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First report on vertical distribution of dissolved polyunsaturated aldehydes in marine coastal waters

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ABSTRACT

Polyunsaturated aldehydes (PUA) are bioactive molecules released by phytoplankton cells which can modify phytoplankton trophic interactions with grazers, bacteria or coexisting phytoplankters. Their ecological significance is still a matter of debate. There have been reports of PUA producers having been investigated at the ocean surface in both coastal and open areas, but there is little information regarding natural ranges and distribution of dissolved PUA (*d*PUA) once they are released. In this report, we provide novel information regarding vertical profiles of *d*PUA for a coastal area under two different hydrodynamical conditions (mixing and stratified waters). Results show significant concentrations of *d*PUA ranging from 0.061 nM to 1.87 nM during both periods. This data demonstrate a significant consistency of these compounds in coastal areas and may prove an indirect evidence of high turnover rates in seawater. The vertical distribution of *d*PUA showed high variability in stratification, and for the first time we describe "patches" of relatively high *d*PUA concentrations in the upper layer. We hypothesize that these patches of *d*PUA, correlated to the flow of phytoplankton-derived sinking organic matter, could be significant for increasing the turnover rates of nutrients by triggering bacterial metabolism.

1. Introduction

Polyunsaturated aldehydes are highly reactive organic molecules released by dead or wounded phytoplankton cells found in marine and freshwater ecosystems. Different marine diatom species are frequent PUA producers (Wichard et al., 2005) although recent research also suggests that smaller size phytoplanktonic groups (pico- and nanoplanktonic taxa) could be important oceanic PUA producers (Vidoudez et al., 2011; Morillo-García et al., 2014). The ecological role of these compounds is still an unanswered question. Several biological functions have been attributed to PUA, most of them involved with intra- and interspecific relationships among coexisting species by acting as infochemicals (Vardi et al., 2006) and/or chemical defences (Pohnert, 2000; Jüttner, 2005; Wichard et al., 2007; Ianora and Miralto, 2010).

In the ocean, PUA producers have been detected in surface waters, from productive coastal waters (Vidoudez et al., 2011; Ribalet et al., 2014; Morillo-García et al., 2014) to nutrient-poor open areas (Bartual et al., 2014). PUA are generated by the lypoxidation of intracellular PUFA after cell breakage (Fontana et al., 2007; D'Ippolito et al., 2004). Therefore, the concentration of dissolved PUA (*d*PUA) has been directly correlated with phytoplankton lysis rates in surface water of the Adriatic Sea (Ribalet et al., 2014). Concentrations up to 0.128 nM of *d*PUA have been quantified in surface waters associated with an intense bloom event of *Skeletonema marinoi* (Ribalet et al., 2014; Vidoudez et al., 2011), a well-known PUA producing diatom. During bloom development, phytoplankton cell concentrations increase 2 to 10 times with non-bloom period. When PUA producers are present, *d*PUA concentration are shown to increase concurrently with bloom ending and senescence (Vidoudez et al., 2011). This suggests that *d*PUAs could play an important infochemical role in the regulation of cell-cell interactions and recycling processes during the final demise of the bloom events.

Under non-bloom conditions, physical processes, such as temperature or density gradients, along the water column can also led to phytoplankton cell aggregation in thin layers, resulting in increased encounter rates and relevant cell-cell infochemical interactions. Thus, the release of *d*PUAs could also be particularly significant in the ocean interior, associated with a ubiquitous sub-surface chlorophyll maximum (Cullen and Eppley, 1981). Data on *d*PUA concentrations have been reported for highly productive waters in the Adriatic Sea (Vidoudez et al., 2011; Ribalet et al., 2014), but there is no information regarding the vertical distribution of *d*PUA in the water column or its ranges of variability during bloom and non-bloom conditions. Knowing these

