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Key Points:
- The dynamics of N, P, and the N:P ratio in the Mediterranean Sea were investigated using ~123,100 data points collected between 1985 and 2014
- The recent dynamics of N in the upper Mediterranean Sea has been sensitive to nitrogen input from atmospheric deposition and rivers
- Air N deposition appeared to be larger than riverine influx, whereas the contributions of other processes were minor

Supporting Information:
- Supporting Information S1

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Temporal nutrient dynamics in the Mediterranean Sea in response to anthropogenic inputs

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Abstract The temporal dynamics of the concentrations of nitrate (N), phosphate (P), and the N:P ratio in the upper water column (200–600 m) of the Mediterranean (MED) Sea were investigated using observational data (~123,100 data points) collected between 1985 and 2014. The studied variables were found to evolve similarly in the western and eastern MED Sea. In both basins, the N concentration increased during the first part of the observational period (1985–1998), and the temporal trend of N was broadly consistent with the history of riverine and atmospheric nitrogen input from populated areas in Europe, with a lag period of 20 years. In subsequent years, the N concentration was high and relatively constant between 1998 and 2005, after which N decreased gradually, although the decreasing trend was indistinct in the western basin. In particular, the trend of constant then declining N after 1998 is consistent with the history of pollutant nitrogen emissions from the European continent, allowing a 20 year lag following the introduction of regulation of pollutant nitrogen in the 1970s. The three-phase temporal transition in P in both basins was more consistent with the riverine phosphorus input, with a lag period of 20 years. Our analysis indicates that the recent dynamics of N and P in the upper MED Sea has been sensitive to the dynamics of anthropogenic nitrogen and phosphorus input from atmospheric deposition and rivers.

1. Introduction

The present-day global ocean is subject to widespread nutrient pollution resulting from human activities [*Duce et al.*, 2008; *Galloway et al.*, 2008; *Kim et al.*, 2011; *I.-N. Kim et al.*, 2014]. The rapid increase in emissions of nitrogen oxides (NO_x) resulting from fossil fuel burning and the intensification of agriculture and associated ammonia (NH_3) emissions have led to a threefold to fivefold increase in nitrogen emission to the atmosphere over the past century [*Dentener*, 2006]. Also, a large fraction of the anthropogenically mobilized nitrogen and phosphorus enter waterways through industrial effluents and nonpoint sources including agricultural and urban runoff. These nutrient pollutants are eventually transported to the marine environment, where they often lead to eutrophication, increase in the frequency and severity of harmful algal blooms, and ocean acidification [*Gruber and Galloway*, 2008]. Coastal and marginal seas located in close proximity to highly populated continental areas are particularly subject to these environmental stresses, because the amounts of nutrients entering these seas are generally 1 or 2 orders of magnitude greater than those introduced to the open ocean [*Rabalais*, 2002; *Kim et al.*, 2011]. Both airborne and riverborne anthropogenic nutrients have entered the Mediterranean (MED) Sea over the past 50 years [*Preunkert et al.*, 2003; *Schöpp et al.*, 2003; *Ludwig et al.*, 2009]. In addition, antiestuarine circulation, the oligotrophic nature of surface waters, and its semienclosed nature make the MED Sea more vulnerable to inputs of anthropogenic nutrients. Therefore, the MED Sea is useful for investigating how anthropogenic factors have affected ocean nutrient dynamics over time.

Differentiating spatial and temporal variations in nutrient dynamics is essential in establishing water quality management plans aimed at mitigating the negative impacts of nutrient pollution. To this end, numerous high-quality oceanographic investigations of the hydrodynamic and biogeochemical nature of the MED Sea have been made. Some modeling studies have hinted at a link between the input of anthropogenic nutrients and a buildup of N and P in the MED Sea [*Macias et al.*, 2014; *Powley et al.*, 2014; *Van Cappellen et al.*, 2014], but reports on decadal trends in nutrient concentration dynamics are limited [*Béthoux et al.*, 1998; *Kress et al.*, 2014; *Pasqueron de Fommervault et al.*, 2015]. Although international programs (e.g., Physical Oceanography of the Eastern Mediterranean, an interdisciplinary study of the Almeria-Oran geostrophic front, the Mass Transfer and Ecosystems Response project, Southern European Seas: Assessing and Modeling Ecosystem changes) have made a major contribution to improving knowledge of the biogeochemical processes in the MED Sea, a basin-scale picture of processes responsible for the biogeochemical functioning of this region remains to be done.

