Human-Driven Atmospheric Deposition of N and P Controls on the East Mediterranean Marine Ecosystem

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ABSTRACT

The historical and future impacts of atmospheric deposition of inorganic nitrogen (N) and phosphorus (P) on the marine ecosystem in the east Mediterranean Sea are investigated by using a 1D coupled physical–biogeochemical model, set up for the Cretan Sea as a representative area of the basin. For the present-day simulation (2010), the model is forced by observations of atmospheric deposition fluxes at Crete, while for the hindcast (1860) and forecast (2030) simulations, the changes in atmospheric deposition calculated by global chemistry–transport models are applied to the present-day observed fluxes. The impact of the atmospheric deposition on the fluxes of carbon in the food chain is calculated together with the contribution of human activities to these impacts. The results show that total phytoplanktonic biomass increased by 16% over the past 1.5 centuries. Small fractional changes in carbon fluxes and planktonic biomasses are predicted for the near future. Simulations show that atmospheric deposition of N and P may be the main mechanism responsible for the anomalous N:P ratio observed in the Mediterranean Sea.

1. Introduction

The atmospheric transport of nutrients like nitrogen (N), phosphorus (P), and iron to the ocean has been identified as a significant source of nutrients to the marine ecosystem (Duce et al. 1991; Jickells et al. 2005; Krom et al. 2010). Interactions between the nutrient atmospheric deposition and the ocean productivity are important for both carbon dioxide storage in the ocean (Mahowald et al. 2005; Krishnamurthy et al. 2007; Okin et al. 2011) and marine ecosystems’ life and functioning (Tyrrell 1999). However, the contribution to the balance of nutrients and the resulting impact of atmospheric deposition on the productivity of the oceans and climate remains uncertain and deserves further investigation (Duce et al. 2008).

Nitrogen and phosphorus are vital elements to marine organisms, being structural and functional components (Tyrrell 1999). Redfield (1958) found that most of the
living organisms in marine ecosystems tend to contain a relatively constant molar proportion of carbon (C), nitrogen, and phosphorus, equal to 106:16:1 (C:N:P). After the industrial revolution, humans have modified, mainly for food and energy production, the biogeochemical cycles of nutrients in terrestrial and aquatic ecosystems (Galloway et al. 2004; Galloway et al. 2008). This change resulted in a higher atmospheric N deposition to the oceans that may account globally for up to ~3% of the annual new oceanic primary productivity (Duce et al. 2009). Atmospheric deposition of nutrients has larger impact in oceanic oligotrophic areas and semienclosed seas where nutrients are the dominant ocean productivity limiting factors (Powley et al. 2014; Van Cappellen et al. 2014). In particular, areas that are either perennially or seasonally depleted in surface nitrate are affected more by anthropogenic N deposition than high-nutrient low-saline oligotrophic ecosystems, where the annual new oceanic primary productivity is further depleted toward the east (Azov 1991) because of the westward transport of the underlying deep Mediterranean return current (Boetius et al. 1996). Thus, the open sea of the Mediterranean is a nutrient-rich, active N have a strong anthropogenic component, the dominant source of total N is of natural origin (86%), with dust particles (48%) and primary biogenic particles (34%) (Mahowald et al. 2008). Overall, there is a net loss of total P from land ecosystems and a net gain by the oceans, with anthropogenic atmospheric inputs of phosphates to the ocean being 15% of total atmospheric inputs and contributing as much as 50% to the deposition over the oligotrophic ocean where productivity may be limited by P. An increase in the N:P ratio in the ocean seems to have been driven by the increase in deposition of atmospheric N, although potential changes in atmospheric P deposition also impact on this ratio.

The Mediterranean Sea is divided into two subbasins with different hydrological and biological characteristics and is characterized by an excess of evaporation over precipitation and river runoff that creates a complex circulation system. Water with a low N:P ratio is penetrating in the Mediterranean from the Atlantic through the Strait of Gibraltar to compensate for the water deficit caused by evaporation (Coste et al. 1988; Gomez et al. 2000). The surface seawater in the Mediterranean is further depleted toward the east (Azov 1991) because of the westward transport of the underlying deep Mediterranean return current (Boetius et al. 1996). Thus, the open sea of the Mediterranean is a nutrient-poor marine environment (Bosc et al. 2004). Unlike other regions, the Mediterranean Sea presents a well-defined decreasing trend in Chl-a from west to east, while the N:P ratio has been measured to increase (up to 27:1) in the same direction following the oligotrophic character of the sea. The diatom and other phytoplankton like Phaeocystis pouchetii and other diatoms (Boschi et al. 2000) concentrations and the resulting low productivity of the eastern Mediterranean Sea. However, it does not explain why the N:P ratios measured in the eastern Mediterranean Sea exceed the 16:1 Redfield ratio.

