



A biogeochemical model for phosphorus and nitrogen cycling in the Eastern Mediterranean Sea

Part 1. Model development, initialization and sensitivity



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ABSTRACT

The Eastern Mediterranean Sea (EMS) is the largest marine basin whose annual primary productivity is limited by phosphorus (P) rather than nitrogen (N). The basin is nearly entirely land-locked and receives substantial external nutrient fluxes, comparable for instance to those of the Baltic Sea. The biological productivity of the EMS, however, is among the lowest observed in the oceans. The water column exhibits very low P and N concentrations with N:P ratios in excess of the Redfield value. These unique biogeochemical features are analyzed using a mass balance model of the coupled P and N cycles in the EMS. The present paper describes the conceptual basis, quantitative implementation and sensitivity of the model. The model is initialized for the year 1950, that is, prior to the large increase in anthropogenic nutrient loading experienced by the EMS during the second half of the 20th century. In the companion paper, the model is used to simulate the P and N cycles during the period 1950–2000. The 1950 model set-up and sensitivity analyses support the following conclusions.

- (1) Phosphorus-limited primary production in the EMS is most sensitive to the P exchanges with the Western Mediterranean Sea (WMS) associated with the anti-estuarine circulation of the EMS. The supply of P through the Straits of Sicily is mainly under the form of dissolved organic P (DOP), while dissolved inorganic P (PO_4) is primarily exported to the WMS. The efficient export of PO_4 to the WMS maintains the EMS in its ultra-oligotrophic state.
- (2) Inorganic molar N:P ratios in excess of the 16:1 Redfield value observed in the water column reflect higher-than-Redfield N:P ratios of the external inputs, combined with negligible denitrification. Model simulations imply that the denitrification flux would have to increase by at least a factor of 14, relative to the 1950 flux, in order for the inorganic N:P ratio of the deep waters to approach the Redfield value.
- (3) The higher-than-Redfield N:P ratios of dissolved and particulate organic matter in the EMS further imply the preferential regeneration of P relative to N during organic matter decomposition.

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1. Introduction

The Eastern Mediterranean Sea (EMS) is a unique part of the global ocean. Although nearly completely surrounded by land, with associated

Abbreviations: EMS, Eastern Mediterranean Sea; WMS, Western Mediterranean Sea; SW, surface water; LIW, Levantine Intermediate Water; EMDW, Eastern Mediterranean Deep Water; EMT, Eastern Mediterranean Transient; MAW, Modified Atlantic Water; ADW, Adriatic Deep Water; PO_4 , dissolved inorganic phosphorus; DOP, dissolved organic phosphorus; POP, particulate organic phosphorus; NO_3 , dissolved nitrate plus nitrite; NH_4 , dissolved ammonium; DON, dissolved organic nitrogen; PON, particulate organic nitrogen.

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significant nutrient inputs (Krom et al., 2004; Ludwig et al., 2009), the EMS is an ultra-oligotrophic marine basin. Annual primary productivity in the EMS ($\sim 60\text{--}80 \text{ g C m}^{-2} \text{ yr}^{-1}$, Berman-Frank and Rahav, 2012; Béthoux, 1989) is even lower than that measured in the low productivity areas of the northwestern Sargasso Sea (Lohrenz et al., 1992). The recent geological past of the EMS, however, was punctuated by episodic accumulations of organic-rich sediments (sapropels), which indicate the potential for rapid and dramatic biogeochemical shifts, including the development of eutrophic conditions, changes in phytoplankton community structure and deep-water anoxia (Cita et al., 1977; De Lange et al., 2008; Sachs and Repeta, 1999). The anti-estuarine thermohaline circulation of the EMS (Astraldi et al., 1999) is generally

considered to be an important factor maintaining the EMS in its current ultra-oligotrophic state (Krom et al., 2003).