The purpose of this study is to provide an integrated description of temporal changes in nutrient dynamics in the MED Sea resulting from anthropogenic causes. To address this issue we compiled observational data on N and P concentrations collected in the MED Sea during the period 1985–2014. As the data were collected by many independent researchers and may therefore include inconsistencies, we performed appropriate adjustments to the entire data set to reconstruct the long-term trends in nutrient concentrations. The temporal evolution of the relative abundance of N over P ($N^* = N - R_{N:P} \times P$, where N and P are the measured concentrations and $R_{N:P}$ is the mean N:P ratio found in the deep water) is also presented. Factors potentially responsible for the observed trends in N, P, and N* are discussed.

2. Data and Methods

2.1. Data Sources

We analyzed hydrography and dissolved inorganic nutrients data (~123,100 data points) archived in the Policy-oriented Marine Environmental Research in the Southern European Seas database (PERSEUS) (http://isramar.ocean.org.il/perseus_data/) and the Scientific Information Systems for the SEA database (SISMER) (http://seadatanet.maris2.nl/v_cdi_v3/search.asp) (Figure S1 in the supporting information). Data collected prior to 1985 were not included in our analysis because few data for the period 1970–1985 were available. Such a data gap prevented us from reconstructing the trends in nutrient concentrations earlier. We only used data with concentrations $>0.1\ \mu\text{mol kg}^{-1}$ for N and $>0.01\ \mu\text{mol kg}^{-1}$ for P, which are the approximate analytical detection limits for these nutrients [*Zhang et al.*, 2001].

The MED Sea data were evaluated separately for the western and eastern basins because the deep water evolves differently in each basin as a consequence of the presence of a sill (400 m depth) extending from Sicily to the North African coast, effectively preventing exchange of deep water between the two basins. The analysis was performed on data collected in Levantine Intermediate Water (LIW) having density values of $\sigma_0 = 28.84–29.16$ (S = 38.47–38.80 and T = 13.1–15.1 °C) in the western basin and of $\sigma_0 = 28.74–29.26$ (S = 38.40–39.00 and t = 13.0–14.5°C) in the eastern basin [*Roether et al.*, 1998; *Millot*, 1999; *Schröder et al.*, 2006; *Hainbucher et al.*, 2014]. LIW formed in the Eastern Mediterranean flows westward across the MED and enters the Atlantic Ocean through the Straits of Gibraltar [*Tanhua et al.*, 2013a]. Since LIW is mostly found in a depth range of 200–600 m, the analysis avoided the large seasonal variability in hydrological and chemical properties observed in water masses shallower than 200 m, which occasionally overwhelms the temporal trends in surface nutrient dynamics. In addition, the analysis is suitable for assessing recent temporal trends in nutrient dynamics because the ventilation ages of LIW (5–40 years; calculated as the mean of the transient time distribution) are broadly consistent with the history of input of anthropogenic nutrients [*Schneider et al.*, 2014; *Stöven and Tanhua*, 2014]. Note that the residence time of the water is typically less than the ventilation age.

2.2. Data Consistency

The accuracy of temporal trends in N and P concentrations detected in our analysis is dependent on the internal consistency of the data sets used. It was therefore essential to check whether the data sets used were internally consistent, given that their underpinning measurements have involved numerous independent investigators and a period of 30 years. Ensuring internal consistency was based on two key assumptions: (1) the concentrations of N and P of the oldest water mass found in the MED Sea (typically centered at approximately 1000 m depth) remained essentially unchanged during the period in which the data used in our analysis were collected (1985–2014) [*Kress et al.*, 2014; *Stöven and Tanhua*, 2014] and (2) data obtained from the 2001 and 2011 Meteor cruises provided a reliable reference against which all data sets were compared, and, if necessary, adjusted (Table 1). The only likely cause for a change in the N and P concentrations of the oldest water mass is the input of anthropogenic N and P. However, such water mass has typically been in place for >100 years [*Lee et al.*, 2011] and thus contain little anthropogenic N and P. Therefore, assumption (1) is probably valid. Assumption (2) was considered reasonable because the group involved in nutrient analyses during the Meteor cruises strictly followed the analytical protocols recommended by the World Ocean Circulation Experiment and Global Ocean Ship-based Hydrographic Investigations Program [*Tanhua et al.*, 2013b].

