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1 **Phosphorus and nitrogen trajectories in the**

2 **Mediterranean Sea (1950-2030):**

3 **Diagnosing basin-wide anthropogenic nutrient enrichment**

4
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19 Mediterranean Sea, phosphorus, nitrogen, nutrient enrichment, thermohaline circulation, primary
20 production

21

22 **Highlights**

- 23 • Marine derived sources dominate nutrient P and N inputs to the Mediterranean Sea
- 24 • Land derived P and N inputs increase by up to a factor of 3 between 1950 and 2030
- 25 • Variable circulation hinders detection of anthropogenic nutrient enrichment
- 26 • Changes in DON concentrations yield the most prominent anthropogenic signatures

27

28 **Abstract:**

29 Human activities have significantly modified the inputs of land-derived phosphorus (P) and nitrogen (N) to
30 the Mediterranean Sea (MS). Here, we reconstruct the external inputs of reactive P and N to the Western
31 Mediterranean Sea (WMS) and Eastern Mediterranean Sea (EMS) over the period 1950 to 2030. We
32 estimate that during this period the land derived P and N loads increased by factors of 3 and 2 to the WMS
33 and EMS, respectively, with reactive P inputs peaking in the 1980s but reactive N inputs increasing
34 continuously from 1950 to 2030. The temporal variations in reactive P and N inputs are imposed in a coupled
35 P and N mass balance model of the MS to simulate the accompanying changes in water column nutrient
36 distributions and primary production with time. The key question we address is whether these changes are
37 large enough to be distinguishable from variations caused by confounding factors, specifically the relatively
38 large inter-annual variability in thermohaline circulation (THC) of the MS. Our analysis indicates that for
39 the intermediate and deep water masses of the MS the magnitudes of changes in reactive P concentrations
40 due to changes in anthropogenic inputs are relatively small and likely difficult to diagnose because of the
41 noise created by the natural circulation variability. Anthropogenic N enrichment should be more readily
42 detectable in time series concentration data for dissolved organic N (DON) after the 1970s, and for nitrate
43 (NO_3) after the 1990s. The DON concentrations in the EMS are predicted to exhibit the largest
44 anthropogenic enrichment signature. Temporal variations in annual primary production over the 1950-2030
45 period are dominated by variations in deep-water formation rates, followed by changes in riverine P inputs
46 for the WMS and atmospheric P deposition for the EMS. Overall, our analysis indicates that the detection
47 of basin-wide anthropogenic nutrient concentration trends in the MS is rendered difficult due to: 1) the
48 Atlantic Ocean contributing the largest reactive P and N inputs to the MS, hence diluting the anthropogenic
49 nutrient signatures, 2) the anti-estuarine circulation removing at least 45% of the anthropogenic nutrients
50 inputs added to both basins of the MS between 1950 and 2030, and 3) variations in intermediate and deep
51 water formation rates that add high natural noise to the P and N concentration trajectories.

52

53	ACRONYMS
54	ASW – Atlantic Surface Water
55	BiOS – Bimodal Oscillation System
56	DON – dissolved organic nitrogen
57	DOP – dissolved organic phosphorus
58	DW – deep water
59	EMDW – Eastern Mediterranean Deep Water
60	EMIW – Eastern Mediterranean Intermediate Water
61	EMS – Eastern Mediterranean Sea
62	EMSW – Eastern Mediterranean Surface Water
63	EMT – Eastern Mediterranean Transient
64	IW – intermediate water
65	LIW – Levantine Intermediate Water
66	MS – Mediterranean Sea
67	N - nitrogen
68	NH ₄ – dissolved ammonium
69	NO ₃ – dissolved nitrate plus nitrite
70	NWM – North West Mediterranean
71	P - phosphorus
72	PDF – probability distribution function
73	PO ₄ – dissolved phosphate
74	PON – particulate organic nitrogen
75	POP – particulate organic phosphorus
76	SGD – submarine groundwater discharge
77	SW – surface water
78	THC – thermohaline circulation
79	WMDW – Western Mediterranean Deep Water
80	WMIW – Western Mediterranean Intermediate Water
81	WMS – Western Mediterranean Sea
82	WMSW – Western Mediterranean Surface Water
83	WMT – Western Mediterranean Transition
84	

85 1 INTRODUCTION

86 Since the industrial revolution, anthropogenic emissions of phosphorus (P) and nitrogen (N) have rapidly
87 increased worldwide (Galloway, 2014; Cordell et al., 2011; Mackenzie et al., 2011), causing widespread
88 changes in the structure, functioning and health of aquatic ecosystems. Anthropogenic inputs of reactive N
89 to the environment have risen roughly nine-fold since 1860, with a large exponential increase since 1950
90 (Galloway, 2014). The resulting N load to the oceans has approximately doubled (Galloway, 2014), while
91 P fluxes to the global ocean are 1.5 to three times greater than estimates for pre-anthropogenic times
92 (Ruttenberg, 2014; Paytan and McLaughlin, 2007; Follmi, 1996). Impacts are particularly severe in semi-
93 enclosed seas such as the Baltic and Black Seas where primary production has increased by factors of four
94 to six in recent decades (Mikaelyan et al., 2013; Gustafsson et al., 2012).

95 Given its large, and growing, coastal population, and the ongoing agricultural and industrial intensification
96 (Micheli et al., 2013; UNEP/MAP, 2012), one may expect widespread evidence of nutrient enrichment in
97 the semi-enclosed Mediterranean Sea (MS). For comparison, land-derived inputs of P and N to the Eastern
98 Mediterranean Sea (EMS) per unit surface area are similar to those entering the Baltic Sea (Van Cappellen
99 et al., 2014). However, despite the high anthropogenic inputs, the MS shows little evidence of increased
100 eutrophication, with the exception of nearshore areas, such as the northern Adriatic Sea, the Gulf of Lions,
101 and the Nile delta region (Karydis and Kitsiou, 2012). The anti-estuarine circulation of the MS and the
102 resulting lateral export of nutrient P and N, ultimately to the North Atlantic Ocean, are usually invoked to
103 explain why the MS remains in its oligotrophic state (Krom et al., 2010; Crispi et al., 2001).

104 The intermediate (IW) and deep (DW) waters of the Western Mediterranean Sea (WMS) and EMS have
105 relatively short residence times (7-150 years; Powley et al., 2016a; Roether and Well, 2001; Stratford et al.,
106 1998; Béthoux and Gentili, 1996; Roether and Schlitzer, 1991). Hence, the dissolved P and N concentrations
107 of these reservoirs could potentially record anthropogenic nutrient enrichment on a decadal time scale.
108 However, although DW temperature and salinity data for the WMS have been systematically increasing
109 since the early 20th century ($0.3\text{-}5 \times 10^{-3} \text{ }^\circ\text{C yr}^{-1}$ and $0.6\text{-}2.2 \times 10^{-3} \text{ PSU yr}^{-1}$; Marty and Chiaverini, 2010 and
110 references therein), the temporal trends of dissolved nutrient concentrations in the IW and DW of the MS
111 are far more uncertain (Karafistan et al., 2002; Béthoux et al., 1998; Denis-Karafistan et al., 1998). For
112 example, Pasqueron de Fommervault et al. (2015) recently reported evidence for increasing dissolved nitrate
113 (NO_3) concentrations between 1990 and 2010 at the DYFAMED site, a permanent mooring station located
114 in the Ligurian Sea, but at the same time they found that the dissolved phosphate (PO_4) concentrations were
115 decreasing.

116 One major difficulty in interpreting temporal trends in water column P and N concentrations is the natural
117 variability of the thermohaline circulation (THC). A well-known example is the Eastern Mediterranean
118 Transient (EMT), when DW supply from the Aegean Sea rose markedly above background values for a
119 period of about ten years (Roether et al., 2007). The changes in properties of IW entering the WMS from
120 the EMS through the Strait of Sicily subsequently led to changes in DW formation within the WMS, termed
121 the Western Mediterranean Transition, or WMT (Schroeder et al., 2006). The average DW formation rate
122 in the WMS during the WMT was several times higher than in pre-WMT times (Powley et al., 2016a).

123 The EMT has recently been proposed to be a manifestation of a bimodal oscillation system (BiOS) in the
124 northern Ionian Sea and the southern Adriatic Sea whereby the North Ionian Gyre switches from
125 anticyclonic to cyclonic on a decadal time scale (Gačić et al., 2010; Pinardi et al., 2015; Malanotte-Rizzoli
126 et al., 1999). BiOS profoundly changes the physical and chemical properties of water masses in the southern
127 Adriatic Sea, as well as those of surface water (SW) that just entered the EMS through the Strait of Sicily
128 and IW entering the Levantine Sea from the Ionian Sea (Civitaresse et al., 2010; Gačić et al., 2010). In
129 addition to these relatively long-term variations in circulation regime, the THC of the MS also demonstrates
130 significant inter-annual variability (Pinardi et al., 2015; Sevault et al., 2014; L'Hévéder et al., 2013; Vervatis
131 et al., 2013).

132 Variations in THC affect the spatial distributions of P and N and can, thus, be a source of variability in time
133 series concentrations measured at given locations in the MS. As an example, changes in PO_4 and NO_3
134 concentrations in Levantine Intermediate Water (LIW) collected off the coast of Israel appear to coincide
135 with changes in circulation due to BiOS (Ozer et al., 2016). Ozer et al. (2016) therefore propose that the
136 observed changes in the dissolved inorganic nutrient concentrations can be explained by variations in
137 circulation driven by BiOS. In contrast, Moon et al. (2016) argue that the temporal trends exhibited by the
138 concentrations of PO_4 and NO_3 in IW across the whole MS are driven by changes in anthropogenic inputs
139 of P and N, mainly from rivers for P and atmospheric deposition for N. These opposing views raise the
140 question whether time series P and N concentration data of offshore (or pelagic) waters of the MS can yield
141 records of anthropogenic nutrient enrichment, or not.

142 The purpose of this study is to evaluate to what extent the trends in dissolved P and N concentrations due
143 to changes in the delivery of anthropogenic nutrients to the MS may be masked by the natural variability in
144 THC. To that end, we first estimate the external reactive P and N inputs to the WMS and EMS between
145 1950 and 2030. Next, we impose these inputs to an existing coupled P and N mass balance model for the
146 MS (Powley et al., 2017), while at the same time considering a number of different water circulation

147 regimes. For the latter, we consider IW and DW formation rates that either remain constant, change
148 randomly from year to year, or follow historical trajectories reconstructed from literature data. The results
149 are used to assess how sensitive temporal trends in aqueous P and N concentrations, N:P ratios and annual
150 primary production in the WMS and EMS are to human-driven changes in land-derived nutrient inputs.
151 Based on our analysis of the modeling results, we formulate recommendations that should help enhance the
152 efficiency of monitoring programs aimed at assessing the impacts of anthropogenic pressures on the
153 biogeochemical state of the MS.

154 **2 METHODS**

155 This paper builds on our previous modeling work on the coupled P and N cycling, first in the EMS (Powley
156 et al., 2014; Van Cappellen et al., 2014), and subsequently extended to include the WMS (Powley et al.,
157 2016a, 2017). The reader is referred to these earlier publications for in-depth presentations of methods,
158 approaches and data sources.

159 **2.1 Mass balance model**

160 The model framework used in this study (Figure 1) is the same as in Powley et al. (2017). The water
161 columns of the WMS and EMS are divided into three horizontal layers: surface water (WMSW, EMSW),
162 intermediate water (WMIW, EMIW) and deep water (WMDW, EMDW). The WMS and EMS models are
163 coupled by the bidirectional water exchanges through the Strait of Sicily. The WMS receives SW inflow
164 from the Atlantic Ocean, while WMIW and WMDW flow back to the Atlantic Ocean. Note that the areas
165 of DW formation in the WMS and EMS are not explicitly included in the model domain; instead the
166 corresponding DW formation fluxes are imposed as boundary fluxes within the model. For the WMS, DW
167 formation occurs in the area of open ocean convection located near to the Gulf of Lions in the northwest
168 Mediterranean and, henceforth, referred to as NWM. For the EMS, DW formation originates in the Adriatic
169 and Aegean Seas. The surface areas of the WMS and EMS model domains (i.e., excluding the DW formation
170 areas) are 815×10^3 and 1336×10^3 km², respectively.