The winter phytoplankton bloom represents the major annual period of carbon fixation in the present-day EMS (Krom et al., 2003). Primary production during the winter bloom is phosphorus (P) rather than nitrogen (N) limited, in contrast to most of the rest of the oceans where N limitation is more commonly observed. In addition, the deep waters of the EMS exhibit anomalously high nitrate to phosphate molar ratios (~28:1; Kress and Herut, 2001; Krom et al., 1991), considerably higher than the Redfield value (16:1, Redfield et al., 1963). Recent work has shown that the very low biological productivity of the EMS, P limitation and the unusual water column nutrient ratios are linked to one another (Krom et al., 2010).

More than 450 million people live in the drainage basin of the Mediterranean, of whom about one-third inhabit coastal regions (FAO, 2003; UNEP/MAP, 2012). Rapid demographic growth and economic development since the 1950s has caused a major increase in nutrient supply to the EMS (Ludwig et al., 2009; Powley et al., 2014). Although significant impacts are observed locally in near-shore coastal areas (e.g., Dell'Anno et al., 2002; Pusceddu et al., 2007), there is little evidence supporting a major evolution in the trophic state of the open waters of the EMS. However, the extent to which the EMS will be able to cope with future anthropogenic nutrient inputs is unknown. Population in the Mediterranean basin is projected to grow an additional 20% during the first quarter of the 21st century (FAO, 2003), while climate change may profoundly modify the thermohaline circulation of the EMS by the end of the century (Somot et al., 2006). A better understanding of basin-scale nutrient cycling will therefore not only help to interpret the present and past biogeochemical conditions in the EMS, but also to evaluate the response of the EMS to ongoing and future anthropogenic pressures (de Madron et al., 2011).

Existing biogeochemical models for the Mediterranean Sea range from 1D biogeochemical (e.g. Béthoux et al., 1992; Sarmiento et al., 1988) and foodweb models (e.g., Allen et al., 2002) to fully coupled 3D physical–biogeochemical models (e.g. Lazzari et al., 2012). Most model applications so far have dealt with ecosystem processes, particularly in the euphotic zone, and their seasonal to interannual variability. In contrast, our work focuses on basin-wide nutrient cycling in the EMS, and its modification by the large changes in anthropogenic nutrient loading in the recent past (i.e., post-1950). To this end, a mass balance nutrient model has been developed, based on our current conceptual understanding of the key processes controlling the biogeochemical cycling of P and N in the EMS (Krom et al., 2010).

The coupled P and N model uses a simple 3-layer representation of the water column (surface, intermediate and deep waters) and accounts for the exchanges between these three water masses, as well as for the external inputs to and outputs from the basin. The model computes annually averaged reservoir sizes and fluxes, and is initialized for the nominal year 1950, assuming relatively limited anthropogenic impact on the biogeochemical functioning of the EMS prior to the second half of the 20th century (Béthoux et al., 1998). The present paper (Part 1) focuses on the development of the model and the reconstruction of P and N dynamics under 1950 conditions. In the companion paper (Part 2) of the study, the model is used to describe biogeochemical changes in the EMS in response to the historical changes in P and N inputs over the period 1950–2000 (Powley et al., 2014).

2. Eastern Mediterranean Sea (EMS): physical description

2.1. Model domain

The Mediterranean Sea consists of two main basins with distinct hydrodynamic and ecological characteristics: the Western Mediterranean Sea (WMS) and the Eastern Mediterranean Sea (EMS). The EMS is connected to the WMS through the Straits of Sicily. In order to account explicitly for the role of deep-water formation in the cycling of P and N in the

EMS, the Adriatic and Aegean seas are excluded from the EMS. The resulting EMS model domain covers a surface area of $1.33 \times 10^{12} \text{ m}^2$ and is divided in three horizontal layers (Fig. 1): surface water (SW: 0–200 m), Levantine Intermediate Water (LIW: 200–500 m) and Eastern Mediterranean Deep Water (EMDW: >500 m). The corresponding volumes are $2.8 \times 10^{14} \text{ m}^3$ (SW), $4 \times 10^{14} \text{ m}^3$ (LIW) and $17 \times 10^{14} \text{ m}^3$ (EMDW). The depth ranges assigned to the three water masses are average values for the entire EMS basin. In detail, there is considerable temporal and spatial variability in the vertical extent of the water masses caused by mesoscale circulation features.