Table 1. Consistency References Used in the Study[a]

	Depth (m)	Potential Density (σ_0)	N (μmol kg^{-1})	P (μmol kg^{-1})
Western MED	900–1100	29.11 ± 0.02	7.69 ± 1.06	0.36 ± 0.07
Eastern MED	900–1100	29.18 ± 0.02	4.97 ± 0.51	0.19 ± 0.03

[a]The reference concentrations were deduced from the data obtained during the M51/2 cruise in 2001 and the M84/3 cruise in 2011 (available at http://cchdo.ucsd.edu/).

The N and P concentrations and hydrographic properties of the deep water in the western and eastern MED Sea are distinctively different [*Pujo-Pay et al.*, 2011; *Tanhua et al.*, 2013a]. In our analysis, only data from individual data sets that fell within the specified depth and density ranges (density range of $29.09 \le \sigma_\theta \le 29.17$ for the western basin and $29.15 \le \sigma_\theta \le 29.30$ for the eastern basin; depth range of 900–1100 m in both basins) were compared against the basin average calculated from Meteor data, which also met the same specifications. The data sets were adjusted based on any differences found. The small difference between the density ranges can be attributed to the differences in salinity and temperature of those water masses [*Özsoy et al.*, 2013; *Tanhua et al.*, 2013a]. The mean corrections for the western MED Sea were -0.27 ± 1.39 μmol kg^{-1} N and -0.01 ± 0.08 μmol kg^{-1} P, whereas those for the eastern MED Sea were 0.02 ± 0.96 μmol kg^{-1} N and -0.01 ± 0.06 μmol kg^{-1} P. When the adjustment was applied, much of the noise in the original unadjusted data was removed, and the adjusted N and P concentrations showed much tighter correlations (Figure S2).

The temporal trends in the relative abundance of N over P were also evaluated by calculating N* at each sampling location, where N* is defined as $N^* = N - R_{N:P} \times P$. Here $R_{N:P}$ is the deep water N:P ratio in the MED Sea, which has been reported to be 23 for the western MED Sea and 28 for the eastern MED Sea [*Krom et al.*, 1991; *Kress et al.*, 2003; *Pujo-Pay et al.*, 2011]. Reasons for the differences between the western and eastern MED Sea N:P ratios remain to be elucidated, but one explanation relates to differences in external N supply [*Krom et al.*, 2010; *Markaki et al.*, 2010].

2.3. Atmospheric Emission and Deposition of Nitrogen and Riverine Inputs of Nitrogen and Phosphorus

For the period 1960–1980, the European atmospheric nitrogen emissions were derived from the Regional Acidification Information and Simulation model of the International Institute for Applied Systems Analysis using European national statistics on economic and agricultural activities, energy consumption levels, fuel characteristics, and emission control measures [*Alcamo et al.*, 1990]. For the years subsequent to 1980, the nitrogen emission data were used [*Adams et al.*, 2012].

The historical atmospheric deposition of nitrogen pollutant was estimated by combining the temporal function of anthropogenic nutrient forcing [*Powley et al.*, 2014] with the chemical transport model of the Meteorological Synthesizing Centre of the European Monitoring and Evaluation Programme.

To assess the riverine fluxes of nitrogen and phosphorus into the MED Sea for the period 1963–1998, we used data estimated from total freshwater discharges, riverine nutrient concentrations, and climatic parameters [*Ludwig et al.*, 2009]. In subsequent years, no relevant data are available.

The data for nutrient input via atmospheric deposition and rivers were used for identifying major source of nutrients in the MED Sea and reconstructing the budget of anthropogenic nutrients (Figure S3).

3. Results

3.1. Temporal Trends of Seawater N, P, and N* in the MED Sea

In the western basin the seawater concentrations of both N and P increased from 1989 until 2000 and remained high (or slightly decreased) thereafter (Figure 1a); the ratio of N change to P change was approximately constant during the study period, resulting in little temporal change in N*. In the eastern basin the concentrations of both N and P increased between 1985 and 1998 (Figure 1b). After a period of high levels of N and P between 1998 and 2005, both N and P gradually decreased thereafter. A similar decrease in N and P concentrations were reported for the easternmost part of the eastern MED [*Ozer et al.*, 2016]. The rate of increase in N was relatively lower than that in P between 1985 and 1998, which resulted in a trend of