171 The model considers three reactive P and four reactive N pools in each horizontal water layer: dissolved
172 inorganic phosphate (PO₄), particulate organic phosphorus (POP), dissolved organic phosphorus (DOP),
173 dissolved nitrate plus nitrite (NO₃), particulate organic nitrogen (PON), dissolved organic nitrogen (DON),
174 and dissolved ammonium (NH₄). The total reactive P input to the model domain equals the sum of PO₄,
175 POP and DOP inputs, plus the fraction of inorganic particulate phosphorus input that becomes soluble after
176 entering the MS (Van Cappellen et al., 2014). The total reactive N input is the sum of NO₃, PON, DON and
177 NH₄ inputs.

178 Internal cycling of P and N within each water layer is modeled using simple first order (or linear) kinetics.
179 Linear expressions are also applied to the denitrification flux, and the sinking and burial POP and PON
180 fluxes. Each rate constant (k) is calculated from the initial source reservoir mass and output flux in the 1950
181 steady state model. The exception is assimilation of NO_3 in the SW reservoirs. The average annual primary
182 production in both WMS and EMS is assumed to be P limited (Powley et al., 2017). Nitrogen limitation
183 may occur during parts of the year and in certain localities, especially in the WMS. However, on an annual
184 basis, P limitation drives basin-wide primary productivity across the MS (Lazzari et al., 2016). In the model,
185 the P and N cycles are therefore assumed to be coupled via the Redfield ratio, that is, N assimilation is
186 computed from the P assimilation flux using a 16:1 molar ratio (Redfield et al., 1963). Similarly, carbon
187 fixation during primary production is calculated from the P assimilation flux assuming a Redfield C:P ratio
188 of 106:1.

189 Fluxes of the various reactive P and N species between water reservoirs are calculated by multiplying the
190 corresponding water flows with the species concentrations in the source reservoirs. The turbulent mixing
191 fluxes are the exception: they are computed by multiplying the difference in concentration between
192 receiving and source reservoirs with an exchange coefficient, where the latter is related to the turbulent
193 diffusion coefficient (Van Cappellen et al., 2014). During the simulations, the concentrations of the various
194 P and N species in the water reservoirs change from year to year. The nutrient fluxes within the MS domain
195 may therefore change over time because of changes in concentrations, changes in water flows, or both.

196 Overall, the model consists of 42 ordinary differential equations solved in MATLAB using solver ODE 15s.
197 Factorial design sensitivity analyses performed by Powley et al. (2017) indicate that primary productivity
198 and the $\text{NO}_3:\text{PO}_4$ ratios within both the WMS and EMS are most sensitive to changes in the fluxes of P and
199 N entering the MS from the North Atlantic Ocean, and changes in the atmospheric deposition fluxes of PO_4
200 and DON. Furthermore, the EMDW $\text{NO}_3:\text{PO}_4$ ratio was found to be more sensitive to processes taking place
201 in the WMS rather than the EMS.

202 **2.2 Reactive phosphorus and nitrogen inputs: 1950 to 2030**

203 The model considers the following sources of reactive P and N to the WMS and EMS: inflows from adjacent
204 marine basins, atmospheric deposition, N_2 fixation, riverine inputs, submarine groundwater discharge
205 (SGD) and direct domestic wastewater discharges. Powley et al. (2017) estimated the magnitudes of these
206 inputs in 1950, that is, before the large increases in anthropogenic P and N emissions that occurred in
207 subsequent decades. These estimates indicated that the inflow of Atlantic Surface Water (ASW) via the
208 Strait of Gibraltar represents the largest input of reactive P and N to the MS. Because our focus is on the

209 detection of anthropogenic signatures in temporal trends of P and N concentrations within the MS, the
210 supply fluxes of reactive P and N associated with ASW inflow are assumed to remain constant over the
211 period 1950-2030. This validity of this assumption is difficult to ascertain given the scarcity of data available
212 to constrain the temporal variability of P and N fluxes through the Strait of Gibraltar. Thus, all the variations
213 in reactive P and N inputs to the MS since 1950 imposed in the model calculations are of anthropogenic
214 origin.

215 Anthropogenic forcing functions for the individual reactive P and N inputs to the WMS and EMS from 1950
216 to 2030 are derived following Powley et al. (2014). The values of the reactive P and N inputs in 1950 of
217 Powley et al. (2017) are used as baseline values. For each input, the forcing function then provides for any
218 given year during the 1950-2030 period the change in input flux relative to that in 1950. Thus, a forcing
219 function value of 1.2 in 1994 means the corresponding annual input in 1994 is 20% larger than in 1950.
220 Powley et al. (2014) provide a detailed account of the forcing functions for anthropogenic P and N inputs
221 to the EMS for the period 1950-2000. Table 1 summarizes how forcing functions for both WMS and EMS,
222 and for the entire 1950-2030 period, are obtained; full details are given in the Supplementary Material.
223 Because direct measurements that constrain the temporal evolution of reactive P and N inputs to the MS are
224 quite limited, relatively large uncertainties are associated with the estimated forcing functions. This is
225 particularly true for the 2000-2030 period, where the forcing functions depend on projections of ongoing
226 trends of anthropogenic drivers into the future, for example, the growth of coastal populations and upgrades
227 to wastewater treatment plants in the various countries surrounding the MS. Therefore, for 2000 to 2030,
228 mean values of the forcing functions are given, as well as estimates of upper and lower limits of the
229 associated anthropogenic drivers. Figure S1 shows the anthropogenic forcing functions applied to the model
230 as a function of time. The total anthropogenic forcing functions for the WMS and EMS are displayed in
231 Figure 2.

232 In addition to the input fluxes described in Table 1, the fluxes of P and N to the DW of the WMS and EMS
233 supplied by DW formation also vary over time, because of 1) the changes in the amounts of P and N carried
234 by the IW and SW that enter the region of DW formation where they mix to form the new DW, and 2) the
235 changes in the nutrients added directly to the DW formation sites via rivers and atmospheric deposition.
236 Here, we derive the forcing functions for the anthropogenic P and N added to each formation site. Changes
237 in the reactive P and N delivered to the DW formation sites from the SW and IW reservoirs are automatically
238 accounted for as the nutrient concentrations in these reservoirs are updated by the model at each time step.
239 Riverine fluxes into the Adriatic Sea and Aegean Sea over the 1950-2030 period are those estimated by
240 Ludwig et al. (2009, 2010). The DON flux entering the Aegean Sea through the Bosphorus is assumed to

241 change proportionally to the reactive N riverine input to the Black Sea (Ludwig et al., 2009, Ludwig et al.,
242 2010). Inflow through the Bosphorus is assumed to be a negligible source of inorganic N and P to the Aegean
243 Sea (Krom et al., 2004). Note that riverine fluxes of reactive P and N are not included for the NWM domain
244 because it corresponds to an area of open ocean convection and thus lacks a coastline. Atmospheric
245 deposition fluxes of P and N to the Adriatic Sea, Aegean Sea and NWM are assumed to follow the same
246 historical trends of those of the entire EMS and WMS.

247 **2.3 Thermohaline circulation (THC)**

248 This study focuses on the inter-annual variability in THC and, more specifically, the year-to-year changes
249 in the rates of IW and DW formation originating from the four main source zones in the MS: the NWM for
250 the WMS, and the Rhodes Gyre, Adriatic Sea and Aegean Sea for the EMS. During any given year, the
251 IW/DW formation rates remain constant. Four different scenarios are considered to illustrate the sensitivity
252 of the P and N distributions to circulation (Table 2): 1) time-invariant circulation, 2) random fluctuating
253 IW/DW formation rates, 3) reconstructed (historical) IW/DW formation rates, and 4) attenuated historical
254 IW/DW formation rates. Each circulation scenario is run separately from, and together with, the 1950 to
255 2030 reactive P and N inputs (Table 2) to separate the contributions of THC from those associated with
256 anthropogenic nutrient enrichment. The observables targeted by our analysis are the reactive P and N
257 concentrations in the IW and DW reservoirs, the corresponding N:P ratios, and primary productivity. Once
258 the prescribed IW/DW formation flows are imposed, the other water fluxes are adjusted to maintain the
259 annual water balance of each reservoir included in the model. The total inflow and outflow water fluxes
260 through the Strait of Gibraltar are kept constant in all model runs, although the proportions of WMIW and
261 WMDW in the outflow to the Atlantic Ocean vary over time. Note that water fluxes between WMSW and
262 WMIW, and WMIW and WMDW, may change direction during some of the model simulations.

263 **2.3.1 Random circulation 1950-2030 (Simulations 1 and 2)**

264 A random normal or lognormal probability distribution function (PDF) is used to generate yearly IW/DW
265 formation rates from each source region between 1950 and 2030 (Table 3). The PDFs are based on modeled
266 IW/DW formation rates in the four regions: DW formation in the NWM has been reported to occur in 53%
267 of years over the period 1959-2001 (L'Hévéder et al., 2013), 63% of years in the Aegean Sea over the period
268 1961-2000 (Vervatis et al., 2013), 80% of years in the Adriatic Sea over the period 1987-2007 (Pinardi et
269 al., 2015), while EMIW formation (also termed LIW in the literature) occurs every year (Vervatis et al.,
270 2013). Mean values and standard deviations of IW/DW formation flows are assigned using long term model
271 estimates from the literature, normalized so that the long term mean value of any given IW/DW formation

272 rate equals the value used in the 1950 steady state water cycle of Powley et al. (2016a). The corresponding
273 THC parameter values are given in Table 3. The variability in P and N concentrations due to random
274 fluctuations in THC are assessed by carrying out 500 model runs with randomly selected values of the
275 IW/DW formation rates. Mean, 10th and 90th percentile concentrations are reported (see below).

276 **2.3.2 Reconstructed (historical) circulation 1960-2000 (Simulations 4 and 5)**

277 Estimates of historical IW/DW formation rates between 1960 and 2000 are obtained from the yearly rates
278 of EMIW (or LIW) and Aegean DW formation reported by Vervatis et al. (2013), and WMDW formation
279 in the NWM by L'Hévéder et al. (2013), normalized as in section 2.3.1 so that the long term mean value of
280 any given IW/DW formation rate equals the steady state value used in the 1950 water cycle of Powley et al.
281 (2016a). The resulting DW and IW formation rates exhibit large year-to-year variations (Figure S3). In
282 particular, intense WMDW formation rates during the first half of the 1980s is followed by a period of
283 relatively little WMDW formation extending into the 1990s.

284 Because of the lack in the literature of long term predictions for DW formation in the Adriatic Sea before
285 1980, we assume that the corresponding DW formation flow follows the observed salinity cycle in the
286 Adriatic Sea due to BiOS (Civitarese et al., 2010). The changes in salinity in the Adriatic Sea caused by
287 BiOS alter the density of Adriatic water and therefore influence the rate of DW formation. To simulate the
288 BiOS driven changes in Adriatic DW formation the following sine wave is used:

$$289 \quad y(t) = (A \sin(\omega t + \varphi) + 1) \cdot 1950_{water}^{Adr} \quad (1)$$

290 where A is the amplitude, ω the frequency, and φ the phase shift of the DW flow out of the Adriatic Sea,
291 and 1950_{water}^{Adr} the 1950 flow (0.32 Sv); A is assigned the value of 0.98 Sv based on the reported range of
292 Adriatic DW flow into the EMS (0.006-0.63 Sv; Pinardi et al., 2015; Sevault et al., 2014), ω is assigned a
293 value of $\pi/8$ to represent a period of 16 years, matching that of salinity variations in the south Adriatic Sea
294 (Civitarese et al., 2010), and φ is equal to 0.7 so that the greatest (smallest) DW formation rate occurs at the
295 highest (lowest) observed salinity. We further discretize the sine wave so that the DW formation rate remains
296 constant throughout a given year to be consistent with the formulations used for the other IW/DW formation
297 sites. The sine wave produced by Equation 1 and the resulting Adriatic DW formation rates are shown in
298 Figures S2 and S3, respectively.

