



Spatial variability of phosphate and nitrate in the Mediterranean Sea: A modeling approach



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ABSTRACT

We present an analysis of the spatial distributions and seasonal dynamics of phosphate and nitrate in the Mediterranean Sea. The analysis involves observations under present conditions and relies on statistical analysis of the output of a state-of-the-art corroborated numerical model. Model results are corroborated with available data from cruises and fixed monitoring stations. The results capture and quantitatively detail the main spatial patterns observed in the Mediterranean Sea, with an east–west gradient in the surface layer for phosphate and a north–south gradient for nitrate. The model results highlight that plankton growth in Mediterranean waters is usually nutrient limited and that such limitation is less frequent in the western sub-basin and is usually due to a lack of phosphate, rather than nitrate, with the exception of the areas close to the Atlantic Ocean, where nitrogen limitation is important. The model simulation illustrates the benefit of a variable stoichiometric formulation of the phytoplankton cell, showing how the ratio of the internal N:P quota adapts to different limiting conditions.

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1. Introduction

In this article we analyze the spatial distributions of nitrate and phosphate in the Mediterranean Sea. The nutrient ratio and the supply rates of these compounds are an important constraint on the dynamics of the Mediterranean Sea lower trophic levels. Several studies have already addressed this topic using spatial-temporal extrapolation of experimental observations (Zavatarelli et al., 1998; Manca et al., 2004; Socal et al., 2008). However, existing datasets offer only limited space-time coverage of the Mediterranean basin (along cruise tracks or fixed stations). As such, important simplifying assumptions have to be made to inter-extrapolate available observations over non-sampled (or poorly sampled) areas. Often, interpolations are implicitly made while interpreting the data based on expert judgment. In some cases statistical methodologies are used, even if the underpinning assumptions (the form of the distribution frequency, stationarity) are hardly verifiable. The knowledge of the physical problem (i.e., general circulation) is seldom considered.

Here, we follow the approach of using available data to corroborate a numerical model and then use the corroborated model to interpolate and extrapolate observations in space and time. By embedding available theoretical information of the physical processes and being able to reproduce the physical environment,

models can be valuable tools for space and time interpolation of experimental findings, as is commonly performed in all physical sciences.

In this study we use OGSTM-BFM, a 3D coupled transport biogeochemical model (Lazzari et al., 2012); there referred as OPATM-BFM) which has already been successfully used to describe the space variability and seasonality of chlorophyll concentrations and primary production in the Mediterranean Sea. Here, we also corroborate our model results against nutrient concentration observational data and then analyze the model outputs. In Section 2, the OGSTM-BFM 3D model is presented together with details of its implementation. In the same section, details about the datasets used for model corroboration are provided. Climatological descriptions of biogeochemical properties resulting from model simulations and their validation with in situ data are presented and discussed in Section 3. In Section 3, climatological maps of nutrient distributions are derived, and N:P ratio and primary producer limiting conditions are also discussed.

1.1. The Mediterranean Sea

The Mediterranean Sea is a semi-enclosed basin surrounded by land and connected to the Atlantic Ocean through the Strait of Gibraltar; other adjacent seas are the Black Sea and Red Sea. Thermohaline circulation is driven by excess evaporation with respect to precipitation and river inputs, making the Mediterranean Sea a concentration basin with an anti-estuarine circulation. Three thermohaline cells can be described as follows: one

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principal open cell at the basin scale and two secondary closed cells at a smaller scale (Lascaratos et al., 1999).

The principal cell involves only the surface and intermediate layers. Atlantic Water (AW), which is characterized by low-salinity and relatively low nutrient content with respect to deeper layers, enters at the surface through the Strait of Gibraltar. During the AW eastward path, its physical properties rapidly change as the high evaporation rate elicits an increase of salinity, giving rise to Modified Atlantic Water (MAW). In the Levantine basin, continental dry winds and a further increase in evaporation rates make the MAW even saltier and denser, such that it sinks down through subduction to the intermediate layer (200–600 m), forming Levantine Intermediate Water (LIW). The LIW outflows at the Strait of Gibraltar after having crossed westward through the entire Mediterranean Sea (Ovchinnikov, 1984).

Contrary to what happens with salinity, nutrient concentrations decrease along the anti-estuarine circulation, starting at the Strait of Gibraltar, where nutrient-poor subtropical AW enters the basin toward the east. The atmospheric and terrestrial inputs (ATIs) of phosphate and nitrate are not able to significantly fertilize MAW, which along LIW, has a short residence time in the basin (Van Cappellen et al., 2014) preventing nutrient accumulation; therefore, the Mediterranean Sea surface layer remains oligotrophic. A numerical analysis (Crispi et al., 2001) demonstrated that the basin nutrient concentrations reach equilibrium with a clear east–west nutrient gradient. This equilibrium is regulated by water mass circulation patterns and ATIs and is characterized by a pronounced oligotrophy, with a clear decreasing gradient in nutrient concentrations from the western to the eastern Mediterranean Sea, the latter of which is characterized by ultra-oligotrophic properties. The Mediterranean Sea is known to be characterized by a peculiarly high N:P ratio with respect to the global ocean both in the deep waters (Krom et al., 1991; d'Alcalà et al., 2003) and for dissolved and particulate matter in the eastern Mediterranean Sea (Krom et al., 2005). This is not surprising because in areas where the imprint of land is pronounced, anomalous N:P ratios can be expected, as has been stated by Redfield (1934). In particular, peculiar explanations for such deviations according to regional conditions must be addressed (Krom et al., 2004, 2010). Moreover, perturbations due to anthropogenic effects over the past 80 years could have altered the situation with respect to the measurements collected by Redfield, especially in an area influenced by ATIs like the Mediterranean Sea.

