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Abstract

The Mediterranean Sea (MS) is a semi-enclosed sea characterized by a zonal west-east gradient of oligotrophy, where microbial growth is controlled by phosphate availability in most situations. External inputs of nutrients including Gibraltar inputs, river inputs and atmospheric deposition are therefore of major importance for the biogeochemistry of the MS. This has long been considered to be driven mainly by nutrient exchanges at Gibraltar. However, recent studies indicate that river inputs significantly affect nutrients concentrations in the Mediterranean Sea, although their resulting impact on its biogeochemistry remains poorly understood.

In this study, our aim was to make good this lack by addressing the large-scale and long-term impact of variations in river inputs on the biogeochemistry of the Mediterranean Sea over the last decades, using a coupled physical-biogeochemical 3D model (NEMO-MED12/Eco3M-Med).

As a first result, it has been shown by the model that the strong diminu-

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tion (60 %) of phosphate (PO₄) in river inputs into the Mediterranean Sea since the end of the 1980s induced a significant lowering of PO₄ availability in the sub-surface layer of the Eastern Mediterranean Basin (EMB). One of the main consequences of PO₄ diminution is the rise, never previously documented, of dissolved organic carbon (DOC) concentrations in the surface layer (by 20% on average over the EMB). Another main result concerns the gradual deepening of the top of the phosphacline during the period studied, thus generating a shift between the top of the nitracline and the top of the phosphacline in the EMB. This shift has already been observed *in situ* and documented in literature, but we propose here a new explanation for its occurrence in the EMB. The last main result is the evidence of the decline in abundance and the reduction of size of copepods calculated by the model over the years 1985-2010, that could partially explain the reduction in size of anchovy and sardine recently recorded in the MS.

In this study, it is shown for the first time that the variations in river inputs that occurred in the last decades may have significantly altered the biogeochemical cycles of two key elements (P and C), in particular in the EMB. To conclude, the magnitude of the biogeochemical changes induced by river inputs and runoff alone over the last thirty years clearly calls for the use of realistic scenarios of river inputs along with climate scenarios for coupled physical-biogeochemical forecasts in the MS.

Keywords: Mediterranean Sea, River inputs, Coupled physical-biogeochemical model, Flexible stoichiometry model, Biogeochemistry, Nutrient

1 1. Introduction

The Mediterranean Sea (MS) is a Low-Phosphate Low-Chlorophyll oligotrophic area characterized by a zonal west-east oligotrophic gradient [1]. The two basins, the Western Mediterranean Basin (WMB) and the Eastern Mediterranean Basin (EMB) are characterized by different biogeochemical properties: deep water phosphate (P) and nitrate (N) concentrations as well as primary production are higher in the WMB than in the EMB [2, 3, 4, 5]. Many studies have addressed the issue of nutrient limitation in the MS, and most of them have pointed out the major role of P availability in the control of phytoplankton growth [6, 7, 4, 8, 5] and bacterial production [9, 10], although N [4, 10, 11] and silicate availability [12] could also be limiting factors ¹² in some areas.

At global scale, it is considered that nutrient availability (and especially that 13 of PO_4) in the surface layer of the ocean is mainly controlled by the exchanges 14 between the deep and the upper layers, with a limited influence of river in-15 puts [13, 14]. Nevertheless, as an inland sea, the MS is strongly connected 16 with the Mediterranean continental region. Four main sources of external 17 inputs of nutrients to the upper layer of the MS can be distinguished : the 18 Gibraltar strait connecting the MS to the Atlantic Ocean, the Dardanelle 19 strait connecting the MS to the Black Sea (BS), rivers and runoff and atmo-20 sphere (dry and wet deposition). In the WMB, the major external sources 21 of nutrients for the upper layer originate from the Gibraltar strait and from 22 the Rhône and Ebro Rivers. For the EMB, the major sources of nutrients 23 are the Po and Nile Rivers and the Dardanelle strait [15]. 24

25

Nutrient inputs in the MS have been estimated using in situ data and 26 numerical models (see Béthoux et al. [16], Huertas et al. [17] for the Gibral-27 tar strait and Ludwig et al. [15] for rivers and the and Kopasakis et al. [18] 28 for Dardanelle strait (Black Sea)). N and P input from the rivers and the 29 Dardanelle strait have undergone significant changes since the early 1960s 30 [15, 19]: due to human activity, they increased by a factor 5 between the 31 1960s and the 1980s. After this period of strong increase, N input remained 32 high until 2000, while P rapidly dropped to reach its 1960s value. 33

Nutrient inputs from Gibraltar have long been considered as the major source
of nutrients for the upper layer of the MS compared to river inputs [20, 21, 22],
but recent studies have shown that N and P concentrations in the MS are
also sensitive to river [23] and atmospheric [24, 25] inputs.

38

Coupled physical/biogeochemical modeling is particularly suitable for as-39 sessing the relative influence of the different nutrient inputs on the biogeo-40 chemical cycles of biogenic elements, and on the structure of the planktonic 41 food web in the MS. Several modeling studies at basin or sub-basin scale have 42 already investigated the biogeochemistry of the MS during the last decades 43 [26, 27, 28], but without specific focus on the relative impact of nutrient 44 sources. One exception is [22], who have shown that the atmospheric inputs 45 could be a major source of nutrient in some areas of the MS. However, at-46 mospheric nutrient inputs remain difficult to quantify and their estimation 47 suffers from considerable uncertainty, particularly regarding the bioavailable 48 fraction of these inputs [22, and references herein]. 49

To the best of our knowledge, only two modeling studies have so far high-50 lighted the large-scale influence of river inputs in the MS. [29] show that 51 primary production over the last decades could be impacted by river inputs, 52 but they mostly focus on the link between biogeochemistry and fisheries data. 53 [30] show that in the EMB primary production is sensitive to river inputs. 54 with an increase of 16 % from 1950 to 2000. They also show that the EMB 55 became more P-limited with the reduction of phosphate in anthropogenic 56 nutrient inputs. 57

58

In this study, our aim was to address the large-scale and long-term influ-59 ence of river inputs on the biogeochemistry of the MS over the last decades 60 using an improved version of the coupled physical-biogeochemical 3D model 61 NEMO-MED12/Eco3M-MED [31, 32, 33, 26]. In order to highlight the effect 62 of river inputs alone, two near-identical simulations were run over 25 years 63 (1985-2010 period), the only difference being that one uses the estimated, 64 interannual river inputs provided by Ludwig et al. [15], while in the second, 65 river inputs are fixed to their 1985s level, i.e. before the decline in phosphate 66 discharge. 67