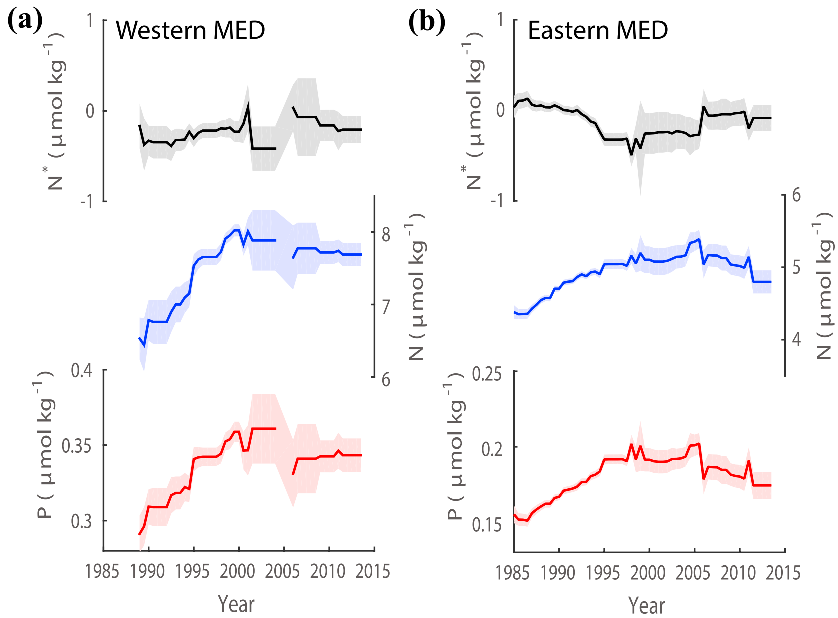

Figure 1. Plot of the 5 year moving average for total N* (black line), N (blue line), and P (red line) data collected in (a) the western Mediterranean (MED) Sea and (b) the eastern MED Sea**.** The color shading indicates the range of the 95% confidence intervals. Note that different numerical scales were used for each plot.

decreasing N*. In subsequent years the rate of N decrease was slightly lower than that of P, resulting in a slight increase of N*.

Examination of only the periods of increasing N and P concentrations (1990–2005 for the western basin and 1985–2000 for the eastern basin) showed that the rate of increase of N and P varied with sampling locations (Figure 2). Both N and P generally increased in all subregions; this trend of increase was particularly pronounced in the open ocean region of the eastern basin, indicating a possible influence of nutrient input from the adjacent eastern European countries.

Overall, the rates of increase in N and P in the western basin (1.89 μmol N kg^{-1} $decade^{-1}$ and 0.07 μmol P kg^{-1} $decade^{-1}$) were considerably higher than those in the eastern basin (0.78 μmol N kg^{-1} $decade^{-1}$ and 0.05 μmol P kg^{-1} $decade^{-1}$).

3.2. Trends of Anthropogenic Nutrient Input Into the MED Sea

The riverine influx of nitrogen continued to increase until the early 1990s and thereafter stabilized at the maximum level (the blue solid lines in Figure 3). However, the riverine input of phosphorus increased until the early 1980s and thereafter decreased because of improvements in wastewater treatment.

Considerable atmospheric emissions of pollutant nitrogen from the European continent began in the 1950s and rapidly increased until the late 1970s. Agreements resulting from the Convention on Long-Range Trans-boundary Air Pollution (1979) came into force in the early 1980s and placed limits on the emissions of pollutant nitrogen. As a result, the temporal trend in emissions of pollutant nitrogen from Europe over the past 50 years has shown a three-phase transition characterized by increase-constant-decline (the solid red lines in Figure 3).

4. Discussion

The results presented here revealed similar patterns in the temporal dynamics of nutrients in the western and eastern basins of the MED Sea. Specifically, in both basins N and P concentrations rapidly increased from 1985 until 2000, plateaued at high levels for a brief interval, and then decreased. The underlying causes for these trends are discussed below.

