



Rare earth element distributions and fractionation in plankton from the northwestern Mediterranean Sea



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HIGHLIGHTS

- REE concentrations were measured for the first time in plankton from Mediterranean Sea.
- REE concentrations in plankton were poorly related to the reported REE concentrations of seawater.
- REE concentrations in plankton correlated well with calculated free REE(III).
- PAAS-REE concentrations are in the same order of magnitude than PAAS-normalized sediment particles.
- PAAS-REE concentrations have similar distribution than PAAS-normalized sediment particles except MREE.

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ABSTRACT

Rare earth element (REE) concentrations were measured for the first time in plankton from the northwestern Mediterranean Sea. The REE concentrations in phytoplankton (60–200 μm) were 5–15 times higher than those in four size fractions of zooplankton: 200–500 μm , 500–1000 μm , 1000–2000 μm and >2000 μm . The concentrations within these zooplankton fractions exhibited the same ranges with some variation attributed to differences in zooplankton taxonomy. The REE concentrations in plankton were poorly related to the reported REE concentrations of seawater, but they correlated well with the calculated REE³⁺, concentrations especially with regard to middle REE (MREEs) and heavy REEs (HREEs). Plankton and seawater revealed different PAAS-normalised REE distributions, with the greatest differences observed in the light REEs. Interestingly, a comparison of PAAS-normalized sediment particles from the study of Fowler et al. (1992) showed concentrations of the same order of magnitude and a similar REE distribution without MREE enrichment. Based on this comparison, we propose a conceptual model that emphasizes the importance of biological scavenging of REEs (especially LREEs) in surface waters.

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1. Introduction

Plankton play a major role in the accumulation, transfer and biogeochemical cycling of trace elements in marine environments (Martin and Knauer, 1973). Phytoplankton directly influence the distribution and availability both of the essential elements upon which these organisms depend and of non-essential elements, such as trace elements (Bruland et al., 1991; Whitfield, 2001; Morel, 2008). Zooplankton play a prominent role in marine pelagic systems due to their trophic position and to their role in organic matter, trace elements and contaminants transfer from phytoplankton

to upper level consumers (e.g. Cushing, 1989; Reinfelder et al., 1997; Saiz et al., 2007; Cossa et al., 2012).

Rare earth elements (REEs) have chemical properties that make them excellent natural indicators of particle-solution interactions and redox reactions on surfaces (Sholkovitz et al., 1994). Because of the systematic changes of chemical properties across the REE series species (La–Lu), increasing carbonate complexation (e.g. the dominant dissolved species; Elderfield, 1988) has been observed from the light REEs (LREEs) to the heavy REEs (HREEs) (Byrne and Kim, 1990). Accordingly, LREEs are preferentially adsorbed onto surfaces, whereas HREEs preferentially remain in solution (Sholkovitz, 1992). The distribution and fractionation of REEs in marine waters and sinking particulate matter have provided insights into the biogeochemical behavior and particle-scavenging processes of REEs (Elderfield and Greaves, 1982; Murphy and Dymond, 1984; Fowler et al., 1992; Sholkovitz et al., 1994).

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The Mediterranean Sea is characterized by trace element concentrations, including REEs, which are higher than those in similar nutrient-depleted surface waters (Boyle et al., 1985; Greaves et al., 1991). An investigation of vertical REE fluxes in the northwestern Mediterranean Sea showed that little, if any, REE scavenging occurs in the water column during a sedimentation pulse (Fowler et al., 1992). However, they also found that deep water particles just after this pulse were enriched in LREEs relative to HREEs and have a positive Ce-anomaly, indicating that time is a key factor in determining REE scavenging by sinking particles. In the open ocean, the vertical profiles of dissolved REEs are mainly governed by biological cycles (Alibo and Nozaki, 1999; Hara et al., 2009). During phytoplankton growth, dissolved REE profiles have shown decreasing concentrations in surface water, with LREEs preferentially adsorbed rather than HREEs (Hara et al., 2009). A large number of studies on dissolved or particulate REE distribution were carried out in the Mediterranean Sea (e.g. Fowler et al., 1992; Bau et al., 1997; Elbaz-Poulichet et al., 2002; Censi et al., 2004, 2007a,b, 2009, 2010a,b; Martinez-Boti et al., 2009), but none of them is interested in the relation between plankton and REE distributions.

Thus, the role of phytoplankton and zooplankton on REE distributions was investigated under the general framework of the COSTAS program (Contaminants in the trophic system: phytoplankton, zooplankton, anchovy, sardine). This multidisciplinary program aimed at studying contaminants transfer along the food webs of the two dominant planktivorous teleosts, the sardine, *Sardina pilchardus*, and the European anchovy, *Engraulis encrasicolus*, two species which rely entirely on planktonic food resources (Costalago et al., 2012). Despite REE are not considered as contaminants and were not included in the original program, we had the opportunity to measure REE concentrations in remaining plankton samples and to conduct the first investigation of its role on REE distribution in the water column.