68

⁶⁹ 2. Material and methods

70 2.1. The biogeochemical model: Eco3M-MED

The biogeochemical model used in this study is embedded in the Eco3M 71 biogeochemical modeling platform, [34] which has been developed with the 72 priority given to (i) mechanistic (i.e. based on underlying processes) descrip-73 tions of biogeochemical fluxes [33, 35, 36, 26], and (ii) modularity, with the 74 aim of easy adaptation of the model to different scientific questions (sev-75 eral configurations already exist, some of them dedicated to studies on the 76 Mediterranean Sea [36, 26], others including diazotrophs [37] for studies in 77 the South Pacific, or *Mnemiopsis leidyi* [38] for a theoretical study on the 78 conditions favoring this comb jelly). 79

80

The Eco3M-Med configuration has been designed to represent the main characteristics of the Mediterranean Sea. It includes 42 state variables grouped in six different plankton functional types (PFTs), namely two phytoplankton compartments (Large and Small), three zooplankton compartments and a compartment of heterotrophic bacteria. The large phytoplankton (PHYL)(>

 $10\mu m$) represents the micro- and the largest nanophytoplankton and is as-86 sumed to be mainly composed of diatoms while the small phytoplankton 87 (PHYS) ($< 10\mu m$) includes picophytoplankton and the smallest nanophy-88 toplankton cells. The three PFT of zooplankton correspond to three size 89 classes, namely nano-, micro- and mesozooplankton, which are respectively 90 associated with heterotrophic nanoflagelate (HNF), ciliate (CIL), and cope-91 pods (COP). Each PFT, except that for copepods, is described by four state 92 variables, namely Carbon (C), Nitrogen (N) and Phosphorus (P) concentra-93 tions, and an abundance (in cell or individuals per liter). Phytoplankton is 94 described by an additional variable (Chlorophyll-a concentration (Chl)), and 95 mesozooplankton is only described through two variables: carbon concentra-96 tion and abundance. Three pools of inorganic matter are also represented, 97 namely nitrate (NO_3) , ammonium (NH_4) and, phosphate (PO_4) as well as a 98 pool of dissolved organic matter (DOM) and two compartments of detrital gc particulate matter, one including small particles (DETS) and the other large 100 particles (DETL). 101

The conceptual model (Fig. 1) is the same as that used in Guyennon et al. 102 [26], except that the compartment of detrital particulate matter has been 103 splitted into large and fast-sinking particles (DETL) and small particles 104 (DETS) with low sinking rate. DETL is fueled by the fecal pellets pro-105 duced by mesozooplankton, and by the mortality of mesozooplankton and 106 large phytoplankton. The hydrolysis of large detrital material, as well as the 107 mortality of CIL, fuel the DETS compartment and the mortality of HNF 108 fuels the DOM compartment. The sinking rates of DETL and DETS are 109 respectively 50 m.d⁻¹ and 2 m.d⁻¹. 110

111

Let X and Y be two biogenic elements among C, N, and P. As in previous versions of the Eco3M-Med model [36, 26], the intracellular ratios $(Q_{X/Y})$ in organisms, as well as their intracellular quotas Q_X (intracellular quantity of X per cell) are flexible and dynamically calculated by the model. These intracellular ratios and quotas are extensively used to regulate the different biogeochemical fluxes represented by the model, and the corresponding equations are given in the previously cited papers.

119

Only the new features of the model as compared to Guyennon et al. [26] and Gimenez et al. [39] are presented in the appendix.



Figure 1: Conceptual model Eco3M-Med.

123 2.2. The hydrodynamic model : NEMO-MED12

In this study, we use an off-line coupling between the hydrodynamic NEMO (Nucleus for European Modelling of the Ocean) model [31] and Eco3M-MED.

¹²⁷ The NEMO-MED12 configuration of NEMO which covers the entire Mediter-¹²⁸ ranean Sea [40] is used. It includes a buffer zone from the Gibraltar strait to ¹²⁹ 11 degrees east, where the open boundary conditions are gradually applied ¹³⁰ to avoid numerical instability. The horizontal resolution is 1/12 degree (6.5 ¹³¹ to 8 km cells), the vertical resolution has 75 z levels of 1 m width at the ¹³² surface to 135 m at the seabed.

133

The hindcast hydrodynamic simulation used in this work is referred to as the NM12-FREE (no reanalysis no data assimilation) which started in October 1979 and ended in June 2013 [32].

In this simulation, the initial conditions for the MS were based on monthly means for temperature and salinity from MEDAR/MEDATLAS [41] and from ORAS4 for the Atlantic part. The runoff and river inputs in the NM12 domain came from the interannual data of [15]. The Black Sea is not included in the NM12 configuration but a fresh water flux from the Dardanelles strait is taken into account [42]. Atmospheric forcing is based on the dynamical downscaling (ALDERA). It has a 12 km spatial resolution and a 3h temporal resolution. For detailed information, the NM12-FREE simulation is extensively described in [32].

¹⁴⁶ 2.3. Characteristics of the hindcast simulation

147 2.3.1. Biogeochemical forcing

148 River inputs

149

Monthly values of NO_3 and PO_4 inputs are provided for the 29 main 150 rivers all around the MS by the study of [15]. The contributions of the other 151 rivers were distributed in their respective sub-basins as runoffs. These nutri-152 ent inputs are available until year 2000. Between 2001 and 2010, nutrients 153 river inputs of the year 2000 are repeatedly used as already done in [26] and 154 [22]. For dissolved organic carbon (DOC) concentration, an annual mean 155 over every watershed calculated by [43] has been used. In the current config-156 uration, the river discharge is distributed over the six first vertical grid cells. 157 Figure 2 shows the phosphate (PO_4) and nitrate (NO_3) inputs to the MS 158 through river and runoff. It can be seen firstly that nutrient inputs are much 159 higher in the EMB than in the WMB. Moreover, since the end of the 1980s, 160 PO_4 input dropped down from more than 120 to less than 40 kt.a⁻¹ in the 161 EMB and from 60 to less than 20 kt.a⁻¹ in the WMB. The significant decrease 162 of PO_4 flux reflects the adoption of new legislation by the surrounding coun-163 tries, such as the prohibition of phosphorus detergents, and the improvement 164 of wastewater treatment plants, as well as other features detailed in Ludwig 165 et al. [15]. By contrast, NO₃ input remains relatively stable over the period. 166



Figure 2: Nutrients inputs from rivers and runoff in $kt.a^{-1}$ [15] used in the model for the eastern basin (dotted line) and for the western basin (plain line). A) PO₄ inputs; B); NO₃ inputs.