2. Methodology

2.1. The physical and biogeochemical models

The numerical tool adopted in this study, the OGSTM–BFM, is based on the system described in Lazzari et al. (2010, 2012). The physical dynamics that drive the biogeochemical processes are pre-computed by an ocean general circulation model (OGCM MED16; Béranger et al., 2005). Therefore, physical–biogeochemical coupling is based on an offline approach. The circulation model supplies temporal evolution fields of horizontal and vertical current velocities, vertical eddy diffusivity, potential temperature, and salinity, in addition to surface data for solar shortwave irradiance and wind stress. The physical fields are then interpolated at 1/8 degree horizontal resolution, which is the resolution of the biogeochemical model outputs produced and analyzed in the present work.

The MED16 model was run using the reanalyzed fields from ERA40 (Uppala et al., 2005) from January 1989 to February 1998 and using the ECMWF analyses from March 1998 to 2006. The biogeochemical model here adopted is the Biogeochemical Flux

Model (BFM; Vichi et al., 2013), which is customized for the Mediterranean Sea. This model has been already applied to explore the dynamics of chlorophyll and primary production (Lazzari et al., 2012), alkalinity spatial and temporal variability (Cossarini et al., 2015), and CO₂ fluxes (Canu et al., 2015) in the whole Mediterranean basin, as well as to explore biogeochemical dynamics in selected sub-regions (Lamon et al., 2014). OGSTM–BFM is also the core of the biogeochemical component of the Mediterranean Monitoring and Forecasting (MED–MFC) system in the Copernicus Marine Environmental Monitoring Service (CMEMS, <http://marine.copernicus.eu>).

The BFM describes biogeochemical fluxes transforming dissolved and particulate organic and inorganic components by processes influenced by temperature, salinity, photosynthetically available radiance and interactions with other biogeochemical properties. The design of this model allows energy and material fluxes to be described through both 'classical food chain' and 'microbial food web' pathways (Thingstad and Rassoulzadegan, 1995). The model can also take into account co-occurring effects of multi-nutrient interactions (Baretta-Bekker et al., 1997). This possibility can be very useful to understand and estimate, for each area and period of the year, what is the most limiting nutrient, according to the resource availability in the Mediterranean Sea.

The model presently includes nine plankton functional types (PFTs). Autotrophic PFTs are diatoms, flagellates, picophytoplankton and dinoflagellates. Heterotrophic PFTs consist of carnivorous and omnivorous mesozooplankton, bacteria, heterotrophic nanoflagellates and microzooplankton. Each of these variables is described in terms of its carbon, phosphorus, nitrogen, and silicon compositions.

Details on the full BFM formulations and their Mediterranean implementation are provided in Vichi et al. (2013) and in Lazzari et al. (2012). Here, we summarize the main assumptions related to nutrient uptake using phosphorus as an example. Similar (but slightly more complex) kinetics describe the nitrogen dynamics.

Carbon assimilation and nutrient uptake are decoupled (Baretta-Bekker et al., 1997). Photosynthesis (primary production) and the uptake of dissolved inorganic carbon depend on light, temperature and carbon to chlorophyll content. As described in Lazzari et al. (2012), the model reproduces the spatial variability and seasonality of this process well.

The uptake of nutrients is then computed as the amount of nutrient required to sustain a 'balanced' growth. Balanced growth means maintaining a 'healthy' stoichiometric composition, which is herein expressed as the nutrient-to-carbon internal ratio of the plankton cell close to the maximum nutrient-to-carbon quota (q_p^{\max}). If the concentration of dissolved inorganic nutrient is not sufficiently high to meet this requirement, nutrient uptake is reduced proportionally to the actual nutrient concentration, and part of the assimilated carbon is released as dissolved organic carbon.

The uptake is based on a two-step procedure. The potential phosphorus uptake is the minimum between two rates:

$$up_p = \min(up_p^{\text{req}}, up_p^{\text{avail}}), \quad (1)$$

where

$$\begin{aligned} \text{nutrient_requirement} &= up_p^{\text{req}} \\ &= npp \, q_p^{\max} + \max(0, (q_p^{\max} - q) r C), \end{aligned} \quad (2)$$

and

$$\text{nutrient_availability} = up_p^{\text{avail}} = \alpha \, PO_4 C, \quad (3)$$

where npp is net primary production, q_p^{\max} is the maximum P:C quota in the phytoplankton cell (in our case twice the Redfield

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