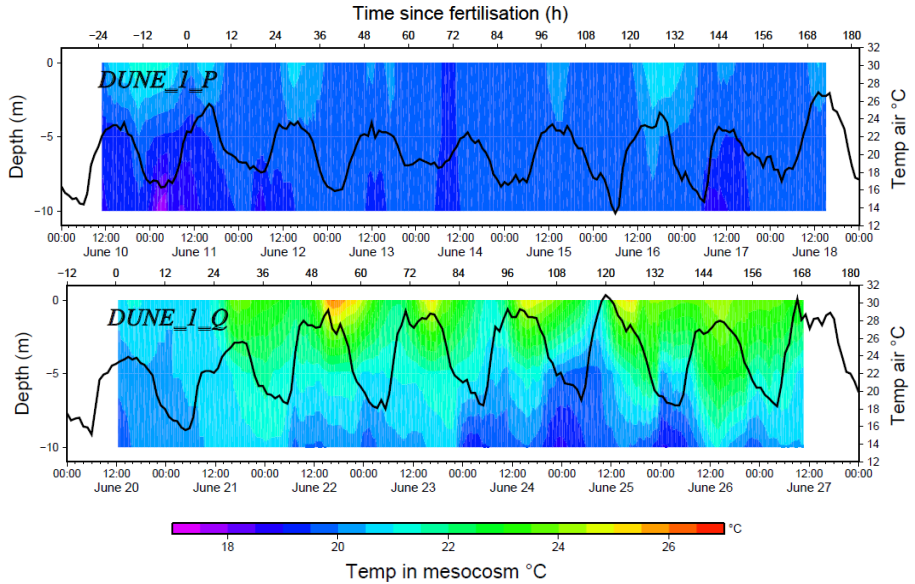

Fig. 11. Evolution of the seawater temperature profile from the surface down to 10 m during the DUNE1 campaign. Top: P-experiment. Bottom: Q-experiment. The superimposed air temperature (black line) indicates how the day/night cycle clearly impacted the intensity of the stratification during the DUNE-Q experiment.

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Fig. 12. The different steps of the seeding: **(a)** on-site preparation of the dust solution in ultra-pure water; **(b)** spraying the dust solution above the surface water of the mesocosm. The mixture is gently pushed through the hose via a manually operated piston pump. (photo: David Luquet, OOV).

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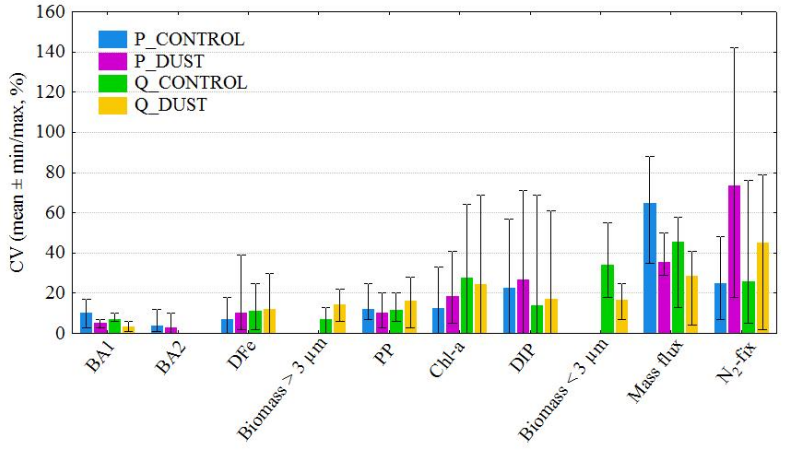

	BA1		BA2		DFe		Biomass > 3 µm		PP		Chla		DIP		Biomass <3 µm		Mass flux		N2 Fix.	
	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST	CONTROL	DUST
P experiment																				
n =	12	12	3	4	23	24	-	-	10	10	21	21	24	24	-	-	4	4	10	10
Q experiment																				
n =	-	-	4	4	27	27	7	7	13	12	25	24	27	27	6	7	4	4	13	12

Fig. 13. Mean coefficient variation along with minimum and maximum values obtained for the measured parameters: mean values were calculated for samples collected at the same depth and time in the 3 mesocosms. The variation coefficients (CV, in %) derived from those calculations (CV = STDEV×100/mean) were then averaged over the whole duration of the experiment. The number "n" of time, three independent measurements from each group of mesocosms were considered in the calculation is reported for each experiment in the table below. ("BA1": bacteria abundance from cytometry;"BA2": bacteria abundance as determined by microscopy after dapi stained cells; "DFe": dissolved iron; "Biomass <3 µm" and "Biomass >3 µm": Phytoplankton biomass in two size classes; "PP": primary production rates; "Chl*a*": chlorophyll *a* concentration; "DIP": dissolved inorganic phosphorus; "Mass flux" : dry weight of material collected in sediment trap ; "N_2 fix": nitrogen fixation rates).