168 Boundary and initial conditions

¹⁶⁹ Nutrient input at Gibraltar is conditioned by the nutrient concentrations in

the buffer zone. Annual climatology data (monthly vertical profiles) are used in the buffer zone for each state variable of the biogeochemical model. For PO₄, NO₃, NH₄ and OXY, these annual climatology data are extracted from the World Ocean Atlas database. The other variables have been computed through a mean chlorophyll profile in order to reproduce seasonal variability. They are derived from the profiles using conversion factors derived from ¹⁷⁶ published works [36]. For the initial conditions, the same procedure has ¹⁷⁷ been applied. More details on this preliminary work can be found in [44] ¹⁷⁸ where it has already been extensively described.

179 2.3.2. Spin-up and Simulation plans

Using the initial conditions as described before, a first 20-years spinup was run, consisting in a 5-years simulation (1982-1987) repeatedly run, allowing most of the variables to reach an equilibrium state. Starting from this equilibrium state, the hindcast simulation was run.

In this study, two simulations were run. The first is the hindcast simulation, starting in 1985 and ending in 2010, described in the previous sections. This simulation will be referred to hereafter as the Riv-ref simulation. The second simulation is identical in all respects to the Riv-ref simulation, except that the monthly river inputs of the year 1985 are used throughout the simulation in order to deconvolute the impact of river inputs from other forcing. This simulation is referred to hereafter as the Riv-85.

¹⁹¹ 3. Results

¹⁹² 3.1. Model skill assessment

Figure 3 shows the modelled (mCHL) for the Riv-ref simulation and ob-193 served (oCHL), i.e. satellite-derived, mean surface chlorophyll a concentra-194 tion over the 1997-2010 period. High chlorophyll clusters can be observed for 195 both oCHL and mCHL in the vicinity of river mouths, but only for oCHL 196 near the Nile, along the western coast of the Adriatic Sea and in the Gulf of 197 Gabes. The well-known east-west gradient of CHL (see oCHL) is also clearly 198 visible in the mCHL pattern. Excluding the coastal areas (i.e. depth < 200190 m) which are more impacted by river inputs, the mean chlorophyll concen-200 trations, oCHL and mCHL, are equal to 0.047 and 0.04 $\mu q.l^{-1}$, and to 0.032 201 and 0.034 $\mu q.l^{-1}$, in the WMB and in the EMB, respectively. 202

Several similar structures can also be observed in both oCHL and mCHL in the WMB, such as i) a well-defined Liguro-Provencal current, ii) an intense Liguro-Provencal bloom, though slightly more expanded for mCHL than for oCHL, iii) a high-chlorophyll gyre to the south-east of Corsica. For the eastern basin, very low chlorophyll concentrations are observed and modelled, except in the Rhodes gyre where higher concentrations can be seen in both oCHL and mCHL patterns.



Figure 3: Average surface chlorophyll a concentration between 1997 and 2010, (top) calculated by the model and (bottom) observed by satellite.

Overall, the model shows a good ability to reproduce the main structures 212 of surface chlorophyll in the MS, and especially all the main productive areas 213 are detected by the satellite. However, in some areas, Chl structures are not 214 well represented by the model, such as i) the Rhodes gyre where mCHL is 215 too high $(+0.05 \ \mu q.l^{-1}$ than oCHL), which can be partially ascribed to the 216 too intense convection estimated by the hydrodynamic model in this area 217 [32], ii) the center part of the Adriatic Sea, which is more productive in the 218 model (+ 0.08 $\mu q.l^{-1}$ than oCHL), iii) the coastal Italian side of the Adriatic 219 Sea, which is less productive in the model than in data. This could be due 220 to insufficient PO_4 inputs from the Po river in the model leading to a too 221 strong PO4 limitation of phytoplankton growth, combined with chlorophyll 222 data which are less reliable in case II waters [45], iv) the gulf of Gabes which is 223 less productive in the model (- $0.5 \ \mu g.l^{-1}$ than oCHL), where high phosphate 224 supply from the land and the seabed are not taken into account in the model, 225 v) the Nile mouth which is less productive in the model (- 1.06 $\mu q.l^{-1}$ than 226 oCHL) where nutrient input is probably poorly represented because of the 227 lack of data [15]. 228

229

A quantitative comparison between *in situ* data and model outputs has 230 also been undertaken using a Taylor diagram [47] that shows the standard 231 deviation, the correlation between the data and the model and the root 232 mean square error (Fig. 4). Mean vertical profiles of four biogeochemical 233 variables, dissolved organic carbon (DOC), CHL, NO₃ and PO₄ measured 234 at the Dyfamed station [46] over the 1990-2002 period, are compared with 235 the model outputs averaged over the same period. For CHL, NO_3 and PO_4 , 236 correlations are higher than 0.95, with relative standard deviations ranging 237 between 0.78 and 1.2, and an error close to 0.2, showing that the model can 238 predict relatively well those variables at Dyfamed station. For DOC, the 239 comparison with data is less favorable. This could be partly ascribed to the 240 number of available DOC data, which is well below the number of data for 241 the other variables, and to the fact that the comparison is partly biased since 242 Dyfamed data concern the whole DOC pool while the modelled DOC only 243 includes the labile and semi-labile pool. The refractory part of the modelled 244 DOC is therefore arbitrarily set to a constant value for the comparison with 245 in situ data, thereby introducing a systematic error. These comparisons and 246 others not shown led us to conclude that the model was able to reproduce 247



Figure 4: Taylor diagram showing the standard deviation of the normalized model outputs, the correlation between *in situ* data and model outputs, and the root mean square error between in situ data and model outputs. Data consist in vertical profiles of NO_3 , PO_4 , DOC and CHL obtained at Dyfamed [46] station during the period 1990-2002. Model outputs are vertical profiles averaged over the same period. In red: dissolved organic carbon (DOC), in light: blue chlorophyll a; in green: PO₄ and in blue: NO_3 .

most of the major biogeochemical features of the MS and could be used to investigate the effects of the variations in nutrient concentration in the river inputs.