299 **2.3.3 Attenuated historical IW/DW formation rates (Simulations 6 and 7)**

300 The mass balance calculations assume that the water fluxes across the entire MS instantaneously adjust to
301 changes in IW and DW formation rates, which is admittedly an oversimplification of the true circulation
302 dynamics inherent to the box modeling approach followed in this study. To relax this assumption and
303 account for attenuation and delays in the propagation of changes in water fluxes, a running average of the
304 previous 5 year IW/DW formation rates is computed and applied to the model for each formation site across
305 the MS. Note that while the 5-year averaging is arbitrary, it is selected to be of similar magnitude as the SW
306 and IW water residence times. Similar to the previous circulation scenarios, resulting changes in the water
307 fluxes throughout the rest of the model are continuously adjusted to maintain the water balance.

308 **3 RESULTS**

309 **3.1 Reactive phosphorus and nitrogen inputs: 1950-2030**

310 For the WMS, our estimates indicate that the reactive P input from land derived sources increases by a
311 maximum factor of three relative to the 1950 input, reaching a peak in the 1980s (Figure 2). However,
312 because of the dominance of marine derived inputs in the nutrient budgets of the MS, the total reactive P
313 input to the WMS only increases by a maximum of 16% between 1950 and 2030, from 13.4×10^9 mol P yr⁻¹
314 in 1950 to a maximum of 15.6×10^9 mol P yr⁻¹ in 1985, largely driven by the increase in riverine supply
315 of PO₄ (Figure 3A). A subsequent decline in the reactive P input occurs until the year 2008 after which it
316 slowly rises again to 14.8×10^9 mol yr⁻¹ by 2030, because of the increasing inputs from riverine and
317 wastewater sources as a result of rapid coastal population growth.

318 For the EMS, the reactive P input from land derived sources increases by a maximum factor of 2.3 (Figure
319 2). The maximum increase of the total reactive P input is 39%, from 5.6×10^9 mol yr⁻¹ in 1950 to 7.8×10^9
320 mol yr⁻¹ in 1984, mainly as a result of increased atmospheric deposition, riverine input and DW inflow from
321 the Adriatic Sea (Figure 3B). Similar to the WMS, the reactive P input to the EMS then decreases until 2000
322 before increasing by an additional 0.4×10^9 mol yr⁻¹ between 2000 and 2030. From 1950 to 2030, most of
323 the reactive P entering the WMS and EMS is associated with inflow through the Straits of Gibraltar and
324 Sicily. The marine derived sources account for 85-94% of the total reactive P input to the WMS, and 62-
325 77% to the EMS. The larger fraction of reactive P from non-marine sources explains why the relative
326 changes in total reactive P input to the EMS are larger than for the WMS.

327 In contrast to P, the reactive N inputs to the WMS and EMS are predicted to continually increase between
328 1950 and 2030 (Figure 3 C and D). By 2030, the land derived reactive N inputs are 3 and 2.5 times higher

329 than in 1950 for the WMS and EMS, respectively (Figure 2). In the WMS, the total reactive N input
330 increases by 51%, from $398 \times 10^9 \text{ mol yr}^{-1}$ in 1950 to $599 \times 10^9 \text{ mol yr}^{-1}$ in 2030 (Figure 3C). As for P, the
331 relative increase in the total reactive N input is greater for the EMS: between 1950 and 2030 it increases by
332 98%, from $208 \times 10^9 \text{ mol yr}^{-1}$ to $412 \times 10^9 \text{ mol yr}^{-1}$ (Figure 3D).

333 Over the 1950-2030 period, inflow through the Straits of Gibraltar and Sicily provides 79 to 87% of the
334 total reactive N input to the WMS; for the EMS, inflow through the Strait of Sicily supplies 48 to 63% of
335 the total reactive N input. Nitrogen fixation, which had been hypothesized to have a significant impact on
336 DW $\text{NO}_3:\text{PO}_4$ ratios of the MS (Béthoux et al., 1992, Béthoux et al. 2002), only accounts for up to 3% of
337 the total reactive N input to the WMS between 1950 and 2030. Submarine groundwater discharge of
338 dissolved reactive N, which is included here for the first time in a dynamic nutrient budget of the MS,
339 becomes increasingly important during the 1950-2030 period, contributing up to 5% of the total reactive N
340 inputs to the WMS and EMS in 2030 compared to only 1% in 1950. Our minimum estimates for the 21st
341 century indicate that the reactive N input may stabilize in the WMS after 2000, and even decrease after 2020
342 in the EMS. The maximum projections have the total reactive N inputs increase approximately linearly from
343 2000 to 2030.

344 **3.2 Dissolved reactive phosphorus and nitrogen concentrations**

345 **3.2.1 Noise from inter-annual THC variability (Simulations 1 and 2)**

346 The areas shaded in red on Figures 4 and 5 encompass the ranges of dissolved reactive P and N
347 concentrations in the water column generated by random changes in inter-annual THC (Simulation 1). Note
348 that we present only results for the IW and DW reservoirs because nutrient concentrations across the photic
349 zone are spatially and temporally extremely variable, making a comparison between long-term model-
350 predicted SW concentrations and near-sea surface observations tenuous. In Simulation 1, PO_4 and NO_3
351 concentrations in WMIW and EMIW exhibit the highest absolute sensitivity to inter-annual variations in
352 THC. For the PO_4 concentrations, the mean difference between the 10th and 90th percentiles in WMIW and
353 EMIW over the course of 1950 to 2030 is 34 nM ($\pm 6\%$ of the mean 1950-2030 value) and 10 nM ($\pm 5\%$ of
354 mean 1950-2030 value), respectively. For the NO_3 concentrations, the difference is $0.7 \mu\text{M}$ ($\pm 5\%$ of mean
355 1950-2030 value) in WMIW, and $0.3 \mu\text{M}$ ($\pm 6\%$ of mean 1950-2030 value) in EMIW.

356 The PO_4 and NO_3 concentrations of the DW reservoirs are more sensitive to THC changes in the WMS than
357 EMS. The mean differences between the 10th and 90th percentiles of the PO_4 and NO_3 concentrations of
358 WMDW are 27 nM ($\pm 4\%$ of mean value) and $0.6 \mu\text{M}$ ($\pm 4\%$ of mean 1950-2030 value), respectively, but

359 only 3 nM ($\pm 1\%$ of mean 1950-2030 value) and 0.1 μM ($\pm 1\%$ of mean 1950-2030 value) for the
360 corresponding concentrations in EMDW. Similar to their inorganic counterparts, the highest absolute
361 sensitivities to THC of DOP and DON concentrations are found for the IW reservoirs: 6 nM ($\pm 7\%$ of mean
362 1950-2030 value) and 0.3 μM ($\pm 5\%$ of mean 1950-2030 value) for DOP and DON, respectively, in WMIW,
363 and 4 nM ($\pm 5\%$ of mean 1950-2030 value) and 0.2 μM ($\pm 3\%$ of mean 1950-2030 value) in EMIW. As
364 expected, for Simulation 2, the variability in concentrations due to the inter-annual variability in THC (blue
365 shaded area; Figures 4 and 5) are of the same order of magnitude as in Simulation 1.

366 **3.2.2 Anthropogenic nutrient enrichment (Simulations 2 and 3)**

367 The temporal trends in the IW dissolved reactive P and N concentrations in Simulation 3 generally reflect
368 those of the P and N inputs to the WMS and EMS over the time period 1950 to 2030 (Figures 3, 4, 5, S4
369 and S5). Relative to the 1950 baseline, IW dissolved reactive P concentrations increase to a maximum of
370 13% in the WMS and 21% in the EMS by the late 1980s to early 1990s (Figures 4, 5 and S5), compared to
371 increases in reactive P inputs of 16% and 39% in the WMS and EMS, respectively (Figure 3). Within the
372 DW reservoirs, dissolved reactive P concentrations in both WMS and EMS increase continuously from 1950
373 to 2030, with the exception of the WMDW DOP concentration, which reaches its maximum in 1993 with
374 an 11% higher value than in 1950. Dissolved reactive N concentrations in both WMS and EMS increase
375 throughout the simulation period reaching their maximum values in 2030 (Figures 4, 5, S4 and S5). In
376 particular IW DON concentrations are predicted to strongly increase by a maximum of 33% in the WMS
377 and 78% in the EMS by 2030 relative to the 1950 concentrations (Figure S5). The NO_3 concentrations in
378 the WMS and EMS increase strongly after the 1980s, with both IW and DW NO_3 concentrations increasing
379 between 2000 and 2030 at almost linear rates of 0.02-0.04 $\mu\text{M yr}^{-1}$ in the WMS and 0.01-0.03 $\mu\text{M yr}^{-1}$ in the
380 EMS (Figures 4 and 5). By 2030, NO_3 concentrations of WMIW are comparable to those of WMDW. The
381 mean dissolved reactive P and N concentrations of Simulation 3 closely match those of Simulation 2 as both
382 simulations use the same anthropogenic forcings.

383 **3.2.3 Reconstructed historical circulation changes (Simulations 4 to 7)**

384 The results of the historical THC changes (1950 to 2000) are shown in Figures 6, S6, S7 and S8. The
385 maximum variations in PO_4 concentrations in Simulation 4 are 75 nM and 29 nM in WMIW and EMIW,
386 respectively, and 33 nM and 4 nM in WMDW and EMDW. For NO_3 concentrations, the maximum
387 variations are 1.6 μM and 0.6 μM in WMIW and EMIW, respectively, and 0.7 μM and 0.1 μM in the
388 WMDW and EMDW. Imposing the 5-year running average of IW/DW historical formation rates
389 (Simulation 6) yields maximum variations in PO_4 and NO_3 concentrations that are 39-53% lower in IW and
390 16-25% lower in DW than in Simulation 4. Note that the P and N concentration trajectories of Simulations

391 5 and 7 are shifted upwards from those of Simulation 4 and 6 respectively, because the former include the
392 post-1950 anthropogenic nutrient inputs (Figures 6 and S6).

393 **3.3 N:P ratios**

394 The dissolved organic P and N pools record the greatest change in N:P ratios over the course of the 1950-
395 2030 period, with the largest changes in the EMS (Figure 7; Table S2). In EMIW, the mean molar
396 DON:DOP ratio increases from 67 in 1950 to a maximum of 100 by 2030 as a result of anthropogenic
397 nutrient enrichment. This increase by 49% far exceeds the variability of only 5% caused by random
398 fluctuations in inter-annual THC. Similarly, increases in the mean $\text{NO}_3:\text{PO}_4$ ratios of WMIW and EMIW of
399 up to 38% exceed changes due to random variations in THC by more than a factor of five. The DW $\text{NO}_3:\text{PO}_4$
400 ratios of the WMS and EMS show the smallest increases with time, although these are the most frequently
401 reported N:P ratios for the MS. In the WMS, the modeled $\text{NO}_3:\text{PO}_4$ DW ratio remains approximately
402 constant at a value 21 until the early 1990s, before increasing approximately linearly to a value of 22.6 by
403 2030 (see also Figure S9). In EMDW the $\text{NO}_3:\text{PO}_4$ ratio slightly decreases from 28.3 in 1950 to a minimum
404 of 28.0 in 1989, as a result of the reduced input from the Nile River after closure of the Aswan Dam, before
405 increasing to 29.5 by 2030. In the historical circulation scenarios, the drop in IW and DW $\text{NO}_3:\text{PO}_4$ ratios
406 of the WMS and EMS during the 1980s and their subsequent recovery during the 1990s primarily reflect
407 the variations in the reconstructed THC (Figure S10).

