Progress in Oceanography xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Progress in Oceanography

journal homepage: www.elsevier.com/locate/pocean

Atmospheric nutrients in seawater under current and high pCO_2 conditions after Saharan dust deposition: Results from three minicosm experiments

J. Louis[a,*], F. Gazeau[a], C. Guieu[a,b]

[a] Sorbonne Universités, UPMC Univ Paris 06, INSU-CNRS, Laboratoire d'Océanographie de Villefranche, 181 Chemin du Lazaret, 06230 Villefranche-sur-mer, France
[b] Center for Prototype Climate Modeling, New York University Abu Dhabi, P.O. Box 129188, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Keywords:
Ocean acidification
Mediterranean Sea
Nutrients
Bioavailability
Dissolution
Scavenging

ABSTRACT

The Mediterranean basin receives among the highest dust fluxes in the world ocean, and also appears to be one of the regions the most strongly impacted by ocean acidification. The aim of this study was to assess, on a short time scale (one-week), the effect of ocean acidification on the dissolution of nutrients (inorganic nitrogen, phosphate and iron) from Saharan dust. Three experiments were performed in three distinct seasons: in May, after the spring bloom with low autotrophic biomass, in September, at the end of the oligotrophic period, and in January, during the winter bloom. On each occasion, a dust flux of 10 g m^{-2} was simulated at the surface of two minicosms (tanks of ~0.3 m^3) filled with filtered (< 0.2 µm) seawater collected in the Bay of Villefranche (NW Mediterranean Sea). One minicosm served as a control and the other was acidified to reach a partial pressure of CO_2 (pCO_2) close to that projected for the end of this century (~1250 µatm). Following a high-resolution sampling protocol, results showed that whatever the season and *in situ* biogeochemical conditions (1) all nitrogen from dust was soluble in seawater, allowing a large and stable increase in the stock of NO_x (nitrate + nitrite) under the two pCO_2 conditions (ambient and future), (2) transient increases in dissolved iron and phosphate concentrations were driven by scavenging processes, with a low dissolution percentage averaging 0.14 ± 0.08 and 4.7 ± 1.2%, respectively. While the absence of pCO_2 effects on the release of atmospheric nitrogen was confirmed in the present study, no clear conclusion could be drawn for phosphate and dissolved iron as a consequence of very low concentrations and rapid (within less than 1 h) dissolved-particulate exchanges. Nevertheless, as the lifetime of these elements in solution is limited to a few hours, whatever the pH conditions, our results suggest that ocean acidification would have only a minor impact on their bioavailability for surface phytoplankton communities in such Low Nutrient Low Chlorophyll areas.

1. Introduction

The Mediterranean Sea is a semi-enclosed sea receiving among the highest fluxes of atmospheric in the world ocean (Guieu and Shevchenko, 2015). In the northwestern Mediterranean area, the dust deposition flux is on average 12 g m^{-2} yr^{-1}, usually punctuated by short intense events, as reported over the past decades (> 10 g m^{-2} over a few days; i.e. Loÿe-Pilot and Martin, 1996; Ternon et al., 2010; Guieu et al., 2010a, 2010b). Due to the chemical composition of source desert soils and subsequent mixing with polluted air masses during atmospheric transport (e.g. de Leeuw et al., 2014), mineral dust is a source of trace metals and nutrients for surface oceanic waters. Artificial Saharan dust deposition experiments using large pelagic mesocosms showed that the dissolution of evapocondensed Saharan dust can be a source of phosphate and nitrate (Pulido-Villena et al., 2014; Ridame et al., 2014), and a sink or a source of dissolved iron, depending on the quality and quantity of dissolved organic matter (DOM) present in the seawater at the time of deposition (Wuttig et al., 2013). In order to discriminate abiotic from biotic post-depositional processes following dust enrichment, minicosm (tank of 0.3 m^3) experiments were performed using filtered seawater to follow the fate of nutrients, under distinct biogeochemical conditions (Bressac and Guieu, 2013; Louis et al., 2015). While the dissolution of nitrate was high and remained in solution over a one-week period, releases of phosphorus and iron were mostly controlled by abiotic scavenging processes, the intensity of which depended on the sampling season. These previous minicosm experiments highlighted the importance of the nature of DOM with regard to the post-deposition process of nutrients from dust (Bressac and Guieu, 2013; Louis et al., 2015).