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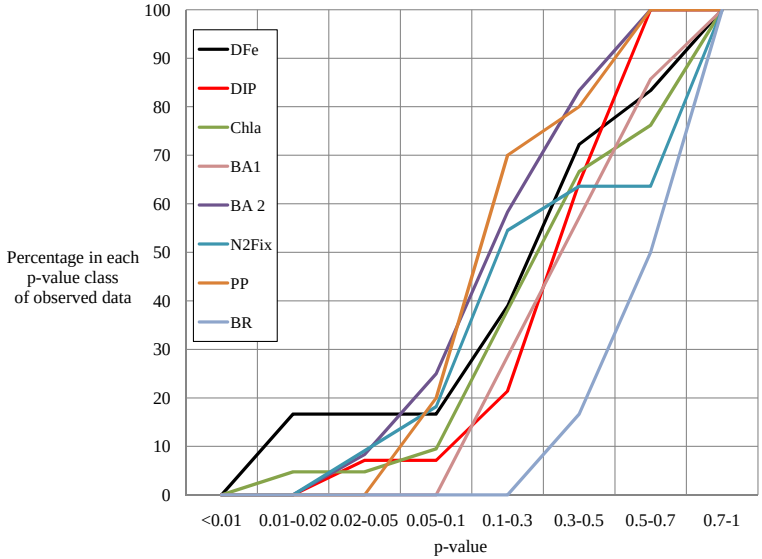

Fig. 14. The cumulative (in %) distribution function of the p-values computed from t-test comparing CONTROL and OUTSIDE data. (labels: same as in Fig. 12 and "BR": bacteria respiration).

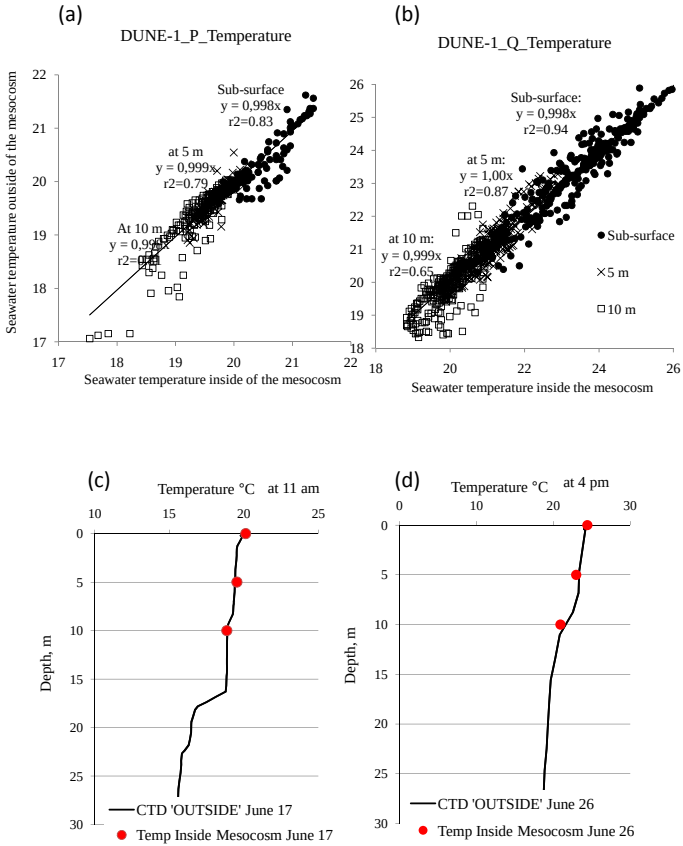

Fig. 15. Comparison of the temperatures (˚C) measured continuously (1 data/h) inside and outside one of the six mesocosms at 3 fixed depths during the DUNE1P experiment **(a)** and the DUNE1Q experiment **(b)**. In addition, a comparison between the temperature inside the bags at 0.1, 5 and 10 m along with the temperature data acquired by CTD at the same time in open waters at the "OUTSIDE" site (b) on 17 June at 11 a.m. and **(c)** on 26 June at 4 p.m.

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