408 **3.4 Primary productivity**

409 According to Simulation 3, the variable inputs of anthropogenic reactive P and N increase primary
410 productivity in the WMS from $148 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 1950 to $166 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 1987 (12% increase), followed
411 by a decrease to $159 \text{ g C m}^{-2} \text{ yr}^{-1}$ by 2011 with little change afterwards (Figure 8). A larger relative increase
412 is seen for the EMS in Simulation 3, with primary productivity rising from $56 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 1950 to 69 g
413 $\text{C m}^{-2} \text{ yr}^{-1}$ in 1989 (22% increase) and settling to a final value of $67 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 2030. The random THC
414 fluctuations in Simulation 1 yield a range in primary productivity in the WMS of around $35 \text{ g C m}^{-2} \text{ yr}^{-1}$
415 ($\pm 12\%$ of mean value), which is nearly twice the maximum change of $18 \text{ g C m}^{-2} \text{ yr}^{-1}$ from the variable
416 inputs of reactive P in Simulation 3. By contrast, for the EMS, the variability produced by random THC (7
417 $\text{g C m}^{-2} \text{ yr}^{-1}$ or $\pm 6\%$ of the mean value) is smaller than the maximum difference of $13 \text{ g C m}^{-2} \text{ yr}^{-1}$ due to
418 increased anthropogenic reactive P inputs after 1950. The historical THC scenarios (Simulations 4 and 5)
419 yield the largest relative changes in primary productivity in the WMS and EMS, with variations of up to
420 60% relative to the 1950 values (Figure S11).

421 4 DISCUSSION

422 4.1 Phosphorus and nitrogen budgets

423 The MS is landlocked and experiences high population growth and seasonal tourism along its coastline
424 (Plan-Bleu, 2005). As a result, the MS has seen significant increases in land derived nutrient inputs since
425 1950 (Powley et al., 2016b, Powley et al., 2014; Ludwig et al., 2009; Guerzoni et al., 1999; this study).
426 Furthermore, the water residence times of the IW and DW reservoirs are relatively short (Figure 1), thus
427 suggesting that anthropogenic nutrient enrichment could potentially be recorded by temporal changes in the
428 reactive P and N concentrations within the IW and DW of the MS. So far, however, long-term trends of P
429 and N concentrations in the deeper water layers of the MS have been inconclusive (Pasqueron de
430 Fommervault et al., 2015; Karafistan et al., 2002; Béthoux et al., 1998; Denis-Karafistan et al., 1998). One
431 key contributing factor is the anti-estuarine circulation of the MS, which buffers the impact of anthropogenic
432 nutrient enrichment on the N and P budgets, and helps explain why offshore waters of the MS have remained
433 oligotrophic, in contrast to, for example, the Baltic Sea.

434 The anti-estuarine circulation causes large, bidirectional water exchanges across the Straits of Gibraltar and
435 Sicily. Based on our estimates, the nutrient fluxes carried by these water exchanges dominate the reactive P
436 and N inputs to the WMS and EMS (Figure 3; Powley et al., 2017). In other words, the nutrients fluxes
437 between the North Atlantic and the WMS, and between the WMS and EMS, dilute the changes in N and P
438 concentrations induced by the inputs from the surrounding land masses. The latter contribute less than 38%
439 of total reactive P inputs and less than 52% of total reactive N inputs into the WMS and EMS between 1950
440 and 2030, despite increases in anthropogenic inputs of P and N by factors of 3 (WMS) and 2.5 (EMS) over
441 the same time period (Figure 2). Additionally, the anti-estuarine circulation efficiently removes a large
442 proportion of the excess anthropogenic nutrients. On the order of 45% of the excess reactive P and N added
443 to the EMS between 1950 and 2030 are removed from the EMS via outflow through the Strait of Sicily
444 (Figure 9). Similarly, outflow to the North Atlantic and EMS exports approximately 60% of anthropogenic
445 P and N supplied to the WMS over the same time period.

446 4.2 Detecting offshore anthropogenic nutrient enrichment

447 The rates of intermediate and deep-water formation in the WMS and EMS vary significantly from year to
448 year (Pinardi et al., 2015; Sevault et al., 2014; L'Hévéder et al., 2013; Vervatis et al., 2013). This creates
449 noise in the spatial and temporal distributions of biogeochemical properties across the MS, including the
450 concentrations of various forms of P and N, N:P ratios and primary productivity. While our analysis focuses
451 on the impact of inter-annual THC variations on the ability to detect basin-wide temporal trends over decadal

452 time scales, we fully recognize that mesoscale and seasonal variability in circulation may cause additional
453 noise in nutrient enrichment signals. These cannot be accounted for in our simple mass balance calculations
454 and require higher resolution modeling approaches (see, for example, Macias et al., 2014).

455 According to our results, the detection of changes in the dissolved reactive P concentrations of WMIW and
456 WMDW directly caused by anthropogenic inputs are expected to be hampered by the random noise created
457 by inter-annual variability of THC (Figure 4). The changes in PO₄ and DOP should be more pronounced in
458 EMIW and EMDW (compare Figures 4 and 5). Nonetheless, the predicted maximum increases in the PO₄
459 and DOP concentrations for the EMS since 1950 are at most of the order of 10 nM, which is close to the
460 analytical precision of 3-5 nM on frozen samples (Pujo-Pay et al., 2011; Krom et al., 2005). Given the sparse
461 measurements of reactive P in the MS, in particular for DOP, together with the analytical limitations, it is
462 unlikely that existing time series PO₄ and DOP data sets can yield unambiguous records of basin-wide
463 anthropogenic nutrient enrichment. Additional practical problems of detecting nutrient changes in the IW
464 is the variable depth of the nutricline, and temporal and spatial variations caused, for example, by mesoscale
465 features.

466 Temporal changes in NO₃ and DON concentrations should be more readily detectable within time series
467 data. The model generated NO₃ concentrations rise above the background noise of random THC variability
468 in the IW and DW reservoirs of both the WMS and EMS after 1990 (Figures 4 and 5). The largest
469 anthropogenic enrichment signatures are predicted for DON, however. In EMIW, the anthropogenic DON
470 signal is already observed after the 1970s, with an increase in the mean DON concentrations of 2.1 μM
471 between 1950 and 2030. The latter is much greater than the 0.18 μM variation in DON concentrations
472 associated with random THC fluctuations (Figure 5). Likewise, anthropogenic enrichment of DON should
473 be detectable in EMDW and WMIW after 1980 and in WMDW after 1990 (Figures 4 and 5).

474 The different temporal trends in reactive P and N inputs imply that N:P ratios should be sensitive indicators
475 of anthropogenic nutrient enrichment, with the largest increases predicted for DON:DOP ratios (Figure 7).
476 Reported DON:DOP ratios in the MS tend to be extremely variable, however. They range from 50 to 84,
477 and from 60 to 220, in the photic zone of the WMS and EMS, respectively, and from 67 to 400, and from
478 25 to 260 in WMDW and EMDW, respectively (Santinelli, 2015). The heterogeneity in reported DON:DOP
479 ratios may largely be due to the difficulty in accurately measuring DOP concentrations, which tend to be
480 very low and require careful blank correction. Our modeling results therefore call not only for a more
481 systematic monitoring of DON and DOP concentrations in the MS, but also for the detailed recording of
482 QA/QC procedures.

483 Higher than Redfieldian $\text{NO}_3:\text{PO}_4$ ratios are a defining feature of the MS: deep water $\text{NO}_3:\text{PO}_4$ ratios are
484 probably the most extensively documented feature of nutrient distributions across the WMS and EMS. The
485 existing observational data further show that DW $\text{NO}_3:\text{PO}_4$ ratios tend to be more coherent than the
486 $\text{DON}:\text{DOP}$ ratios; they cluster around 20-23:1 in WMDW and 28:1 in EMDW (Pujo-Pay et al., 2011;
487 Schroeder et al., 2010; Ribera d'Alcalà et al., 2003; Moutin and Raimbault, 2002; Kress and Herut, 2001;
488 Béthoux et al., 1998; Krom et al., 1991). The greater spatial consistency of the DW $\text{NO}_3:\text{PO}_4$ ratios are
489 likely due to the higher concentrations of PO_4 in DW (170-400 nM for PO_4 in DW, compared to 25-60 nM
490 for DOP in IW and DW) leading to lower relative errors on the $\text{NO}_3:\text{PO}_4$ ratios compared to the $\text{DON}:\text{DOP}$
491 ratios. Our mass balance calculations predict that anthropogenic nutrient enrichment should be detectable
492 in the $\text{NO}_3:\text{PO}_4$ ratios of WMDW and EMDW after 2000 and 2010, respectively (Figures 7 and S9).

493 Variations in THC are predicted to cause significant noise in the annual primary production rates of the
494 WMS (Figure 8). A key role of circulation in controlling primary production in the north-west
495 Mediterranean is highlighted by two open ocean convection events that took place in spring 2011: these two
496 events supplied the same amount of PO_4 to the SW as annual riverine discharge and atmospheric deposition
497 together (Severin et al., 2014). In the WMS, DW formation is linked to upwelling of WMIW into WMSW.
498 A similar coupling is absent in the EMS where little upwelling into the SW occurs (Figure 1). This explains
499 why the range of primary productivity associated with random variations in THC is much broader in the
500 WMS than EMS (Figure 8). Overall, our results imply that the relative increase in primary productivity due
501 to anthropogenic nutrient enrichment should be more easily detectable in the EMS than WMS.

502 The largest driver of the predicted changes in the mean primary productivity of the WMS over the period
503 1950-2030 is the riverine supply of reactive P input (Figure S12). For the EMS, variations in atmospheric
504 deposition are the main cause of changes in primary productivity until the beginning of the 21st century. By
505 2030, however, direct wastewater discharges and riverine discharge may catch up with atmospheric
506 deposition as non-marine sources of reactive P to the EMS. Interestingly, the model predicts that riverine
507 inputs to the WMS are as important in controlling primary productivity in the EMS as riverine inputs directly
508 to the EMS, because of the large contribution of inflow of WMSW via the Strait of Sicily to the reactive P
509 budgets of the EMS (Figure 3, see also Powley et al., 2017).

510 **4.3 Historical trajectories**

511 The reconstructed historical changes in THC between 1960 and 2000 significantly affect the distributions
512 of P and N, as well as primary productivity (Figure 6, S6, S7, S8, S10 and S11). The combination of
513 anthropogenic P and N inputs plus historical THC (Simulation 5) yields primary production rates ranging

514 from 125 to 234 g C m⁻² yr⁻¹ in the WMS, and from 55 to 86 g C m⁻² yr⁻¹ in the EMS. These values fall
515 within the observed ranges compiled by Berman-Frank and Rahav (2012) for the period 1970-2009: 37-475
516 g C m⁻² yr⁻¹ for the WMS and 10-143 g C m⁻² yr⁻¹ for the EMS. Equally important, Berman-Frank and Rahav
517 (2012) did not observe clear temporal trends in time series data on primary productivity in the WMS and
518 EMS between 1970 and 2009, which is consistent with the model predictions (Figure S11). Thus, the noise
519 in primary productivity data due to the relatively large variations in THC masks the effect of excess
520 anthropogenic nutrient inputs on primary production during the last decades of the 20th century.

521 A comparison of the results of Simulations 3 and 5 implies that time series data on dissolved inorganic P
522 and N concentrations in the WMIW primarily record the impact of variations in THC, while a long-term
523 increasing trend between 1960 and 2000 linked to anthropogenic nutrient enrichment may be inferred for
524 the EMIW (Figure 6). Nevertheless, even for EMIW, the variations in PO₄ and NO₃ resulting from the
525 reconstructed circulation are much greater than those resulting from nutrient enrichment as also proposed
526 by Ozer et al. (2016). Note that all P and N concentrations in the historical simulation scenarios, and indeed
527 all model simulations in this study, are within the range of dissolved reactive P and N concentrations
528 reported across both the WMS and EMS (Table S3).