²⁵¹ 3.2. River input and the biogeochemistry of the MS

252 3.2.1. Nutriclines

According to the model, over time, the evolution of continental nutrient inputs has various effects on the biogeochemistry of the MS.

One of them concerns nutriclines, and more specifically the top of nutriclines. Let us first define how the top of the nitracline (Ncline) and phosphacline (Pcline) are determined. The top of the Ncline is located at the first depth, starting from the sea surface, at which NO₃ reaches 0.05 μ mol.l⁻¹. This threshold corresponds to the classical quantification limit of nitrate measurement using an autoanalyser [48].Such determination of the top Ncline has already been used by Pujo-Pay et al. [2] and Bahamón et al. [49].

The depth of the top of the Pcline is based on a threshold value of 3 262 $nmol.l^{-1}$. The latter value corresponds to the nitrate threshold (i.e. 0.05) 263 μ M) divided by 16, that is, by the Redfield proportion between N and P. 264 Figure 5 shows the patterns of change over time of the top of the Pcline 265 for the WMB (A) and the EMB (B) over the period 1985-2010. There is 266 no clear trend over this period in the WMB (Fig. 5 A). The top of the 267 Pclines seasonally reaches the surface in winter and deepens to around 60 m 268 in Summer (Fig. 5 A). In the EMB (Fig. 5 B), the top of the Pcline never 269 reaches the surface, not even during winter convection. Moreover, there is 270 a clear trend towards a deepening of the Pcline between the 1980s and the 271 year 2000s. This deepening can be better quantified in figure 5 D where 272 the difference between the depths of Pcline for the Riv-ref simulation (using 273 realistic changes in river input) and the Riv-85 simulation is reported for the 274 EMB. It can be seen there that the top of the Pcline can deepen as far as 275 40m. A similar result (not shown) is obtained for the 0-150 m integrated PO_4 276 concentration (referred to as I - PO_4 hereafter). In the WMB, this deepening 277 is far less marked, that is less than 10 m (Fig. 5 C). Concerning the top of 278 the nitracline (not shown), it exhibits the same seasonal variations as the 279 Pcline, but no clear trend could be evidenced, either in the WMB, or in the 280 EMB. 281



Figure 5: Patterns of change in the depth of the top of the phosphacline (see the definition in the text) for (A) the western basin and (B) the eastern basin and difference between the top of the phosphacline for the Riv-ref and the Riv-85 simulations for the (C) western basin and (D) the eastern basin over the period 1985-2010. Each line corresponds to a two-year average. The line colors progressively change from blue (1985) to red (2010) in order to highlight the temporal changes during that period. The grey area delimits the maximum standard deviation of the 1985-2010 averaged depth of Pcline (throughout period 1985-2010).

In the model, the biogeochemical processes controlling the depth of the Pcline are the different production and consumption fluxes: uptake of PHYS (Fig. 6 A); uptake of PHYL (Fig. 6 B); uptake of BAC (Fig. 6 C); excretion of CIL and HNF (Fig. 6 D) and mineralization by BAC (Fig. 6 C). The mean depth at which production and consumption fluxes of PO₄ are balanced is

also represented (Fig. 6 F). PO_4 uptake by PHYS in the upper surface (0-50 287 m) decreases from $0.6 \pm 0.1 \times 10^{-15}$ mol.l⁻¹.s⁻¹ in 1985 to $0.89 \pm 0.1 \times 10^{-16}$ 288 in 2010 (Fig. 6 A). The maximum uptake rate, corresponding to the maxi-289 mum abundance (not shown), is a little bit weaker and deeper in 2010. For 290 PHYL, the maximum uptake decreases from $3.3 \pm 0.1 \times 10^{-16}$ in the 1980s to 291 $5.14 \pm 0.1 \times 10^{-17}$ mol.l⁻¹.s⁻¹ in the years 2000s (Fig. 6 B). PO₄ uptake by 292 bacteria (Fig. 6 C) decreases only at the surface and becomes deeper over 293 the years. The maximum uptake deepens slightly between 1985 and 2010, 294 but its intensity remains stable around 4×10^{-14} mol.l⁻¹.s⁻¹. 295

The excretion by microzooplankton (CIL) and nanozooplankton (HNF) decreases progressively over the period (Fig. 6 D) and the maximum excretion deepens (though this is barely visible in this figure). The maximum remineralization by heterotrophic bacteria also deepens from less than 200 m in the 1980s to almost 300 m in the years 2000's and is also less intense (Fig. 6 E). The depth where a balance between production and consumption fluxes is reached also deepens from 200 m in 1985 to almost 300 m in 2010 (Fig. 6 F).



Figure 6: Patterns of change in the different production and consumption fluxes of PO_4 playing a role in the position of the phosphacline in the eastern basin; A) Uptake by small phytoplankton; B) Uptake by large phytoplankton; C) Uptake by bacteria; D) Excretion by micro and nanozooplankton; E) Remineralization by bacteria; F) Depth where a balance between production and consumption fluxes is reached. The line colors progressively change from blue (1985) to red (2010) in order to highlight the temporal changes during that period. Negative values refer to fluxes from water towards organisms and positive ones from organisms towards water.

304 3.2.2. Surface Dissolved Organic Carbon

Surface DOC concentration exhibits a clear seasonal pattern, not only for the WMB (Fig. 7 A) but also for the EMB (Fig. 7 B). To highlight a potential trend in surface DOC concentrations over the 1985-2010 period, the difference between DOC concentration for the Riv-ref and the Riv-85 simulations is plotted for the two basins. The trend is tenuous in the WMB (Fig. 7 C), while there is a regular and significant DOC concentration increase of nearly

$_{311}$ 20% in the EMB over the same period (Fig. 7 D).



Figure 7: Patterns of change in surface DOC concentration in μ mol.l⁻¹ for (A) the western basin and (B) the eastern basin and difference between the top of the phosphacline for the Riv-ref and the Riv-85 simulations for the (C) western basin and (D) the eastern basin over the 1985-2010 period, as calculated by the model. The line colors progressively change from blue (1985) to red (2010) in order to highlight the temporal changes during that period.