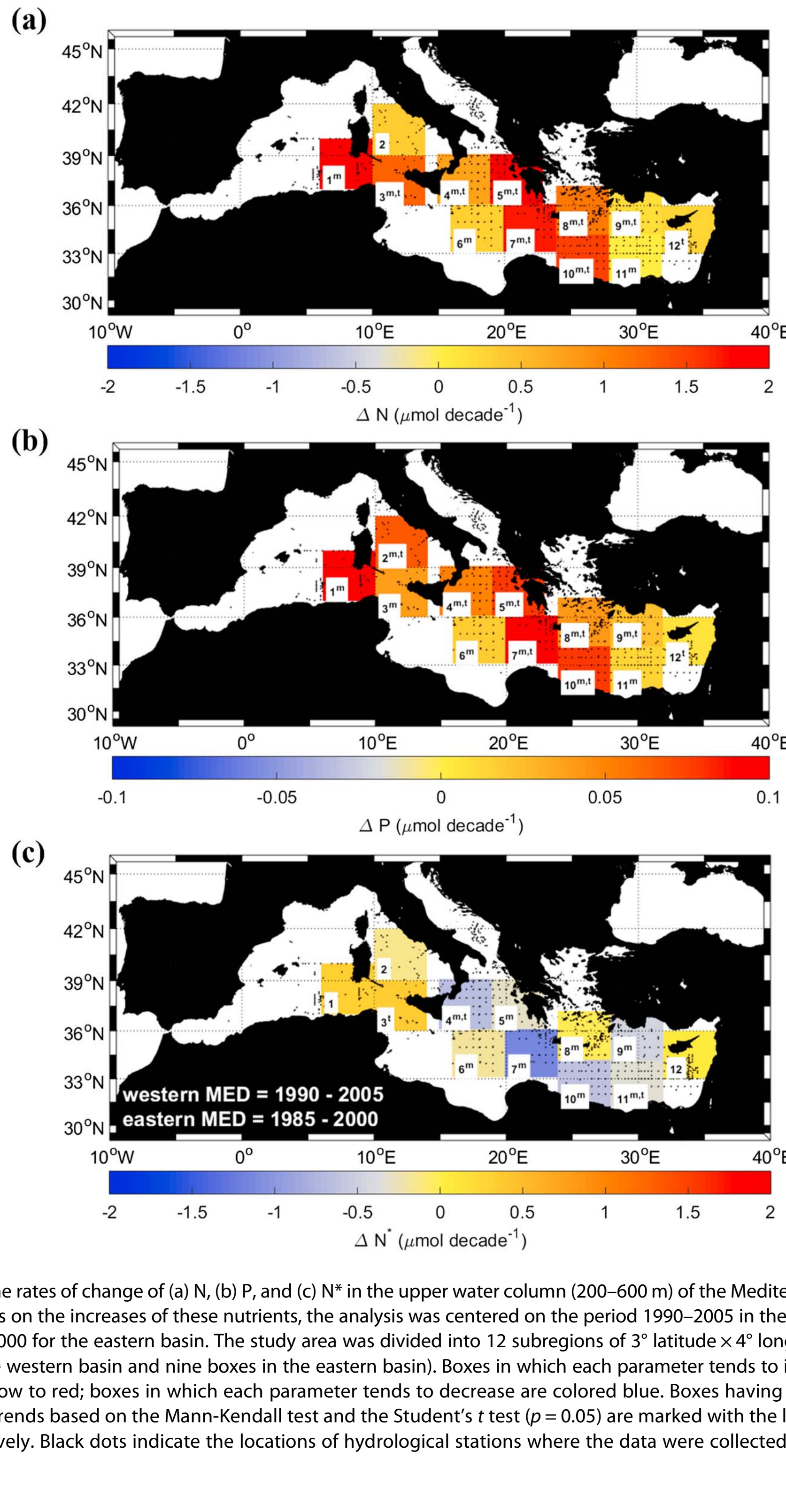

Figure 2. The rates of change of (a) N, (b) P, and (c) N* in the upper water column (200–600 m) of the Mediterranean (MED) Sea. To focus on the increases of these nutrients, the analysis was centered on the period 1990–2005 in the western basin and 1985–2000 for the eastern basin. The study area was divided into 12 subregions of 3° latitude × 4° longitude (three boxes in the western basin and nine boxes in the eastern basin). Boxes in which each parameter tends to increase are colored yellow to red; boxes in which each parameter tends to decrease are colored blue. Boxes having statistically significant trends based on the Mann-Kendall test and the Student's *t* test ($p = 0.05$) are marked with the letters "m" and "t," respectively. Black dots indicate the locations of hydrological stations where the data were collected.