529 For WMIW, Moon et al. (2016) recently reported that, between 1990 and 2005, PO₄ and NO₃ concentrations
530 rose on average by 70 nM and 1.98 μM per decade, respectively. For EMIW, the same authors report
531 increases of 50 nM PO₄ and 0.78 μM NO₃ per decade, over the period 1985-2000. They further propose that
532 increasing anthropogenic inputs of PO₄ and NO₃, via riverine discharge and atmospheric deposition,
533 respectively, are responsible for the observed concentration trends. This hypothesis contrasts with our
534 analysis, which suggest that circulation changes mostly modulate the PO₄ and NO₃ trajectories in the IW
535 reservoirs, rather than changing anthropogenic inputs. For example, according to Simulation 3, the
536 maximum increases in PO₄ concentrations of WMIW and EMIW during the 1950-2030 period that can be
537 attributed to nutrient enrichment alone are 27 nM and 17 nM, respectively, that is, much less than the
538 observed decadal increases.

539 When historical changes in THC are accounted for, however, the model-derived trajectories are consistent
540 with the observed PO₄ and NO₃ concentration changes reported by Moon et al. (2016). In Simulation 5, the
541 PO₄ concentration of WMIW increases by 49 nM between 1990 and 2000, and that of EMIW by 27 nM
542 between 1985 and 2000. Over the same time periods, the increases in NO₃ concentrations are 1.4 μM and
543 1.0 μM in WMIW and EMIW, respectively (Figure 6). These predicted increases in concentration are of
544 comparable magnitudes as those observed by Moon et al. (2016). Even with attenuated water fluxes

545 (Simulation 7), the variations in IW PO_4 and NO_3 concentrations during the last decade of the 20th century
546 markedly exceed those due to anthropogenic nutrient inputs alone (Simulation 3). We therefore propose that
547 variations in THC are a major contributor to the observed increases in PO_4 and NO_3 concentrations in the
548 IW reservoirs from 1985 to 2000. This is in line with Ozer et al. (2016) who suggest that temporal trends in
549 observed EMIW NO_3 and PO_4 concentrations are primarily driven by circulation changes.

550 The lack of substantial change in the predicted DW $\text{NO}_3:\text{PO}_4$ ratio of the WMS prior to 1990 (Figure S10)
551 is in agreement with the observations of Béthoux et al. (1998; 2002). Pasqueron de Fommervault et al.
552 (2015) further report an increase by 4.2 units between 1990 and 2010 in the $\text{NO}_3:\text{PO}_4$ DW ratio at the
553 DYFAMED station located in the WMS. Although this increase is significantly larger than the
554 corresponding WMS-wide DW increase of the $\text{NO}_3:\text{PO}_4$ ratio predicted by our model in both the ensemble
555 and historical simulations, it could reflect DYFAMED's location close to the land-derived nutrient inputs
556 along the northern coast of the WMS.

557 **5 CONCLUSIONS**

558 At first the MS would seem the ideal setting to observe whole-basin impacts of anthropogenic nutrient
559 enrichment: it is almost entirely surrounded by land with a large and rapidly growing coastal population.
560 However, as shown here, several factors complicate the unequivocal detection of anthropogenic signatures
561 in time series P and N concentrations in the offshore waters of the MS. First, marine sources play a dominant
562 role in the P and N budgets of the MS. For the WMS, reactive P and N are overwhelmingly supplied by
563 inflow of ASW through the Strait of Gibraltar and EMIW through the Strait of Sicily. For the EMS, the
564 major reactive source of reactive P and N is WMSW flowing in through the Strait of Sicily, although
565 atmospheric deposition represents a reactive N input of comparable magnitude as the WMSW inflow.
566 Second, the anti-estuarine circulation of the MS efficiently removes a large fraction of newly added
567 nutrients, thus further diluting potential anthropogenic signatures in the temporal and spatial distributions
568 of P and N concentrations. Third, significant variability in IW and DW formation rates introduces noise in
569 time series reactive P and N concentrations. Ignoring the effects of variations in THC therefore greatly
570 increases the possibility of false detection of anthropogenic nutrient enrichment in the water column of the
571 MS.

572 Over the 1950-2030 period, we estimate that the total reactive P and N inputs to the WMS (EMS) increase
573 by up to 16 (39) and 51 (98) % relative to their 1950 values, respectively. According to our simulation
574 results, however, the accompanying changes in water column PO_4 and DOP concentrations between 1950

575 and 2030 should hardly be discernible over the background noise created by random inter-annual variability
576 in THC. By contrast, the temporal trajectories of DON concentrations should yield more reliable records of
577 the changes in anthropogenic inputs, especially in the EMS. Within the IW and DW, anthropogenic nutrient
578 enrichment should be detectable in DON time series after around 1970 and 1980 in the EMS and WMS,
579 respectively, assuming that the DON concentration data are acquired using artifact free sampling and storage
580 techniques, and high accuracy analytical methods.

581 Following from the above, the model calculations predict relatively large changes in the molar DON:DOP
582 ratio with time. Nevertheless, the existing time series data on DON:DOP ratios may not yield reliable
583 records of anthropogenic nutrient inputs because of measurement artifacts. For instance, we predict that
584 between 1950 and 2030 the mean molar DON:DOP ratio in EMIW should increase from 67 to 100, a change
585 exceeding the DON:DOP variability produced by inter-annual THC fluctuations. However, the existing
586 observational data show a very high spatial heterogeneity of DON:DOP ratios across the MS, which we
587 attribute in large part to the difficulties associated with accurately measuring the low concentrations of DOP
588 in the waters of the MS, and, to a lesser extent, those of DON. In comparison, the reported $\text{NO}_3:\text{PO}_4$ ratios
589 in the DW of the WMS and EMS are much more consistent, likely because of the much higher quality of
590 dissolved inorganic P and N concentration data compared to their organic counterparts. According to the
591 model calculations, the increases in $\text{NO}_3:\text{PO}_4$ DW ratios driven by anthropogenic P and N inputs supplied
592 by land-based sources should be discernable after 2000 in the WMS and after 2010 in the EMS.

593 The model simulations imply that variations in the annually averaged primary production of the WMS are
594 dominated by the year-to-year variations in DW formation rates rather than by changing anthropogenic
595 nutrient inputs. In the EMS, however, annual primary production should be more sensitive to the changes
596 in nutrient inputs from the surrounding land. These differences between the WMS and EMS are further
597 reflected in the broader ranges of dissolved reactive P and N concentrations produced by inter-annual THC
598 variability in the WMS compared to the EMS. Thus, basin-wide anthropogenic nutrient signals and
599 responses to nutrient enrichment are more likely to be detected in time series data from the EMS than the
600 WMS, provided the data have sufficient spatial and temporal coverage, appropriate sampling and accurate
601 analytical procedures are used, and variations in THC are taken into account.

602 By unraveling the relative roles of anthropogenic nutrient enrichment and thermohaline circulation in
603 driving inter-annual changes in nutrient distributions of the MS, our mass balance model provides a
604 quantitative framework to (1) hind- and fore-cast nutrient trajectories under changing P and N inputs and
605 THC regimes, (2) interpret existing time series data on reactive P and N concentrations and ratios in the

606 WMS and EMS, and (3) explain why the trophic state of the MS responds differently to anthropogenic
607 nutrient inputs than other landlocked marine basins, such as the Baltic Sea. Additionally, and equally
608 important, the model results yield practical recommendations for a more effective monitoring of the
609 biogeochemical state of the MS. In particular, we strongly recommend the sustained acquisition of water
610 column P and N data over decadal time periods using appropriate methods that are able to accurately
611 determine the low concentrations of P and N encountered in the offshore water masses of the MS.
612 Furthermore, the monitoring programs should include measurements of DOP and DON, because the
613 concentrations of DON and the DON:DOP ratios are predicted to be among the most sensitive indicators of
614 changing nutrient inputs to the MS (if properly measured!). Especially useful would be time series nutrient
615 data obtained at fixed locations (similar to the DYFAMED site) spread across the entire WMS and EMS.
616 Given the importance of the bidirectional exchanges through the Straits of Gibraltar and Sicily for the
617 reactive P and N budgets, the Straits should be priority locations for systematic nutrient analyses and flow
618 determinations.

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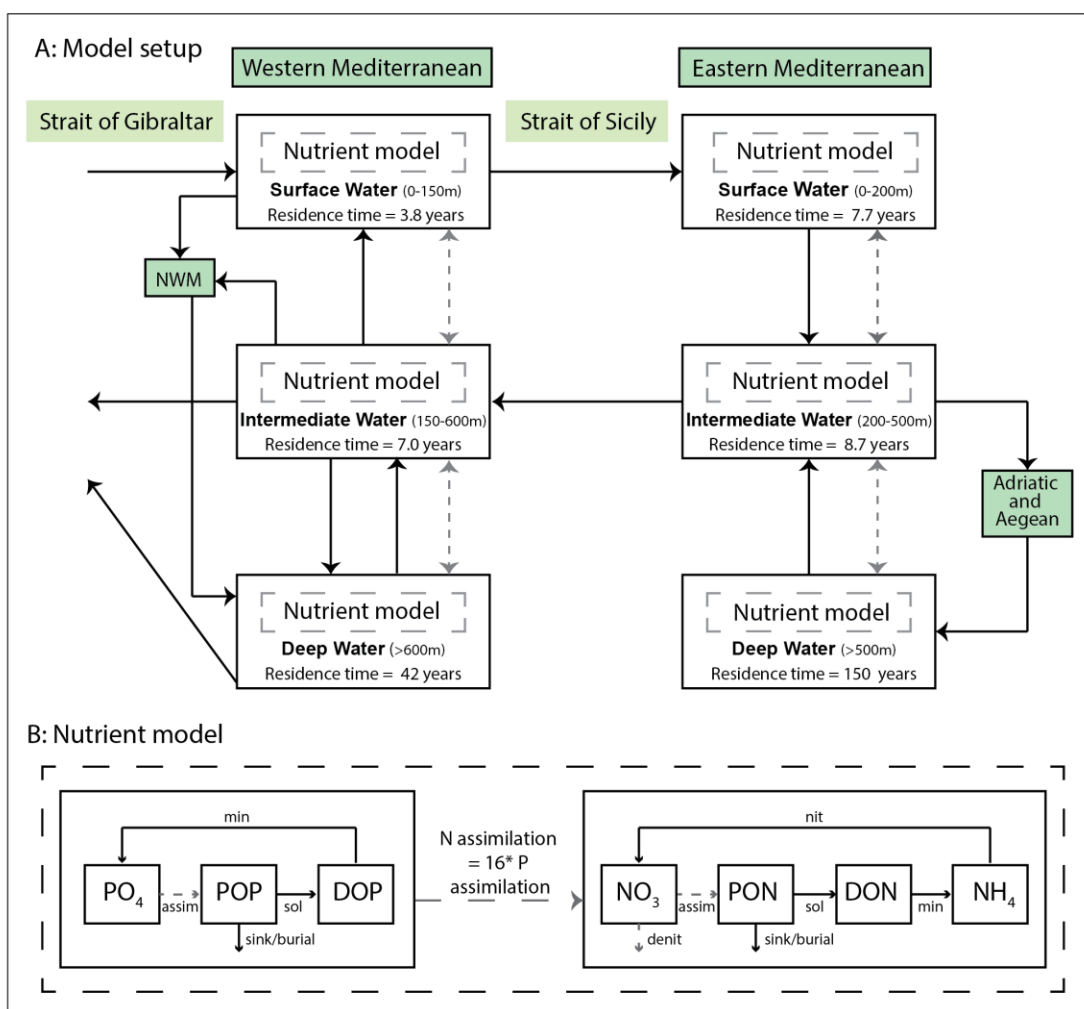
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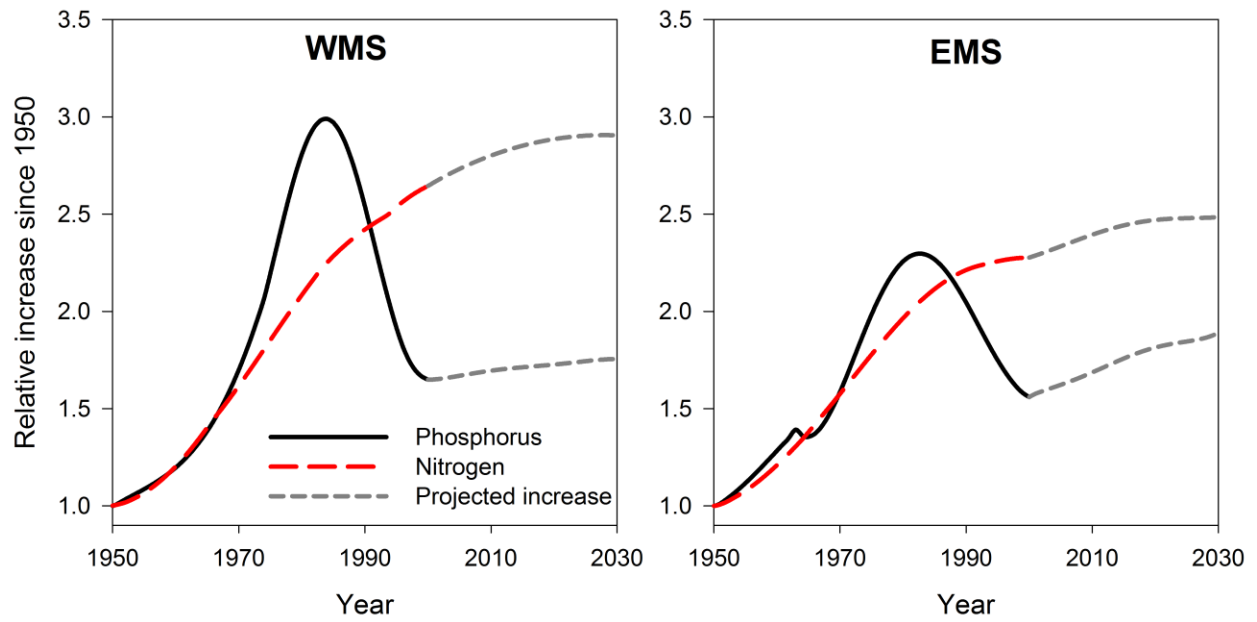
825 **FIGURE CAPTIONS:**