313 3.2.3. Time and spatial distribution of certain biogeochemical variables at 314 basin scale

Figure 8 shows that during the simulated period, I-PO₄ drops everywhere 315 in the EMB (Fig. 8), except near the Sicilian strait and to the south of 316 Rhodes due to very strong and deep vertical mixing. This decrease in $I-PO_4$ 317 can be as high as 40 % (Fig. 8). In the WMB, the spatial variability of the 318 difference in $I-PO_4$ between 1985 and 2010 is slightly more noticeable but 319 remains weak. The difference in $I-PO_4$ remains close to 0 % except near the 320 coastal areas where the decrease in $I-PO_4$ over the period can reach up to 321 30 %, and offshore of the Gulf of Lions where I-PO₄ is higher in 2010 than 322 1985. It can also be seen that DOC concentration at the surface progressively 323 increases between 1985 and 2010 in the EMB (Fig. 8) and reaches more than 324 40 % in some areas, while DOC concentration remains nearly constant in the 325 WMB. 326

The patterns of change over with time of the 0-150 m integrated carbon 327 biomass of copepod (I-COP-C) is also reported in the same figure, showing 328 that I-COP-C decreases mostly in the EMB between 1985 and 2010 (Fig. 8). 329 In the same period, we observe a decrease in COP abundance (not shown). 330 Furthermore, I-COP-C exhibits wide mesoscale variability over the MS (Fig 331 8) with a decrease in the EMB in coastal areas and an increase in the gulf of 332 Gabes and near the Algerian coast. This result highlights the importance of 333 mesoscale activity with regard to the biogeochemistry of the Mediterranean 334 sea. 335

336

337 4. Discussion

$_{338}$ 4.1. The decrease in PO₄ input by rivers strongly impacts the biogeochemistry $_{339}$ of the eastern basin

The hindcast simulation over the period (1985-2010) using the coupled 340 model NEMO-MED12/Eco3M-Med shows a significant decrease in the 0-150 341 m integrated PO_4 concentration (I-PO₄), especially in the EMB (Fig. 8). 342 At first glance, several factors could explain this decrease, namely (i) a drift 343 of the model, (ii) changes in PO_4 surface inputs at Gibraltar strait, (iii) 344 changes in the vertical exchanges between the upper and the deep layers, or 345 (iv) changes in river input and runoff, or possibly a combination of all these 346 factors. The three former causes have been ruled out: it has been verified 347



Figure 8: Patterns of change at basin scale between 1985 and 2010 of: (top) the 0-150 m integrated PO_4 concentration(I-PO_4), (middle) the surface DOC concentration, (bottom) the carbon biomass of copepods (I-COP-C) integrated between 0 and 150 m. The first three columns refer to the years 1985, 2000 and 2010, respectively, and the last column shows the difference between 1985 and 2010 (i.e. 2010 value - 1985 value)

first that the model drift was negligible after having run the spin-up, and that 348 PO_4 surface inputs at Gibraltar strait were approximately constant during 349 the simulated period. Concerning vertical mixing, it has been confirmed that 350 the mean position of the mixed layer depth (MLD) did not significantly vary 351 over this period, that the seasonal and annual standard deviation of the ML 352 did not show any trend, and that vertical velocities as well as the vertical 353 eddy diffusivity at the bottom of the ML did not exhibit any trend either. 354 As a result, changes in river input and runoff is the only factor in the model 355 able to explain the decrease in integrated PO_4 concentration in the EMB. In 356 order to confirm this assumption, a twin simulation only differing by nutrient 357 input from rivers and runoffs has been run. In the second simulation, PO_4 358 input remains at the 1985s level. 359

360

The comparison between the two simulations confirms the major influence of changes in PO_4 river input and runoff on the integrated PO_4 concentrations and beyond on the MS biogeochemistry, especially in the EMB. The decrease in I-PO₄ probably results from the combination of a direct and an indirect effect. The direct effect is a consequence of the decrease in PO₄ input ³⁶⁶ by Mediterranean rivers between 1985 and 2000 [15]. PO_4 input from rivers ³⁶⁷ and runoff strongly decreased during this period in the WMB and in the ³⁶⁸ EMB (see Fig. 2), while NO₃ input remained roughly unchanged. Moreover, ³⁶⁹ this decrease is stronger in the EMB: PO_4 inputs indeed decreased from 140 ³⁷⁰ kt.a⁻¹ to less than 40 kt.a⁻¹ between the 1980s and the 2000s in the EMB, ³⁷¹ and from 50 kt.a⁻¹ to less than 20 kt.a⁻¹ in the WMB during the same pe-³⁷² riod.

Overall, the model shows, on time scales of a few decades, a strong relation-373 ship between nutrient input via rivers and nutrient availability in the surface 374 layer, as already pointed out by Powley et al. [30], as well as the link be-375 tween the decrease in PO_4 input by rivers and the increase of P depletion in 376 the EMB. It is nevertheless in contradiction with the study of [14] showing 377 similar annual PO₄ input by the Rhône River and annual PO₄ storage in the 378 upper sediment of the Gulf of Lions, indicating no strong influence only close 379 to the river mouth of one of the major rivers in the MS. 380

Furthermore, a decrease in surface PO_4 has been recently reported in the 381 Levantine basin [50]. This decrease is however rather a shift in phosphate 382 concentrations than a progressive decrease over years, which may be caused 383 by decadal reversals in the North Ionian Gyre, i.e. Bimodal Oscillation Sys-384 tem (BiOS). Such alterations of the MS circulation, as well as many other 385 factors that are not necessarily included or well represented in our model may 386 indeed contribute to an impact on the biogeochemistry of the MS. However, 387 considering that our results rely on two identical simulations only differing by 388 river inputs and runoff, the unavoidable inaccuracies in the aforementioned 389 model do not call into question the unexpected conclusions they lead to on 390 the major influence of river inputs on the biogeochemistry of the MS. 391

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The indirect effect of changes in PO_4 river input and runoff is the deepen-393 ing of the top of the phosphacline (i.e. Pcline as defined in section 3.3) which 394 occurs only in the EMB (from 60 m in 1985 to 90 m in 2010). This deepening 395 exacerbates the decrease in PO_4 in the surface layer by restricting the PO_4 396 flux brought to the surface through winter mixing. Investigating the reasons 397 for this deepening requires to describing in detail all PO_4 fluxes shaping the 398 Pcline. The position of the Pcline within the water column (during stratified 399 conditions) results from an equilibrium between PO_4 production and con-400 sumption fluxes [3, 2, 51]. 401