2.2. Circulation

The water cycle imposed in the model calculations is summarized in Fig. 1. Water flow rates are given in Sverdrup units ($1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$). The imposed flow rates are based on estimates for the time period prior to the early 1990s, when circulation in the EMS underwent a major disturbance due to a large increase in deep-water formation in the Aegean Sea (Roether et al., 2007). This event is known as the Eastern Mediterranean Transient (EMT), whose effect on nutrient cycling is assessed in the companion paper (Powley et al., 2014).

Relatively low salinity Modified Atlantic Water (MAW) enters the EMS from the WMS via the Straits of Sicily (Krom et al., 2003; Robinson et al., 2001). This SW becomes progressively more saline as it flows across the EMS from west to east due to intense evaporation and limited precipitation. Ultimately, the SW sinks close to the Turkish coast and forms LIW (Lascaratos, 1993). LIW then returns westwards while accumulating nutrients and eventually flows out via the Straits of Sicily below the MAW. Part of the LIW is diverted into the Aegean and Adriatic seas where it becomes incorporated into the deep waters forming in these basins.

Estimates of LIW outflow through the Straits of Sicily are between 0.6 and 1.5 Sv (Roether and Schlitzer, 1991), with some higher reported values (up to 3.2 Sv, Manzella et al., 1988). We assign a value of 1.10 Sv based on the work of Astraldi et al. (1999). The inflow of MAW into the EMS is on the same order of magnitude as the outflow of LIW. Based on conservation of heat and salt, MAW inflow is estimated to be 4% higher than the outflow of LIW (Astraldi et al., 1999; Manzella et al., 1988). Hence, MAW inflow is set at 1.14 Sv. The flow rates of LIW into the Adriatic Sea and the outflow of Adriatic Deep Water (ADW) to the EMS through the Strait of Otranto are not statistically different (Astraldi et al., 1999) and are therefore assigned the same value of 0.36 Sv (see below).

Residence times of EMDW based on CFC and tritium distributions as well as oxygen consumption rates fall in the range of 100–150 yr (average: 126 yr; Roether and Schlitzer, 1991; Roether and Well, 2001). However, these estimates only consider the deeper part of the EMDW reservoir (>1200 m, volume $8.6 \times 10^{14} \text{ m}^3$). To account for the larger EMDW reservoir considered in the present model (volume $17 \times 10^{14} \text{ m}^3$), we use the highest residence time estimate ($150 \text{ yr} = 4.7 \times 10^9 \text{ s}$). Under steady state conditions, mass balance then implies a total rate of deep-water formation of 0.36 Sv ($= 17 \times 10^{14} / 4.7 \times 10^9 = 0.36 \times 10^6 \text{ m}^3 \text{ s}^{-1}$). This is in good agreement with estimates in the order of 0.3 Sv for the formation rate of ADW (Lascaratos et al., 1999), which is generally acknowledged to be the dominant pre-1987 source of EMDW, with only a minor contribution of Aegean Deep Water formation (Roether and Schlitzer, 1991). In the model, we assign 10% of EMDW formation to Aegean-derived Cretan Deep Water, based on the observations for the central EMS reported by Zervakis et al. (2004). Thus the inflows into the EMDW from the Adriatic and Aegean seas are 0.32 and 0.04 Sv, respectively.

A small surplus of Adriatic water is exported as surface flow to the EMS. The assigned flow rate is on the same order of magnitude as the average yearly flow of the Po river ($1500 \text{ m}^3 \text{ s}^{-1}$, Vilibić and Supić, 2005). The general circulation within the Aegean Sea is cyclonic with Levantine Water (probably a mix of surface and intermediate water)

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