826
 827 **Figure 1:** Conceptual model framework. A) Circulation structure and water reservoirs: black arrows
 828 represent water fluxes, grey dashed arrows turbulent mixing fluxes. Residence time represents the water
 829 residence time in the 1950 steady state model. B) Nutrient model: assimilation of P and N only occur in the
 830 surface water (SW) reservoirs and denitrification in the deep water (DW) reservoirs (grey dashed arrows).
 831 Abbreviations: NWM = Northwest Mediterranean; assim = assimilation; sol: solubilisation; min:
 832 mineralization; nit: nitrification; denit: denitrification. Modified from Powley et al. (2017).



834 **Figure 2:** Total anthropogenic forcing functions for phosphorus (black continuous line) and nitrogen (red
835 dashed line) inputs into the WMS and EMS. See text for detailed discussion.

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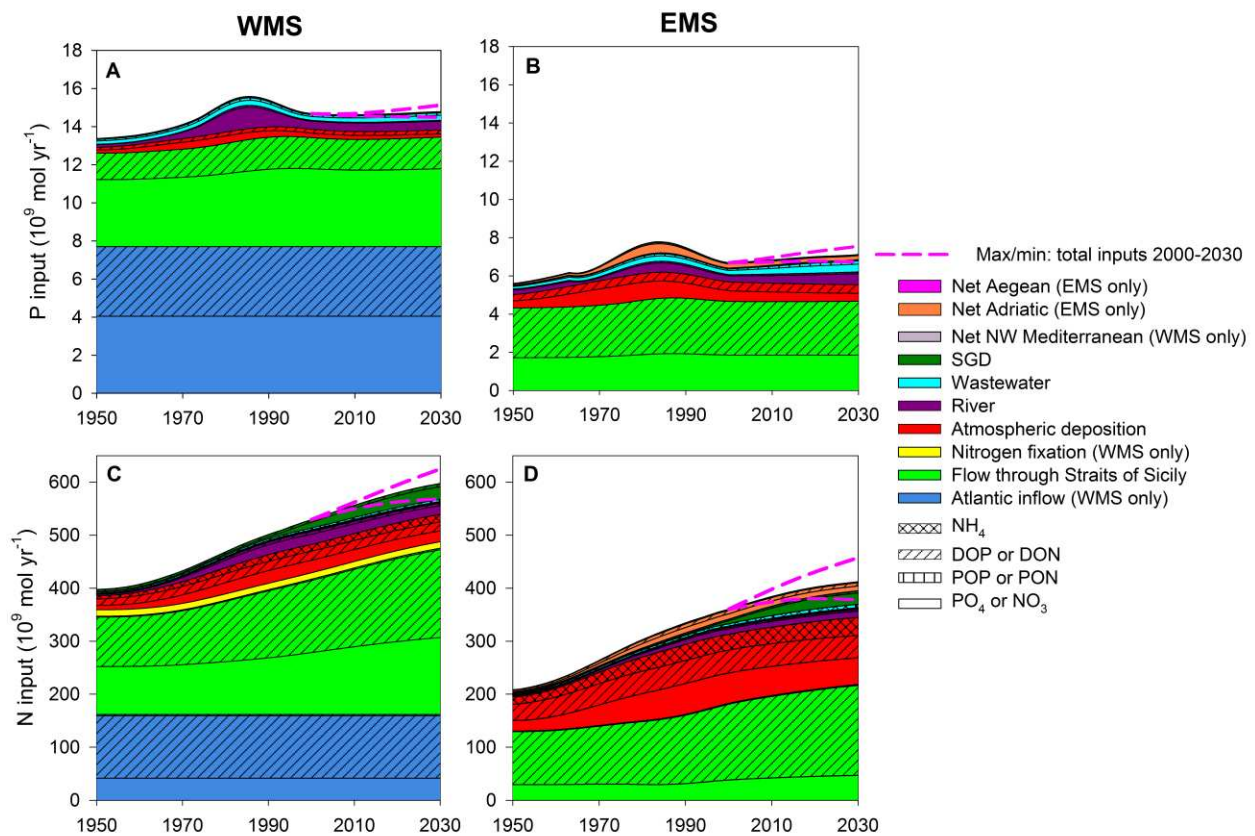


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838

839 **Figure 3:** Sources and speciation of reactive phosphorus (A+B) and reactive nitrogen (C+D) inputs into the
 840 WMS (A+C) and EMS (B+D) between 1950 and 2030. The changes with time are calculated from the
 841 forcing functions described in Table 1, Table S1 and Figure S1, with the exception of the P and N exchanges
 842 through the Strait of Sicily. The later are based on the model results of Simulation 3 (constant circulation).
 843 Colours refer to the sources of external P and N inputs, hatchings to the chemical speciation of P and N.
 844 Pink dashed lines are maximum and minimum estimates of predicted total inputs between 2000 and 2030
 845 (see text for details).