402

 $_{403}$ The consumption of PO₄ in the model is driven by PHYS, PHYL and

BAC uptake. Phytoplankton and bacteria need nutrients (NO_3, PO_4) to 404 grow, as well as carbon. Carbon essentially comes from DIC uptake (photo-405 synthesis) by phytoplankton and from DOC uptake by heterotrophic bacteria 406 [52]. This uptake progressively decreased over time in surface waters because 407 of the gradual depletion of PO_4 (Fig. 6). The maximum PO_4 uptake rates at 408 depth (around 100 m) for PHYS and PHYL also decrease with time, mostly 409 for PHYL (Fig. 6) because sufficient nutrient concentrations to sustain the 410 growth of organisms are only found at greater depth. However, the efficiency 411 of photosynthesis decreases with depth since light energy decreases as well, 412 leading to an increase in carbon limitation for phytoplankton and to lower 413 cell abundance, and in turn to a decrease in nutrient uptake rates. 414

PHYL is more sensitive to nutrient variations in the model. Because 415 of the scaling relationship between nutrient uptake and organism size [53], 416 PHYL is characterized by a higher half-saturation constant than PHYS [33], 417 making it less adapted to ultra-oligotrophic conditions. The uptake of BAC 418 is deepening over the period (Fig. 6 c) but it does not strongly decrease at 419 depth since, unlike phytoplankton, bacteria use DOC as carbon source and 420 are therefore not limited by light. Bacteria follow the deepening of the Pcline 421 as long as labile DOC is available. 422

 PO_4 is produced by zooplankton excretion and bacteria remineralization. 423 Excretion of CIL and HNF is regulated by Q_P , their intracellular P quota 424 (i.e. excretion non-linearly increases with Q_P). Since the abundance and 425 the Q_P of CIL and HNF's preys (namely PHYS and BAC for HNF, and 426 PHYS, BAC and HNF for CIL) decline over the period (not shown), the Q_P 427 of CIL and HNF decrease as well. As a result, PO_4 excretion by HNF and 428 CIL decreases. The deepening of PO_4 production by BAC remineralization 429 could also be explained by the P quota of BAC. BAC reach their maximum P 430 quota (i.e. the value allowing remineralization of organic P) deeper because 431 of the increasing P depletion in the surface layer. Moreover, the decrease in 432 remineralization intensity with depth is also due to the diminution of BAC 433 abundance associated with the lower concentration of labile DOC at depth. 434 435

To sum up, PO₄ consumption fluxes show a clear decreasing trend in the surface layer while the maximum of consumption deepens and its intensity remains almost unchanged. PO₄ production fluxes also show a clear decreasing trend in the surface layer, as well as in depth. As a result, the equilibrium between all those processes occurs deeper in the water column, resulting in a Pcline that deepens over the years. Furthermore, the amount of PO₄ brought to the surface layer annually during winter mixing also decreases, thereby reinforcing the lower availability of PO₄ in the surface layer.

To the best of our knowledge, no deepening of the top of the phosphacline 444 in the EMB during the last decades has yet been reported in the literature. 445 The lack of data and the quantification limit issue associated with PO_4 mea-446 surement probably explains why this question has not been addressed so far. 447 We gathered the few available NO_3 and PO_4 data recorded in the center of 448 the Levantine Sea and collected during five cruises over our simulation pe-449 riod, namely POEM 05 (1987), LBD01 (1989), MINOS (1996), PROSOPE 450 (1999) and BOUM (2008). The vertical PO_4 and NO_3 profiles measured dur-451 ing these cruises have been reported in figure 9 in order to test the hypothesis 452 of the deepening of the Pcline using in situ data. According to the POEM 453 and BOUM cruises data, PO₄ concentration between 100 and 200 m seems to 454 decrease between 1987 and 2008 while NO_3 concentration remains constant 455 during the same period. Given the limited set of data available in the open 456 EMB, and taking into account the issue of the relatively high quantification 457 limit for PO_4 measurements, those data are obviously not a sufficient basis 458 for any definite conclusions, but they do however seem to confirm the deep-459 ening with time of the top phosphacline simulated by the model, as well as 460 the roughly constant position of the top nitracline. 461

462

In the model, the fact that only the top Pcline deepened in the EMB be-463 tween 1985 and 2010 results in the appearance of a shift between Pcline and 464 Ncline which increases with time. During the BOUM cruise in 2008, [2] mea-465 sured a maximum shift between nutriclines of 130 m in the Levantine basin, 466 and a mean shift of around 60 m if we exclude the eastern stations sampled 467 in the center of an anticylonic eddy characterized by specific hydrodynamic 468 conditions [1]. To calculate the position of the top of the nitracline [2] use, 469 as we do (see section 3.3), the threshold of 0.05 μ mol.l⁻¹, leading to a mean 470 nitracline top located at approximately 75 m, which is consistent with the 471 top of the nitracline depth calculated by our model (between 70 m and 75 472 m). For the determination of the depth of top of the phosphacline, [2] use the 473 threshold value of 0.02 μ mol.l⁻¹, resulting in a mean top phosphacline depth 474 at around 130 m if we exclude the eastern stations for the reason previously 475 mentioned. In the model, we find a phosphacline top depth at around 90 m 476 in the EMB with the more restrictive threshold of 0.003 μ mol.l⁻¹. However, 477



Figure 9: NO_3 (left) and PO_4 (right) data from five cruises in an area located in the center of the Levantine sub-basin, namely : i) POEM 05 (June 1987) in blue; ii) LBD01 (April 1989) in cyan; iii) MINOS (June 1996) in pink; iv) PROSOPE (September 1999) in green; v) BOUM (July 2008) in red. The black dotted line shows the quantification limit, except for the BOUM cruise during which sensitive methods of analysis were used.

⁴⁷⁸ if we apply the same threshold value as [2], the model calculates a phospha-⁴⁷⁹ cline top depth between 110 and 125 m in the EMB, which is consistent with ⁴⁸⁰ *in situ* data.