In the context of climate change, the accurate parametrization of dissolved-particulate exchanges of nutrients requires taking into account the potential effects of major environmental factors such as

---

[*] Corresponding author at: Université de Rennes 1, IUT de Saint Brieuc, Département Génie Biologique, 22004 Saint Brieuc, France.
E-mail address: justine.louis@univ-rennes1.fr (J. Louis).

http://dx.doi.org/10.1016/j.pocean.2017.10.011

Please cite this article as: Louis, J., Progress in Oceanography (2017), http://dx.doi.org/10.1016/j.pocean.2017.10.011

seawater pH. The human-driven increase in atmospheric CO_2 leads to an acidification of the ocean: a decrease in pH and concentrations of carbonate ion (CO_3^{2-}) and an increase in concentrations of carbon dioxide (CO_2) and bicarbonate ion (HCO_3^-) (Gattuso and Hansson, 2011). Since the start of the industrial era, the pH of surface waters of the world ocean has already decreased by ~0.1 units, and it is expected to decrease by another 0.06–0.32 units by the end of this century (Ciais et al., 2014). With an estimated pH decrease higher than 0.1 since the industrial revolution, the western Mediterranean basin appears to be one of the regions the most impacted by ocean acidification (Touratier and Goyet, 2011; Mermex Group, 2011). In order to assess the future strength of the biological pump in this area, it is therefore of the utmost importance to assess the potential effects of ocean acidification on the bioavailability of atmospheric new nutrients for Mediterranean plankton communities.

As Saharan dust is rich in calcium carbonate ($CaCO_3$), it has a high capacity to absorb anthropogenic nitric acid (HNO_3) onto its surface, leading to the formation of calcium nitrate $Ca(NO_3)_2$ (Usher et al., 2003; Krueger et al., 2004; Formenti et al., 2011). Given that $Ca(NO_3)_2$ is a water-soluble salt and that the dissolution percentage is close to 100% in seawater under natural pCO_2 conditions, our first working hypothesis was that ocean acidification would not affect the release of NO_x from dust.

In contrast, the fraction of phosphorus (P) and iron (Fe) naturally contained in dust particles that can be released in seawater would appear to be dependent on pH (i.e. Ridame and Guieu, 2002; Baker and Croot, 2010). Phosphorus is mainly present under inorganic forms in Saharan soils. This includes a large fraction associated with iron oxyhydroxides coated on clay minerals and quartz particles (Guieu et al., 2002), and another fraction bound with calcium (Aghnatios et al., 2014). Since crustal P is poorly soluble under basic pH conditions (Bergametti et al., 1992), it has been shown that acidic conditions (at pH 2), prevailing in rainwater drops, significantly increase P solubility (Nenes et al., 2011). In contrast, to our knowledge, no experimental work has focused on the effect of pH decrease in seawater, in the range ~8.1–7.4, on the release of P from desert dust. Based on the diagram of solubility of iron phosphate and calcium phosphate (Stumm and Morgan, 1996), the dissolution of Ca-bound-P would be theoretically higher under future seawater pH, while the dissolution of Fe-bound-P would decrease. In addition, the adsorption of phosphate (PO_4^{3-}) onto mineral particles rich in iron and aluminum oxyhydroxides has been shown to be strongly pH-dependent (Fox, 1989). Chitrakar et al. (2006) showed that the uptake of PO_4^{3-} onto synthetic goethite and akaganeite in phosphate-enriched seawater was the highest at pH values around 7, and then decreased with an increase in pH. Therefore, our second working hypothesis was that the decrease in seawater pH, as projected for the coming decades, could favor the adsorption process of PO_4^{3-} onto dust.