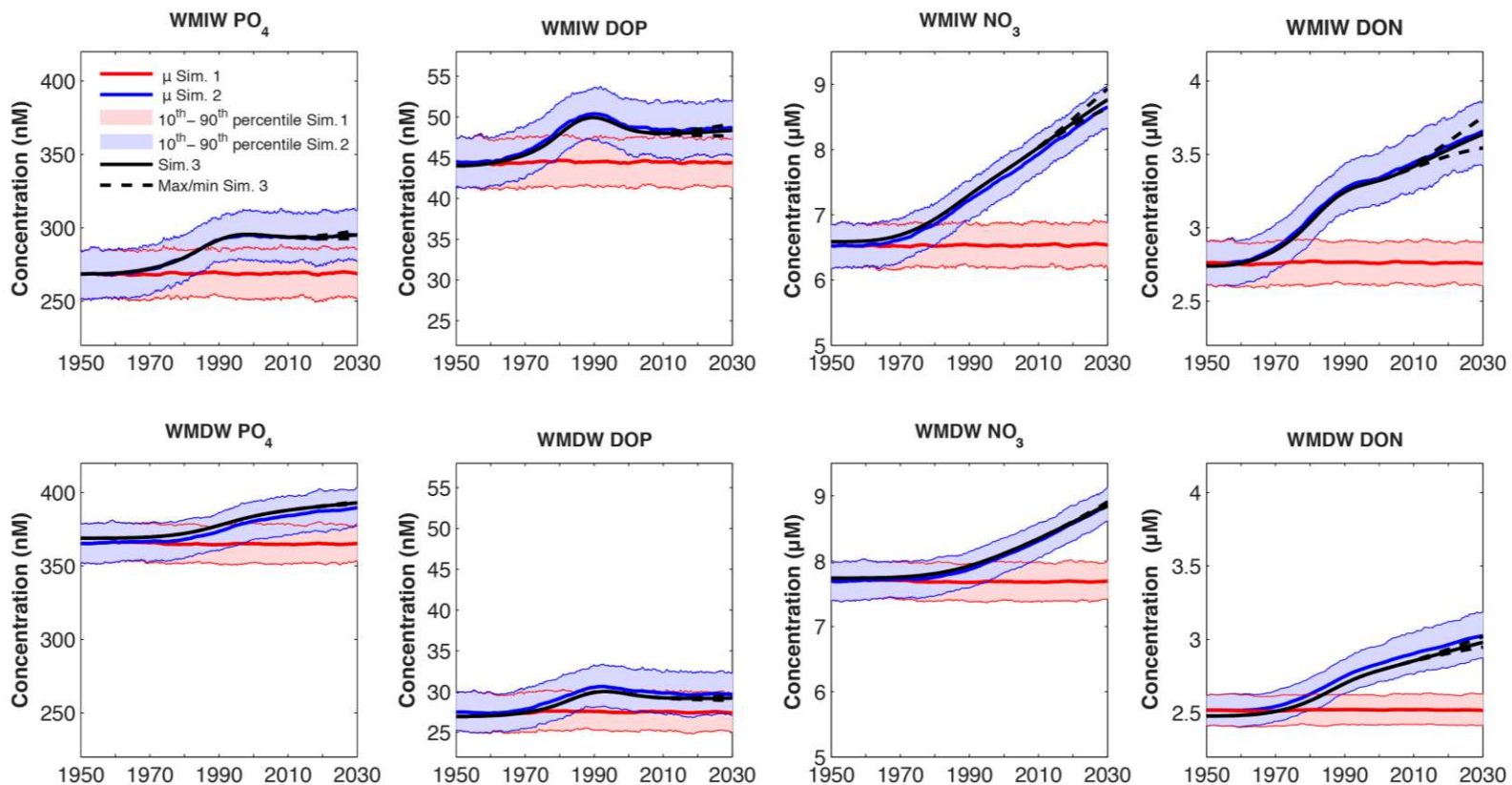
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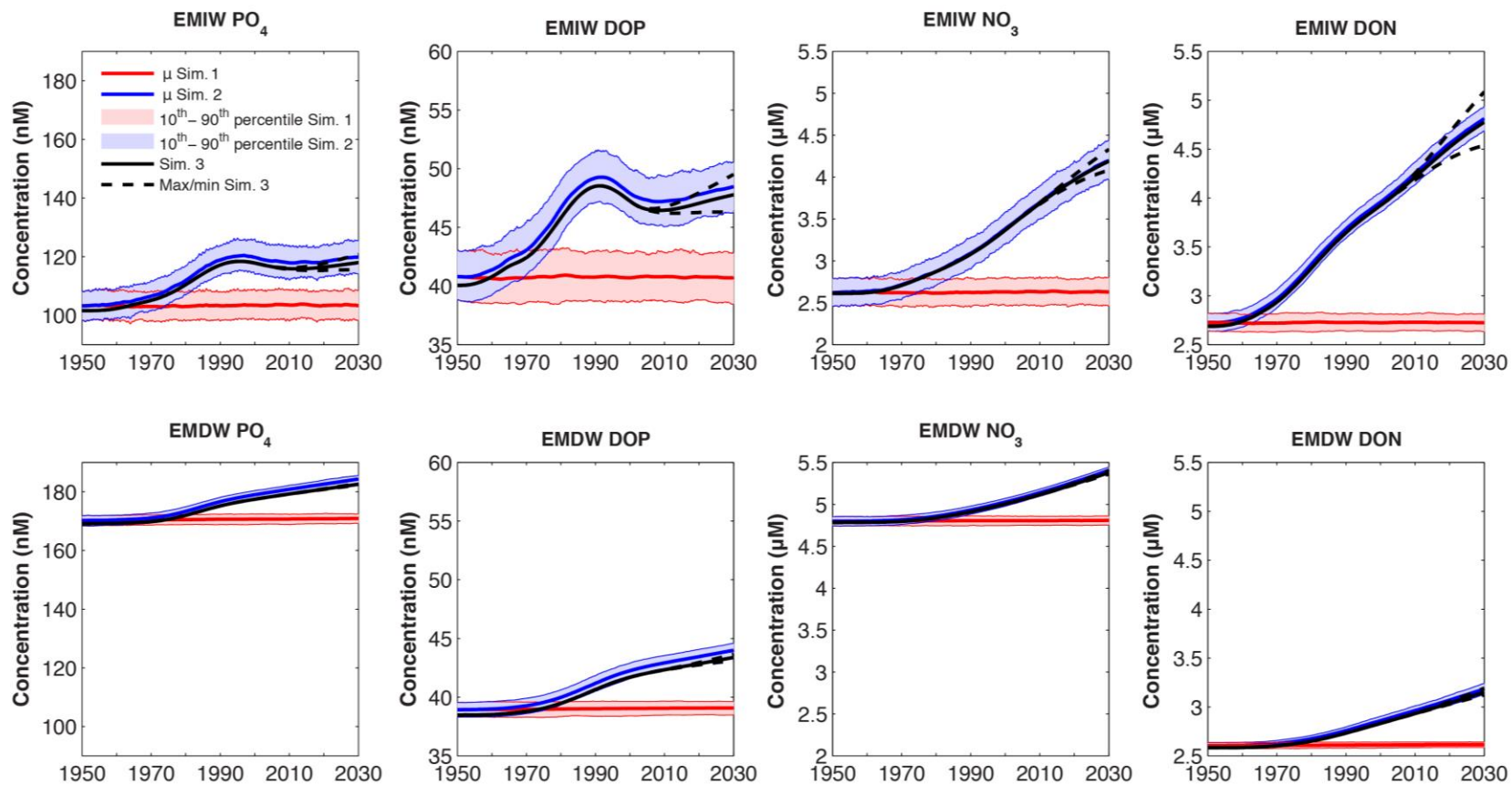
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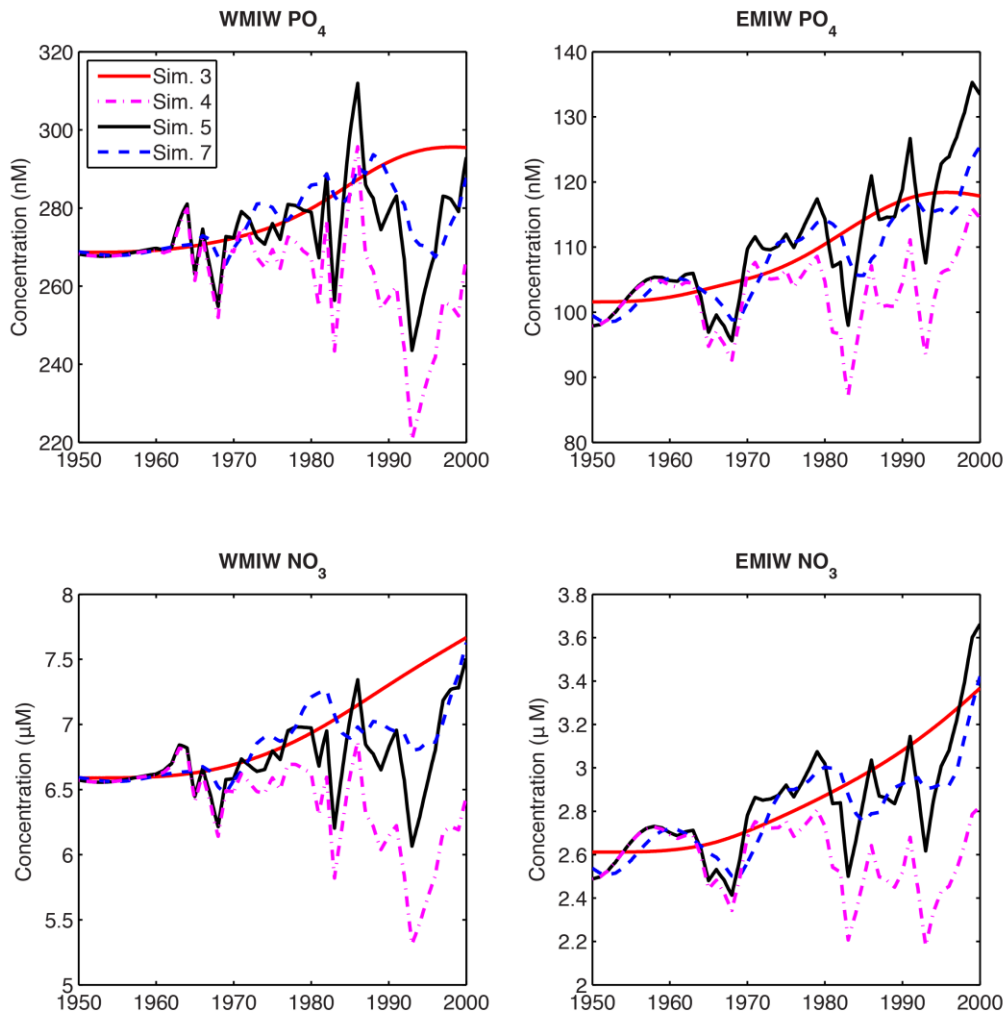
849 **Figure 4:** Comparison of 1950-2030 trajectories of intermediate (IW) and deep water (DW) P and N concentrations for the WMS generated
 850 by the different scenarios: inter-annual variability of thermohaline circulation (THC) alone (Simulation 1; red shading and red lines),
 851 anthropogenic nutrient enrichment plus inter-annual THC variability (Simulation 2; blue shading and blue lines), anthropogenic nutrient
 852 enrichment alone (Simulation 3; black line). Mean, 10th and 90th percentiles of 500 model runs are shown. Dashed lines between 2000 and
 853 2030 represent the ranges obtained by considering maximum and minimum estimates of reactive P and N inputs for this time period. Note y-
 854 axis changes in scale for different species. See text and Table 2 for details on the model runs. Small discrepancies between the mean
 855 concentration trajectories in Simulation 2 and Simulation 3 arise from a change in direction of fluxes between WMIW and WMDW when the
 856 flow through the Strait of Sicily drops below 0.53 Sv.
 857



859 **Figure 5:** Same as Figure 4 but for the EMS.

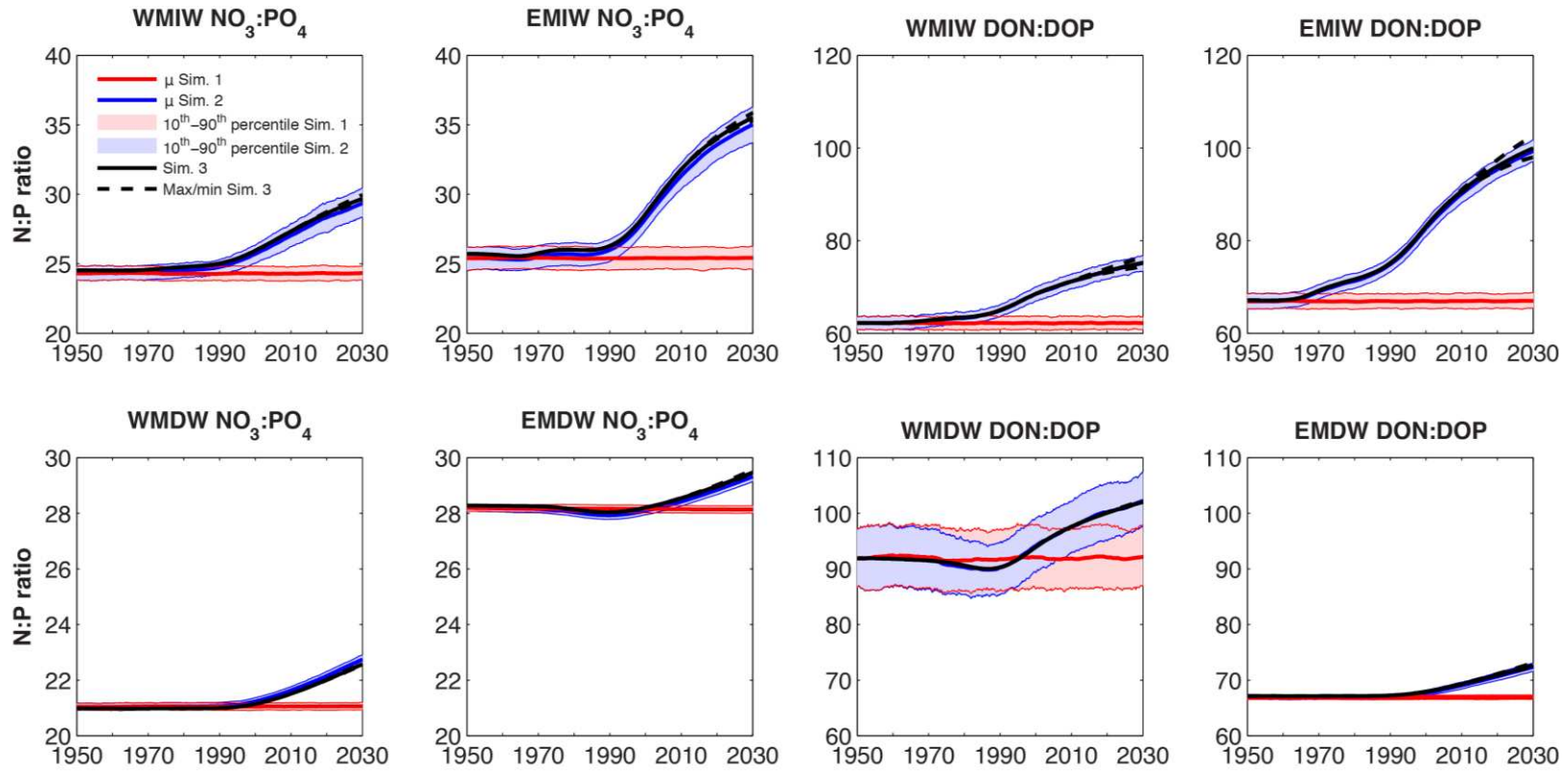


861 **Figure 6:** Trajectories of intermediate water (IW) PO₄ and NO₃ concentrations in WMS and EMS based on
862 reconstructed deep water (DW) formation rates between 1960 and 2000 with constant reactive P and reactive
863 N inputs (Simulation 4); variable (1950-2000) reactive P and reactive N inputs (Simulation 5); and imposing
864 5-year running average DW formation rates with variable reactive P and reactive N inputs (Simulation 7).
865 Also shown are the trajectories for variable (1950-2000) reactive P and N inputs with constant thermohaline
866 circulation (Simulation 3; red line). See text and Figure S3 for details on the historical DW formation rate
867 reconstructions.