4.1. Anthropogenic Nutrient Inputs

The major sources of nutrients to the MED Sea include atmospheric deposition and riverine runoff [*Krom et al.*, 2004]. Although submarine groundwater discharge may be an additional source of nutrients to the MED Sea [*Rodellas et al.*, 2015], it is not known if it varied with time unlike the atmospheric and runoff

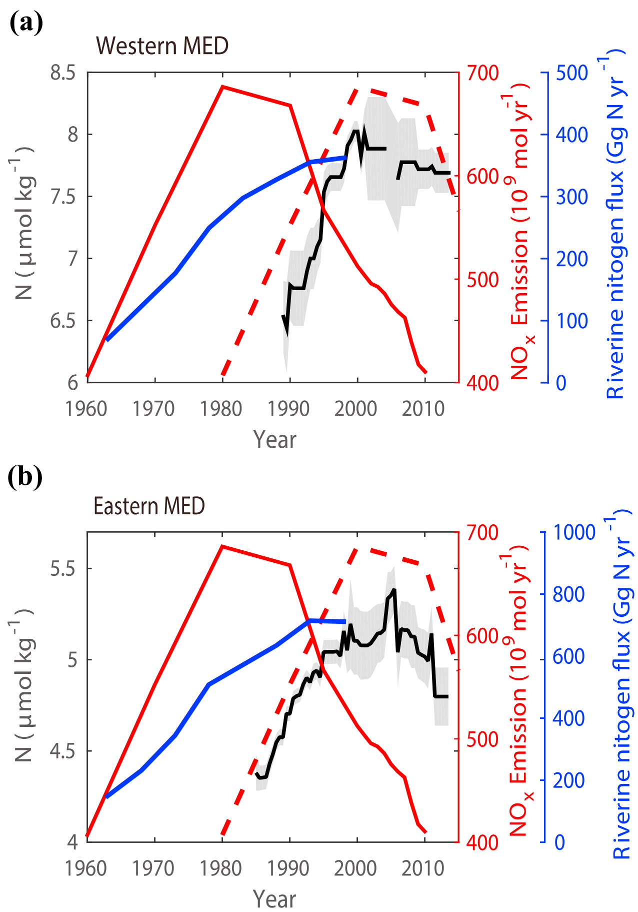

Figure 3. Long-term trends in N concentrations (a) in the western Mediterranean (MED) Sea, and (b) in the eastern MED Sea, compared with the anthropogenic nutrient inputs. The black line is the temporal trend of N in each subbasin, showing the 95% confidence interval (shaded). The blue and the red solid lines represent the riverine nitrogen influx to the MED Sea and the NO_x emission from Europe, respectively. Red dotted line is the temporal trend of European NO_x emission shifted considering the time lag of 20 years.

introduction. Temporal trends of N input into the MED Sea from the two former sources were similar in the western and eastern basins (Figure 3). The rapid increase in N in both basins for the earlier period (1985–1998) coincides with increases in riverine nitrogen input and emissions of reactive nitrogen from Europe, with a lag period of 20 years. Such good agreement strongly indicates that the riverine and atmospheric sources contribute to the observed increase in N concentration in the MED Sea, although the exact contributions of the two N sources are not easily quantifiable. During the later part of the study period (1998 onward), a two-step temporal transition (constant-decline) was observed in the N concentration in the eastern basin and to a lesser degree in the western basin, in agreement with the temporal trend in pollutant nitrogen emissions in Europe (constant-decline).

It should be noted that the temporal trends (increase-constant-decrease) of P in both basins may be more closely associated with the input history of riverine phosphorus, with a lag period of 20 years.

As reactive nitrogen emissions from Europe have declined, and the inputs of riverine nutrients appear to have stabilized since the early 1990s, the concentrations of N and P in the intermediate water of the MED Sea are expected to decline in the coming decades. The predicted decline in N and P concentrations illustrates how preventive action to address pollutant emissions can mitigate anthropogenic impacts on oceanic environments.

4.2. Marine N_2 Fixation, Overturning Circulation, and Dust Input

Another source of N that may have contributed to N availability in the MED Sea is marine N_2 fixation. However, the majority of recent measurements of N_2 fixation indicate that the N_2 fixation rate is small (~1 nmol N L^{-1} d^{-1}) in this region (Table S1 and Figure S4). Such low rate of N_2 fixation activity was attributed to the limitations of phosphorus or other elements [*Krom et al.*, 2010; *Ridame et al.*, 2011]. Given that the low rate is representative of N_2 fixation in the MED Sea, the contribution of N_2 fixation to the trend of increasing N would be minor, and thus, N_2 fixation cannot be considered as a major N source to the MED Sea [*Ibello et al.*, 2010].