Most of the iron present in dust originates from crystalline Fe oxides incorporated in clay minerals (Shi et al., 2010). According to Schroth et al. (2009), the low seawater solubility of iron from dust is due to the presence of poorly soluble Fe oxides. Several factors, including pH, are known to control the solubility of Fe in atmospheric rainwater drops and in seawater. The simulation of atmospheric processing showed that the dissolution of Fe in rainwater drops is minimal above a pH threshold of 3.6–3.8 (Desboeufs et al., 2014; Mackie et al., 2005). As rainwater pH (pH ~ 5.5) is usually far below seawater pH (pH ~ 8), mixing of rainwater with seawater leads to a decrease in Fe solubility (Spokes and Jickells, 1995). In the ocean, the solubility of Fe(III) species is theoretically controlled by pH, and appears to be particularly low at pH ~ 8 (Liu and Millero, 2002). At this pH, Fe(III) is mostly under the poorly soluble iron form $Fe(OH)_3$, and is removed from seawater by particle scavenging (Boyd and Ellwood, 2010). With respect to Fe(II) which is considered more bioavailable than Fe(III), it is rapidly oxidized under ambient conditions, leading to low concentrations in the ocean (Millero et al., 1987). Furthermore, in the ocean, dissolved iron (DFe) is mainly chelated by organic compounds (van den Berg, 1995; Rue and Bruland, 1995). According to Breitbarth et al. (2010), ocean acidification would lead to an increase in Fe solubility through a change in organic iron complexation and an increase in Fe(II) half-life time. Our third working hypothesis was that a decrease in seawater pH could enhance the solubility of Fe originating from dust.

As emphasized by Guieu et al. (2014), an expansion of Low Nutrient Low Chlorophyll (LNLC) areas and a decline in the autochthonous inputs of nutrients by changing ocean physics under future climate conditions, would increase the contribution of atmospheric inputs for fueling surface waters' new primary production and capacity to pump anthropogenic CO_2. Thereby, in the present study, we tested the above-mentioned hypotheses and assessed the effects of a realistic ocean acidification scenario on the post-depositional processes of nutrients after a Saharan dust event in the Mediterranean Sea. Three minicosm experiments using 0.2 µm filtered seawater, sampled in distinct seasons, were conducted under two different pCO_2 conditions (present and future). Following an artificial Saharan dust wet deposition at the surface of the minicosms, the patterns of change of inorganic nutrient concentrations (N, P, Fe) were monitored following a high-resolution sampling protocol. Results of the same experiments, and focused on the impact of ocean acidification on the formation of transparent exopolymer particles (TEP) and particulate organic carbon (POC) export, are presented and discussed in a companion paper (Louis et al., 2017). A large and rapid abiotic formation of TEP was stimulated for all experiments after dust addition. No major impact of ocean acidification on POC export, associated with aggregation process between TEP and dust, was observed during the CHIPIE experiments.

2. Material and methods

2.1. Experimental setup and sampling

Three experiments were conducted in three distinct seasons: 'CHIPIE 1' (water sampling on May 21th 2013) at the start of the stratification period, 'CHIPIE 2' (water sampling on September 30th 2013) at the end of the stratification period, and "'CHIPIE 3'" (water sampling on January 28th 2014) during the winter mixing period. For each experiment, two minicosms (High-density polyethylene, HDPE, tanks with a height of 1.09 m, a diameter of 0.68 m, a surface area of 0.36 m^2 and a volume of 0.28 m^3), previously cleaned (protocol described by Bressac and Guieu, 2013), were used and installed inside a dark, clean, temperature-controlled room. A weak turbulence was generated by a rotating a PVC blade (9 rpm) in order to mimic natural conditions. At the base of each tank, a polyethylene (PE) bottle collecting the exported material from above was screwed onto a polyvinyl chloride (PVC) valve that remained open during the duration of the whole experiment. Minicosms were filled with seawater collected at 5-m depth in the Bay of Villefranche (France) using trace-metal-clean Teflon pumps and an inline filtration system with a 0.2 µm cartridge (Sartorius Sartobran-P-capsule). Dissolved inorganic nitrogen ($NO_x = NO_2^- + NO_3^-$), phosphate (PO_4^{3-}) and iron (DFe) concentrations, as well as the abundance of heterotrophic prokaryotes and the concentration in chlorophyll *a* were determined from *in situ* water sampled before each experiment. The abundance of heterotrophic prokaryotes was determined from a 2 mL aliquot of seawater, preserved with 80 µL of glutaraldehyde, snap-frozen in liquid nitrogen and kept at −80 °C pending analysis.

One minicosm, referred to as 'non-acidified', was not manipulated in terms of carbonate chemistry with ambient pCO_2 levels of ~460 µatm. The second minicosm, referred to as "acidified", was enriched with CO_2-saturated filtered (0.2 µm) seawater to reach a pCO_2 of 1250 µatm. No further regulation of pCO_2 was performed during the experiment and pH levels increased gradually due to air-sea exchanges. This pCO_2 level is above that projected for 2100 following RCP8.5 (~1000 µatm; Ciais et al., 2014) and should be considered as an extreme scenario.