In this study we investigate how the increase in atmospheric deposition of N over the past 1.5 centuries, together with a smaller increase in atmospheric P deposition onto the surface seawater, affected the nutrient stoichiometry and the marine ecosystem in the eastern Mediterranean Sea and how this impact will change in the near future. For this, a one-dimensional marine physical–biogeochemical model is used to estimate the impact of atmospheric deposition of dissolved inorganic nitrogen (DIN) and phosphorus (DIP) on the N:P ratio in the seawater and on the biomasses and C fluxes in the planktonic community over time, from preindustrial times (1860) to the near future (2030). For the present-day simulation, atmospheric deposition observations are used, while for the hindcast and forecast simulations, estimated deposition flux changes are based on results from global transport–chemistry models (Duce et al. 2008; Mahowald et al. 2008).

2. Method description

a. Marine ecosystem model

The study focuses on the Cretan Sea as a representative open-sea area of the oligotrophic ecosystem of the eastern Mediterranean. The 1D water column model (Fig. 1) used here has been adapted by Christodoulaki et al. (2013) to simulate the entire eastern Mediterranean basin. The model extends down to 1000-m depth and is discretized in the vertical by 25 grid layers, with a finer resolution in the euphotic zone. The hydrodynamic properties of the water column (temperature, salinity, and vertical diffusivity coefficient) were obtained (offline) on a daily basis from the Poseidon operational 3D hydrodynamic Mediterranean basin-scale model (www.poseidon.hcmr.gr; Korres et al. 2007).

The biogeochemical model based on European Regional Seas Ecosystem Model (Blackford et al. 2004; ERSEM-2004) accounts for seawater stratification or mixing and all key biogeochemical processes affecting the flow of C, N, P, and silica in the water column. The food-web representation (Baretta et al. 1995) considers functional groups (producers, decomposers, and consumers) that are further subdivided on the basis of trophic links and/or size and has been modified from the
standard configuration to represent the eastern Mediterranean ecosystem. Additionally, the breakdown of particulate matter and the remineralization of dissolved organic matter have been modified to permit preferential P remineralization [details in Christodoulaki et al. (2013)]. Selective removal of P reflects the nutrient demands of marine microorganisms in oligotrophic P-limited regions (Clark et al. 1998). Seawater DIN and DIP exchange through the Sicily Straits, rivers, and Black Sea water nutrient inputs are taken into account into the marine model as well as losses due to sediment deposition and sediment denitrification, following Krom et al. (2004). Riverine fluxes of DIN and DIP contribute 37% of DIN and 17% of DIP sources with N:P ratio of 57, DIN and DIP influxes through the Sicily Straits contribute 9% of DIN and 42% of DIP sources with N:P ratio of 16, and Black Sea water nutrient inputs contribute 5% of DIN sources. Atmospheric deposition fluxes are introduced to the marine model based on monthly mean measurements of DIN and DIP. For the present-day simulation, considering the inputs of all sources of DIN and DIP into our model, the atmospheric flux of DIN is about 35% higher than riverine input, while rivers provide about 4 times more DIP to the ocean than the atmosphere. The detailed description and validation of the model can be found in Christodoulaki et al. (2013).

Three different simulations have been performed that only differ in the atmospheric deposition fluxes: one for the present environment (2010), one for the preindustrial period (1860), and one for the near future (2030) (section 2b). Data of NO$_3^-$ and PO$_4^{3-}$ riverine fluxes into the east Mediterranean Sea are scarce and limited in time [Ludwig et al. (2003); Kocak et al. (2010) and references therein]. The limited observational data suggest that Greek river discharges to the east Mediterranean Sea have been reduced to about half between 1960 and 2000 [Ludwig et al. (2009) and references therein]. DIP concentration in these discharges, after a dramatic increase in the 1960s and 1970s, rapidly declined back to early 1960s levels, while DIN concentrations almost continuously increased over the last 50 yr and only recently started to decrease as a
result of legislation. However, there is not enough information to enable an estimate of the overall change in the riverine fluxes of nutrients, accounting for the change in both the nutrient concentration and the volume of water discharge. Thus, apart from the changes in the atmospheric deposition fluxes of DIN and DIP (Figs. 2a and 2b) that vary seasonally but not interannually, for the hindcast and forecast scenarios, the absence of relevant data all other nutrient fluxes into the eastern Mediterranean Sea are kept unchanged with time. For each simulation the model has been run for 50 yr, the results of year 50 are here compared and discussed.