So, in the present study, we presented for the first time data of REE concentrations measured in different size classes of phytoplankton and zooplankton at different seasons (May 2010 and February 2011) and in different environments of the Gulf of Lion. In this context, the aims of this study were to (i) determine REE concentrations in phytoplankton and zooplankton from surface waters of the Gulf of Lion, Northwestern Mediterranean Sea; (ii) characterize any fractionation patterns within the plankton; and (iii) investigate the interactions of the REE distributions in the plankton with data of REE distributions in the seawater and particles from previous references in the Mediterranean Sea.

2. Study area and methods

2.1. The Mediterranean Sea

The Mediterranean Sea is considered an oligotrophic sea, with low nutrient concentrations and relatively moderate levels of primary production (Estrada, 1996). The Gulf of Lion (GoL), Northwestern Mediterranean Sea, exhibits complex hydrological dynamics. The circulation is driven by the cyclonic Northern Current, which flows westward along the continental slope, and by a combination of wind-driven processes (coastal upwelling and dense shelf water formation) and freshwater dynamics associated with the large discharge from the Rhone River (Ulises et al., 2003), which is the most important river in the Mediterranean (with a mean annual discharge of approximately $1700 \text{ m}^3 \text{ s}^{-1}$). Composition, biomass and seasonal variations of zooplankton have been well studied in the Northwestern Mediterranean Sea (Razouls and Kouwenberg, 1993; Champalbert, 1996; Calbet et al., 2001; Gaudy et al., 2003; Saiz et al., 2007; Fanelli et al., 2011). Its diversity is generally lower in coastal waters than in offshore waters, whereas the

biomass is higher near the coast due to terrestrial inputs of nutrients by rivers (Champalbert, 1996; Gaudy et al., 2003).

2.2. Sampling and handling

Two cruises were conducted in the GoL in May 2010 and February 2011 by the RV 'L'Europe' within the framework of the ANR-COSTAS program. On each cruise, three sites were sampled from east to west: the site "SOMLIT", in the eastern part and near the coast, the site 'RHONE', located in the axis of the mouth of the Rhône and the site PLN (Port La Nouvelle) in the western part of the Gulf of Lion (Fig. 1). At each sampling site, a chlorophyll-a (chl-a) profile was sampled using a CTD probe to determine the depth of the maximum chl-a and the sampling depths. Plankton was then sampled using a pumping system or a trawling system depending on the particle size. In the first method, which was used to obtain plankton within the size range of (60–200 μm), seawater was pumped through a tube with a diameter of 8 cm, and plankton were retrieved onboard using two nets of 200- and 60- μm mesh. In the second method, plankton were collected with the trawling system (200- μm mesh for 30 min) and sieved onboard in a clean laboratory through three different meshes (500 μm , 1000 μm and 2000 μm) to obtain the plankton size fractions of (200–500 μm), (500–1000 μm), (1000–2000 μm) and (>2000 μm). During sieving, each plankton size class was carefully rinsed for a couple of hours with filtered seawater from the sampling site, to remove any terrigenous or inorganic particles and to keep biogenic materials only. Then, each plankton size class was collected in acid pre-cleaned PE tubes and was frozen at -18°C . An aliquot was kept in a 20 ml recipient at 4°C for plankton determination analysis. Back in the laboratory, the samples were freeze-drying and kept at room temperature.

2.3. Analyses

Representative sub-samples of plankton (100–150 mg of dried and homogenized material) were digested into acid pre-cleaned Teflon tubes using 8 ml HNO_3 (14 M, ultra-pure grade, Eco-Research, Korea) heated at 100°C for 4 h. All of the Teflon tubes and bombs had been pre-cleaned using 5% HNO_3 in a hot acid bath and then rinsed with Milli-Q water. After cooling, the digested solution was diluted with Milli-Q water, and the REEs were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (Model X-II, Thermo Scientific Inc., UK). As Certified Reference Materials are not provided for REE analyses in plankton, we could not test the recovery of the digestion method. However, we tested the reproducibility of nitric acid digestion on sample replicate of different plankton size classes, and obtain reproducibility better than 5%. The instrumental detection limits of our REE analyses ($n = 10$) were: 0.55 (La), 0.08 (Ce), 0.14 (Pr), 0.18 (Nd), 0.23 (Sm), 0.07 (Eu), 0.42 (Gd), 0.03 (Tb), 0.15 (Dy), 0.07 (Ho), 0.12 (Er), 0.05 (Tm), 0.10 (Yb), and 0.02 (Lu) ppt (which are 3-times the standard deviation of the Rh values in de-ionized water). The BaO/Eu and CeO/Ce ratios were found to be less than 2% and 1%, respectively, and the analytical precisions of the REEs were lower than 2%, 3%, and 5% of the relative standard deviations (RSD) for L-, M-, and HREEs, respectively. The blank values ($n = 11$, including reagent values) were less than 0.62 (La), 1.92 (Ce), 0.19 (Nd), 0.07 (Sm), 0.11 (Tb), and 0.09 (Lu) ppt and were non-detected for other elements.

3. Results

3.1. REE concentrations

The detailed measured REE concentrations in each plankton size classes from each sampling site and season are summarized in Table 1. From these data, we determined mean/SD ratios for each

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