The shift between the top of nutricline depths in the EMB has been 481 previously reported in literature [4, 54, 2] and explained by several processes 482 but changes in river input were never suspected of playing a significant role 483 in this shift. So far, the most common explanation for this shift (and for 484 the associated high subsurface $NO_3:PO_4$ ratio) was related to the high deep 485 $NO_3:PO_4$ ratio, i.e. higher than the Redfield value, as a result of nutrient 486 budgets regulated by nutrient exchanges at straits, and especially at the 487 Gibraltar strait [55]. Upward diffusion of deep nutrients taken up biologically 488 at a constant molar N:P ratio of 16:1 may theoretically lead to subsurface 489 ratios as high as those observed at depth [7, 4]. External atmospheric inputs 490 were also recently suggested to play a role in the high surface and subsurface 491 $NO_3:PO_4$ ratio [25, 24]. 492

⁴⁹³ This study suggests that the N:P ratio in nutrient input by rivers, and its

deviation from the Redfield ratio, may partly explain the shift between the top of the nitracline and phosphacline in the MS as a result of a deepening of the Pcline (due to the strong decrease in PO₄ inputs from rivers), without a similar deepening in the Ncline.

4.2. Patterns of change in DOC concentration between 1985 and 2010 and 499 consequences for the biological carbon pump

⁵⁰⁰ DOC surface concentration increases strongly over the simulated period, ⁵⁰¹ especially in the EMB (Fig. 7 and 8). At the scale of the EMB, this increase ⁵⁰² reaches 20 % (Fig. 8) but it is far higher in the Levantine sub-basin, reaching ⁵⁰³ there more than 40 %. An inverse trend for PO₄ concentrations was observed ⁵⁰⁴ (Fig. 8) reinforcing the west to east oligotrophy gradient in the EMB.

This increase in DOC is driven by the same mechanisms as those in-505 volved in the surface DOC accumulation observed every summer in the MS 506 [8, 9]. The latter, namely an increase in DOC exudation by P-limited phyto-507 plankton exceeding bacterial DOC demand, since bacteria are also strongly 508 P-limited, have already been extensively described in Guyennon et al. [26]. 509 Over the simulated period, the EMB upper waters become more and more P-510 depleted (Fig. 8) which induces a rise in DOC exudation by phytoplankton 511 (Fig. 8). Furthermore, because of the strong P-limitation of both phyto-512 plankton and heterotrophic bacteria, the abundance of bacteria decreases in 513 the surface layer, as has been evidenced in situ [9]. The decrease in bacte-514 rial abundance probably also leads to a decrease in DOC consumption by 515 bacteria and reinforces DOC accumulation. 516

A DOC concentration increase between 1985 and 2010 cannot be validated 517 with any certainty since very few DOC measurements in the EMB before the 518 years 2000 are available, and most of them were carried out in coastal areas. 519 Moreover, as already mentioned, the comparison is not easy since DOC in 520 situ data refer to total DOC, while the modelled DOC does not include 521 the refractory part, making necessary an approximation for refractory DOC. 522 Overall, the model seems to provide realistic DOC values as suggested by 523 comparison with in situ data from the DyFaMed station over the 1992-2002 524 period (see Fig. 4) or from the BOUM cruise (not shown). The modelled 525 increase in dissolved organic carbon is not observed in the detrital particulate 526 carbon, which even slightly decreases. However the total organic carbon 527 increases, indicating that the pool of organic carbon available for export has 528 increased during the period. Since, as already shown by [26], the export 529 of DOC in the eastern basin is the main component of the exported organic 530

carbon, the strong DOC increase in the EMB has significantly increased DOC
export during this period.

4.3. A simulated decrease in mesozooplankton abundance and biomass with expected consequences for higher trophic levels

Despite the wide variability associated with mesoscale activity (Fig. 8), 535 a strong decrease in biomass (I-COP-C) and abundance of copepods was 536 modelled in the EMB, as well as in the offshore part of the WMB, between 537 1985 and 2010. The carbon intracellular quota (Q_C) of COP decreases as 538 well in the same regions. In the model, COP are the top predators. Their 539 intracellular carbon is directly related to the abundance and the carbon con-540 tent of their prey, namely PHYL, CIL and HNF, with a preference for PHYL 541 over the two others. Because of strong phosphate limitation, abundance of 542 PHYL decreases (not shown), thereby limiting the number of prey available 543 for COP. The abundance of HNF and CIL also decreases, because of the 544 decrease in prey abundance. Such depletion of COP preys explains the de-545 crease in COP biomass and abundance. A similar decreasing trend in COP 546 abundance due to increasing land-based N:P nutrient load has already been 547 observed in the San Francisco Estuary Bay Delta [56]. 548

The decrease in COP abundance could have a significant effect on small 549 pelagic fishes such as sardine and anchovy. Copepods are indeed an impor-550 tant link in marine food webs as prev for larger pelagic predators [57]. As 551 an example for the MS, [58] highlighted changes in biomass and fish mean 552 weight of sardine and anchovy in the Gulf of Lions around 2008. They showed 553 that the bottom-up control exerted by the plankton community played an 554 important role in those changes through a decrease in fish energy income. 555 They also showed that copepod abundance was directly linked to fish char-556 acteristics (size and weight). Those results are difficult to reproduce with 557 our model since the Gulf of Lions is too small and too coastal an area with 558 regard to the size of the horizontal grid used, but they nevertheless seem to 559 confirm the general trend predicted by the model at larger scale. In the same 560 way, [59] showed a decrease in the mean length of sardines between 1996 and 561 2000 in the EMB. They pointed out that, among other factors, the quality 562 of their preys (among which copepods) could have decreased, leading to a 563 diminution of the size of sardine. This could be linked to the decrease in 564 COP abundance and Q_C predicted by the model (Q_C can indeed be seen as 565 a proxy of the nutritional quality of copepods and of their size) during the 566 same period and at least partially explained by the changes in river outputs 567

during the last decades. Furthermore, this suggests that COP abundance and Q_C , as calculated by the model, could be used as one indicator among others of the stocks and size of small pelagic fish in the MS in future modeling scenarios.