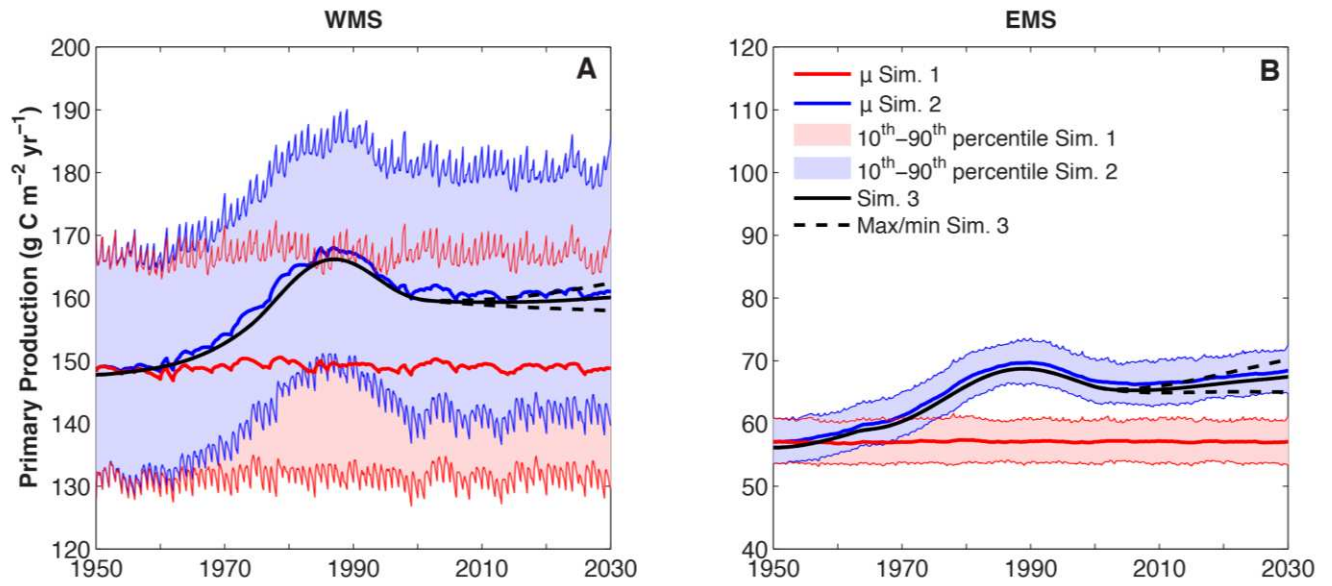
868 **Figure 7:** Same as Figure 4, but for the N:P ratios in the intermediate (IW) and deep water (DW) reservoirs of the WMS and EMS.

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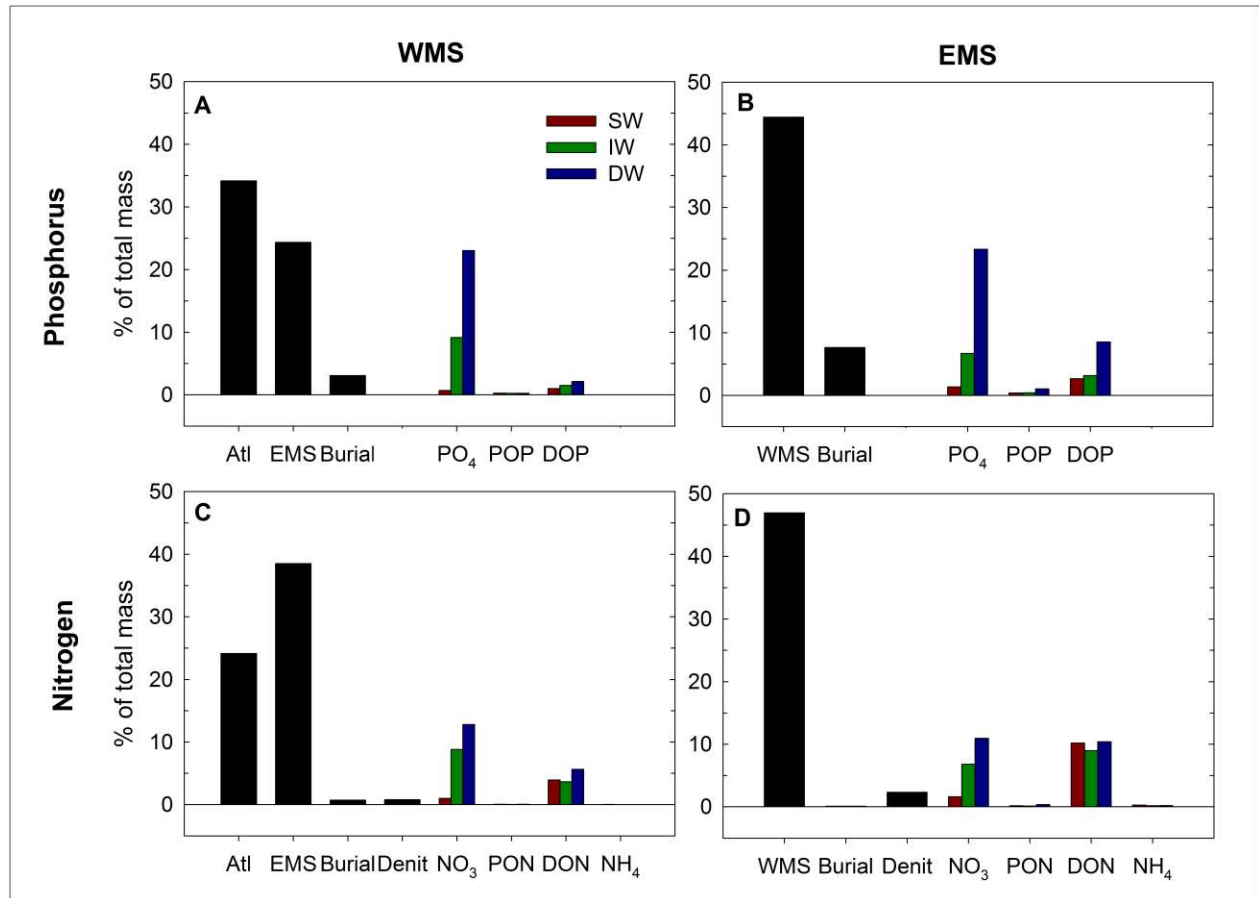


870 **Figure 8:** Same as Figure 4 except for annual primary productivity in WMS and EMS.

871



872 **Figure 9:** Fate of anthropogenic P and N supplied between 1950 and 2030 to the WMS (A and C) and EMS
 873 (B and D), expressed as percentages. Burial, denitrification (Denit) and outflow to Atlantic (Atl), EMS and
 874 WMS refer to the percentages of the total reactive P and N supplied, while accumulation in the water column
 875 reservoirs differentiates between the different chemical species of P and N



877 **TABLE CAPTIONS:**

878 **Table 1:** Summary of the methods used to calculate the 1950 to 2030 anthropogenic forcing functions applied
879 in the mass balance model calculations.

880 **Table 2:** Model simulations combining the various circulation scenarios with constant or variable and reactive
881 P and reactive N inputs.

882 **Table 3:** Parameters of deep and intermediate water formation used to initiate the random circulation scenarios.
883 See text for details. ^aFrom Powley et al. (2016a)

884

885 **TABLE 1:**

Forcing function	Species	Method and data sources
Atmospheric deposition	PO ₄	Deposition of leachable PO ₄ in the WMS and EMS is assumed proportional to changes in acid availability in the atmosphere above the Mediterranean basin (Nenes et al., 2011), estimated through emissions of NO _x and SO ₄ to the atmosphere in Europe, Africa and the Middle East. For 1950-2000 the forcing function is justified in Powley et al. (2014) and references therein. For 2000-2030 data are taken from Lamarque et al. (2013).
	DOP and DON	Deposition of organic matter in both WMS and EMS is assumed proportional to the relative change in 1) organic carbon emissions from biomass burning in the northern hemisphere over 1950 to 2000 (Powley et al., 2014 and references therein), and 2) anthropogenic global organic carbon emissions for 2000-2030 (IPCC, 2013).
	NO ₃ and NH ₄	Deposition estimates in both the WMS and EMS are calculated from the relative changes in 1) NO _x and NH ₄ deposition rates in French and alpine ice core records from 1950 to 2000 (Powley et al., 2014 and references therein) and 2) model predicted dry and wet deposition rates for NO _x and NH ₄ from Africa, Europe, and former USSR and Middle East (2000-2030).
Rivers	P and N	Ludwig et al. (2009) report riverine inputs of P and N to the WMS and EMS for every 5 years between 1963 and 1998. We assume minimal changes in riverine P and N inputs from 1950 to 1963. The relative changes in riverine inputs from 2000 to 2030 are those of Ludwig et al. (2010) based on the Millennium Ecosystem Assessment Scenarios. The relative speciation of P and N are assumed to stay constant with time.
Direct wastewater discharges	N	Wastewater discharges are assumed proportional to the coastal population of each Mediterranean country (FAOSTAT, 2016), weighted towards each country's individual wastewater total N input into the MS (Powley et al., 2016b). A ±5% error is assigned to the 2030 population estimates to represent upper and lower limits.
	P	The N:P ratio of direct wastewater discharges is assumed to follow the same trajectory as the N:P ratio of riverine discharge.
SGD	NO ₃ and NH ₄	The change in inorganic N in SGD is assumed to follow that of inorganic N fertilizer inputs on land with a 30 year time lag (Powley et al., 2017). The forcing function is created using the relative change in total N fertilizer consumption rate in the EU for the WMS and in rest of the world for the EMS between 1920 to 1960 (Erisman et al., 2011), while nitrogenous fertilizer consumption rates per country (FAOSTAT, 2015a), weighted to regional GW discharges (Zekster et al., 2007), are used for the period 1960 to 2000.
	DON	The change in DON in SGD is assumed to follow the application of manure on land with a 30 year time lag (Powley et al., 2017). Manure application rates in the EU are used for the WMS, and in the rest of the world for the EMS, over the 1920 to 1960 period (Erisman et al., 2011) and for each individual country (FAOSTAT, 2015b) weighted to regional GW discharges (Zekster et al., 2007) for 1960 to 2000.
	P	Assumed constant with time as the 2000 P concentration in SGD is very small suggesting that P from fertilizer input is retained within the aquifers.
N ₂ fixation	N	Assumed constant with time due to lack of correlation between nitrogen fixation and nutrient availability (Berman-Frank and Rahav, 2012; Sandroni et al., 2007).

887 **TABLE 2:**

888

Simulation	1	2	3	4	5	6	7
Randomized perturbations in circulation (constant mean): 1950-2030	✓	✓					
Constant circulation: 1950-2030			✓				
Reconstructed historical circulation (year by year): 1960-2000				✓	✓		
Reconstructed historical circulation (5-year moving average):1960-2000						✓	✓
Constant 1950 P and N inputs	✓			✓		✓	
Variable 1950-2030 P and N inputs		✓	✓		✓		✓

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891 **TABLE 3:**

Area	Mean IW/DW rate of formation events (Sv)	Standard deviation (σ) of formation events (Sv)	Probability distribution function	Range (Sv)	% of years IW/DW formation occurs	Mean formation rate (Sv) (all years) ^a	Reference
<i>Years when IW/DW formation occurs</i>					<i>All years</i>		
NWM	1.20	0.68	Lognormal	$0 < x < 3.3$	53	0.61	L'Hévéder et al. (2013)
Levantine	1.10	0.83	Normal	$x - \sigma < x < \sigma + x$	100	1.10	Vervatis et al. (2013)
Adriatic	0.455	0.25	Lognormal	$0 < x < 0.8$	80	0.32	Pinardi et al. (2015)
Aegean	0.069	0.08	Lognormal	$0 < x < 0.38$	62.5	0.04	Vervatis et al. (2013)

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