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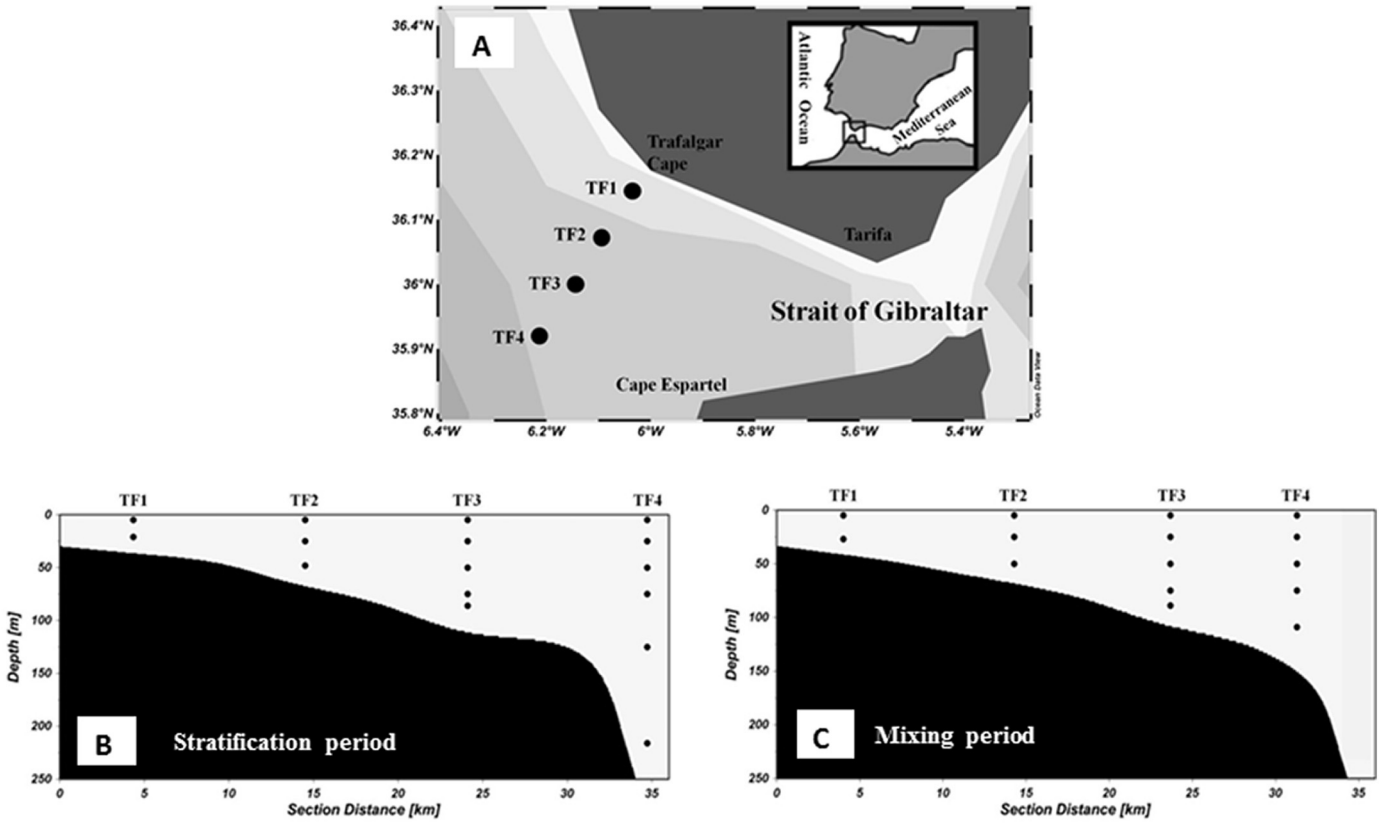

Fig. 1. A) Map showing the location and main geographical points of the study area. Black dots indicate the sampling stations. B, C) Sampling stations at both sampling periods. Black dots indicate depths at which discrete samples were collected (see Supplementary Table S1 for detail). Note that the position of station TF4 is different for both sampling periods (Table S1).

ranges is key in order to relate laboratory experiment data on PUA effects with its ecological significance in nature. The present study reports, for the first time, vertical profiles of *d*PUA to provide a picture of concentrations ranges and composition across the water column under different scenarios, stratification and mixing.

2. Methods

2.1. Field sampling

Data were obtained in two different cruises along a coastal transect consisting of 4 stations from Trafalgar Cape to offshore waters. This is a productive coastal area located in southwestern Spain (Fig. 1). The first cruise was carried out from 4 to 5 of August of 2011 (stratification period) and the second one was on 31 of March of 2012 (mixing period), both aboard the research vessel B/O "Cornide de Saavedra". During the mixing period, the position of the offshore station (TF4) was modified due to meteorological difficulties as indicated in Supplementary Table S1.

A CTD probe (Seabird SBE-911) was used to register continuous profiles of temperature, salinity, oxygen and fluorescence in the water column. At each station, 5 L samples of natural seawater were collected using Niskin bottles mounted on a rosette sampler at different depths (Table 1) to quantify chemical and biological variables such as: concentration of nitrate, phosphate, silicate, nitrite, total Chlorophyll a (TChla), fractionated Chlorophyll a > 20 µm, fractionated Chlorophyll a > 10 µm, and dissolved polyunsaturated aldehydes (*d*PUAs). Additionally, at each station, 50 L of natural seawater were collected at surface for the quantification of particulate PUA (*p*PUA) of two phytoplankton sizes; *p*PUA > 10 µm and *p*PUA < 10 µm.

2.2. Discrete samples

2.2.1. Polyunsaturated aldehydes (PUAs)

2.2.1.1. Sampling procedures. We collected samples for quantifying two different fractions of PUA: particulate PUA (*p*PUA) and dissolved PUA (*d*PUA). *p*PUAs were measured after artificial phytoplankton cell disruption by sonication as explained below. For *p*PUA, two fractions were collected: *p*PUA for large phytoplankton (> 10 µm) and *p*PUA for small phytoplankton (< 10 µm). For pPUA > 10 µm 50 L of seawater were collected at the surface at each station during both sampling periods. This volume was collected in order ensure enough large-sized phytoplankton biomass was present. The water was passed through two consecutive meshes: the first one of 200 µm (to remove zooplankton and to reduce its residue for the extractions) and a second one of 10 µm to collect phytoplankton larger than 10 µm. We checked that there was not phytoplankton retention at 200 µm mesh by optical checking. The phytoplankton retained in the second mesh was diluted in 125 mL of filtered seawater and passed through a nucleopore polycarbonate filter with a 0.4-µm pore size (GE Poretics™). The filter was then transferred to a 25 mL glass vial (Teknokroma) and was rinsed using 1 mL of a 25 mM *O*-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine (PFBHA, Fluka, Basel, Switzerland) solution in Tris-HCl 100 mM, pH 7.2 (Trizma, Sigma). These samples were stored at −80 °C until further analysis. *p*PUA for small phytoplankton (< 10 µm) was obtained from 1 L of seawater passed through a 10 µm mesh, and then through a nucleopore filter. This filter with small phytoplankton retained was then immersed in PFBHA following the above explained protocol, and finally stored at −80 °C until examination.

To analyse dissolved *d*PUA, 1 L of seawater was collected at the surface and different depths, and carefully filtered through a Whatmann GFF filter at very low pressure (< 500 mbar), a protocol that do not