572 5. Conclusion

This study provides new insight into the possible effects of changes in 573 nutrients provided by river inputs on the biogeochemistry of the MS over 574 the last decades. The strong reduction of PO_4 input by river and runoffs, 575 that occurred over the last decades in the EMB, induces a lowering of PO_4 576 availability in the sub-surface layer of this basin. An indirect consequence of 577 these strong variations in river inputs lies in the deepening of the top of the 578 phosphacline, as an adjustment of organisms and biogeochemical cycles to 579 the sub-surface PO_4 decrease. Since the position of the top of the nitracline 580 remains unchanged during that period, a shift between the two nutriclines 581 gradually emerges. This provides a new explanation for the shift between 582 the top of the nutriclines already mentioned in literature. 583

Another result provided by this modelling study concerns the rise of the 584 DOC concentration in the surface layer between 1985 and 2010, as evidenced 585 by the model in the EMB. The increasing P limitation in this basin results 586 in higher DOC accumulation in the surface layer, and therefore in increas-587 ing DOC export fluxes over the last decades (not shown). This is of major 588 importance since DOC export represents the major part of the total (dis-589 solved and particulate) carbon export in the MS, as has been evidenced in 590 Guyennon et al. [26]. 591

Finally, we have highlighted the decline over the years 1985-2010 in copepod abundance and intracellular content, the latter being a proxy of copepod size. Those decreases could have had an important impact on the higher trophic levels, and potentially provide an explanation to the smaller size of sardine or anchovy recently observed in the MS. Broadly speaking, the model underlines a trend towards the decline of large organisms in favour of small organisms.

Overall, this study emphasizes the fact that the biogeochemistry of the 599 two basins of the MS did not exhibit the same response to the variation 600 of rivers inputs. Significant biogeochemical trends were simulated over the 601 period 1985-2010 in the eastern basin. By contrast, the WMB seems to be less 602 sensitive to changes in river inputs, but it is difficult within the scope of this 603 study, to determine whether this is due to the difference in the characteristics 604 of the two basins, or whether it is due to the lower variations observed in 605 river inputs in the WMB as compared to those in the EMB. It is probably 606 a combination of these two factors. It has also been evidenced that these 607 variations in river inputs and runoff may affect not only the coastal areas 608

and the direct vicinity of river mouths, but also offshore areas. Finally, the magnitude of the biogeochemical changes induced by river inputs and runoff alone over the last thirty years clearly calls for the use of realistic scenarios of river inputs along with climate scenarios for coupled physical-biogeochemical forecasts in the MS.

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⁶²² Appendix A. New features of the biogeochemical model

Since the Alekseenko et al. [36] first version of the Eco3M-Med model, 623 some features of the original model were improved and some new features 624 were introduced to correct the model major flaws or to add some realism 625 to the model. In [26], it has been shown that the position of the nitracline 626 and the phosphacline were not well represented by the model (Figures S3 627 and S4 in the Supplement). A deep work has then been undertaken on the 628 remineralization process which was up to now function of the N:C and P:C 629 ratios in bacteria. In the present version of the model, the outflow of N 630 and P associated with the uptake of dissolved organic matter (DOM) is still 631 function of the N:C and P:C intracellular ratios (i.e. it is maximum when the 632 N:C or the P:C ratio takes its maximum value), but the intracellular carbon 633 quota Q_C will redirect this outflow either towards the DOM pool when Q_C 634 is high or towards the mineral pool otherwise. Concerning parameters, in 635 [39], the half-saturation constants (Ks) for the DOP uptake were divided by 636 1 order of magnitude in order to better match in situ data. However, Ks 637 values in the original model were all calculated using a similar method and 638 mechanistic considerations based on the shape of cells and the control of the 639 uptake rate by molecular diffusion at low nutrient concentrations. Here, we 640 consider a more realistic cells shape to derive new values of the Ks for NO_3 , 641 NH_4 , PO_4 , LDON and LDOP involved in the model in a similar way. Using 642 the diffusion flux established by Kiorboe [60] for cigare-shaped (ellipsoid) 643 cells, we derive the following relationship between the maximum uptake rate 644 (V^{max}) of a given nutrient and the associated half-saturation constant as 645 done in Mauriac et al. [35]: 646

$$K_s = \frac{V^{max} Ln(\frac{2a}{b})}{4\pi \mathcal{D}a} \tag{A.1}$$

where a and b stand for the semiaxes of the cigare-shaped ellipsoid $(a^2 >> b^2)$ and \mathcal{D} for the molecular diffusion coefficient (see Tab. Appendix A).

Table A.1: Parameters for the half-saturation constant			
Variable	Value		
\mathcal{D}_{NO_3} diffusion coefficients $[m^2.s^{-1}]$	$1.7 \ 10^{-9}$		
\mathcal{D}_{PO_4} diffusion coefficients $[m^2.s^{-1}]$	$7.5 \ 10^{-10}$		
\mathcal{D}_{NH_4} diffusion coefficients $[m^2.s^{-1}]$	$1.9 \ 10^{-9}$		
\mathcal{D}_{DON} diffusion coefficients $[m^2.s^{-1}]$	$3.0 \ 10^{-10}$		
\mathcal{D}_{DOP} diffusion coefficients $[m^2.s^{-1}]$	$3.0 \ 10^{-10}$		

Table Appendix A gives the values for a associated which each functional group. The ratio a/b has been set to 10. Finally, the K_s values derived from Eq. A.1 provide a consistent set of K_s values and they were all multiplied by the same number (50) to match the range given by literature.

Table A.2: Parameters for the half-	saturation	constant	
Variable	PHYL	PHYS	BAC
a Semi major axis of the ellipsoid $[\mu m]$	$2 \ 10^{-5}$	$2.5 \ 10^{-6}$	$4 \ 10^{-7}$

Other parameter values were modified (see table A.3), either to improve the consistency between the model parameters (for photosynthetic parameters), or to better integrate the knowledge from literature (hydrolysis rates), or to improve the model outputs (costs of DOC uptake, sinking rates).

Table	A.3: Other parameters	
Variable name		Value
PHYL PSII cro	ss section $[m^2.J^{-1}]$	2.5
PHYS PSII cro	ss section $[m^2.J^{-1}]$	2.0
MOPL specific	hydrolysis rate $[d^{-1}]$	15
MOPS specific	hydrolysis rate $[d^{-1}]$	7.5
Sinking rate of	MOPL $[m.d^{-1}]$	50
Sinking rate of	MOPS $[m.d^{-1}]$	2.0
Cost of DOC u	ptake	0.15
Cost of SLDOC	^l uptake	0.25

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