Denitrification, which represents a natural sink of N, is not an explanation for the trend of decreasing N in the MED Sea between 2005 and 2014, because the conditions of high O_2 concentration and low organic carbon content would not have supported the denitrification process [*Krom et al.*, 2004; *Granéli and Granéli*, 2008].

Another possible factor that could affect the distribution of nutrients in the studied depth range (200–600 m) is a change in overturning circulation. One such event that occurred in the early 1990s was the Eastern Mediterranean Transient [*Roether et al*., 2007]. During this event the concentrations of N and P in the Eastern MED Sea intermediate waters (water masses of interest in this study) probably increased because of the uplift of nutrient-rich deep waters [*Klein et al*., 1999; *Kress et al*., 2003]. This event may in part contribute to the rapid increase in the N and P concentrations found in the eastern MED Sea during the 1990s.

The deposition of dust from the Saharan Desert may increase total phosphorus [*Morales-Baquero et al*., 2013]; however, it is difficult to estimate its contribution because of large interannual variability in dust input into the MED Sea [*Wong et al*., 2008; *Rodríguez et al*., 2015].

4.3. Anthropogenic N Budget in the MED Sea

A potentially powerful approach to assess whether nutrient change in the MED Sea was attributed to human impacts is to calculate anthropogenic N budget for the area. In this calculation we compared the change in the water column nutrient inventory for the period 1985–2000 with the nutrient influx via atmospheric deposition and riverine discharge between 1965 and 1980, given that a 20 year lag period was required for the nutrient inventory to be fully adjusted to these external nutrient inputs. The rate of increase in the N inventory of the intermediate water layer (200–600 m) was calculated by multiplying the rate of N increase per unit volume of seawater by the entire volume of the intermediate water layer influenced by anthropogenic nutrient inputs.

Across the western and eastern basins combined, the increase in the N inventory of the intermediate water layer was estimated to be 1.20 Tg N yr^{-1}, which was inconsistent with the nitrogen influxes from atmospheric and riverine sources (1.37 Tg N yr^{-1}; Table S2). Assuming that all other factors influencing primary and new production remained constant, one important implication of anthropogenic nutrient input into the MED Sea is an increase in primary and new production [*Okin et al*., 2011]. In particular, the rate of N increase was equivalent to 22% of the new production [*Béthoux et al*., 2005]. Interestingly, a similar magnitude of contribution of atmospheric nitrogen deposition to the new production was found in the South China Sea [*T.-W. Kim et al*., 2014], which is also located downwind of the heavily populated and economically dynamic countries. Those high contributions suggest that anthropogenic N and P can be an important source of new nutrients in the oligotrophic marginal seas.

5. Conclusion

Our results provide a compelling indication that human activities have largely shaped the temporal dynamics of nutrient concentrations in the MED Sea through multifaceted pathways. Interestingly, the contributions of atmospheric deposition and riverine influx were not homogeneous. Overall, the contribution of atmospheric deposition appeared to be larger than that of riverine influx. For a more thorough evaluation of the relative contributions of atmospheric deposition and riverine input to the nutrient dynamics in the MED Sea, the riverine nutrient input for the period 1998 onward should be further evaluated. In the eastern MED Sea, nutrient dynamics were also influenced by an extreme hydrological event in the early 1990s. The contributions of other natural processes (e.g., N_2 fixation and denitrification) were shown to be minor.

The observed sensitivity of the nutrient dynamics in the MED Sea to human activities highlights the importance of building an observational network, which will eventually provide high-quality biogeochemical and physical data. To this end, it is critical that the Mediterranean Sea Ship-based Hydrographic Investigations Program builds long-term data sets for the MED Sea, through regular measurement of marine physical and biogeochemical variables [*Schröeder et al*., 2015]. A decrease in the anthropogenic nutrient inventory of the MED Sea is projected to occur in the near future, driven primarily by the recent stabilization of release of nutrient pollutants from the European continent. Our findings for the MED Sea provide an important focus on how the regulation of inputs of anthropogenic nutrients can be a key driver affecting seawater nutrient dynamics in the future.

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