b. Data

Atmospheric deposition present-day fluxes are observations at the monitoring station of the University of Crete at Finokalia, Crete, Greece (35°24′N, 25°60′E; http://finokalia.chemistry.uoc.gr/; Mihalopoulos et al. 1997). This is the only location in the east Mediterranean with available long-term atmospheric deposition data for DIN and DIP. Measurements during intensive campaigns using ship and aircraft have shown that observations at Finokalia are representative of a larger area of the east Mediterranean (Kouvarakis et al. 2001; Lelieveld et al. 2002). Deposition of airborne DIN (Fig. 2a) and DIP (Fig. 2b) have been measured between June 2001 and March 2005 (Markaki et al. 2010). Particulate ammonium, NO$_3^-$, and PO$_4^{3-}$ have been measured in rainwater (collected on an event basis). Dry-deposition samples (sum of gases and particles) have been collected on glass beads and analyzed to determine atmospheric samples (sum of gases and particles) have been collected in rainwater (collected on an event basis). Dry-deposition fluxes of DIP have been estimated either from observations of size-segregated atmospheric aerosol concentrations and deposition velocities obtained from literature or after collection of atmospheric aerosols on glass beads (Markaki et al. 2003). Maximum DIP deposition fluxes (dry and wet) are associated with intensive Saharan dust outbreaks occurring in the region during February and during the transition periods of spring (April) and fall (November). According to Markaki et al. (2003, 2010), wet deposition contributes by about 78% to the total DIN deposition while for DIP this contribution is only 60%, indicating a significant difference in the behavior and sources of DIN and DIP.

To evaluate uncertainties in the model results, additional sensitivity simulations have been performed to assess the effect of the year-to-year variability of the atmospheric deposition fluxes of DIN and DIP (Fig. 2c) on the model results. Extreme scenarios of DIN and DIP atmospheric deposition fluxes (maximum, minimum, or average) from the 5-yr atmospheric deposition flux measurements at Finokalia are compared to the present-day simulation (average monthly deposition data) (see supplementary material, Table S1).

DIN atmospheric deposition fluxes for the hindcast and forecast simulations are based on the present-day observed deposition fluxes and the global annual-mean changes in these fluxes due to human activities calculated for DIN by ensemble chemistry transport models (CTM) (Dentener et al. 2006; Duce et al. 2008; ~90% in 1860 and +15% for 2030) and for DIP by the Model of Atmospheric Transport and Chemistry (MATCH, version 4.2; Mahowald et al. 2008) (only past estimates: −15% for 1860). Thus, in the past, atmospheric deposition of DIN was contributing less than 15% to the external source of DIN to the ocean (flux from the atmosphere and the rivers) compared to about 60% contribution nowadays. In our model, the increased atmospheric deposition of DIN is the main driver of the studied changes in the marine ecosystems. However, DIP global simulations by Mahowald et al. (2008) do not account for the effect of atmospheric acidity on the solubility of total P contained in dust aerosols. Indeed, the increase of nitrogen oxides and sulfur dioxide from the 1860s to present have enhanced the acidity of aerosol particles and thus increased the soluble fraction of P atmospheric deposition (Nenes et al. 2011). This enhancement has not been taken into account when deriving the 15% change in DIP deposition since 1860. Furthermore, for the present study we assume no change in DIP deposition from present day to 2030 due to the large contribution of the natural source of DIP and the absence of DIP future emissions estimates. Indeed, assuming a proportional to DIN increase in DIP anthropogenic emissions would result in an overall 2.5% increase in the total DIP emissions. This increase is relatively small compared with the natural emissions variability that has been reported to vary by up to a factor of 6 (Gong et al. 2006; Rodriguez et al. 2015) and with the observed year-to-year variability at Finokalia, shown in Fig. 2c.

3. Results and discussion

Figure 3 shows the calculated evolution of the ratio of DIN to DIP (DIN:DIP) in the upper 200 m of the water column in the eastern Mediterranean basin. DIN has increased as a result of human activities during the past 1.5 centuries by 20%–45% because anthropogenic atmospheric deposition is rich in DIN compared to DIP. The DIN:DIP ratio in the atmospheric deposition for the present-day range is between 77:1 and 380:1.
FIG. 2. Monthly atmospheric deposition data (total = wet + dry) of (a) DIN and (b) DIP (mmol m\(^{-2}\) month\(^{-1}\)) for the past (1860), the present-day (2010), and the future (2030) simulations. Present-day atmospheric deposition fluxes are monthly averages from January 2002 to December 2006. Mean scaling factors have been applied to the present-day deposition to derive past and future deposition fluxes. These are ~90% and ~15% for past and future DIN deposition, respectively (Duce et al. 2008), and ~15% for past DIP deposition (Mahowald et al. 2008). (c) Year-to-year variability of DIN and DIP atmospheric deposition fluxes at Finokalia during the 5-yr sampling period.
while in the hindcast simulation range is between 10:1 and 47:1. It is remarkable that in the hindcast simulation the system reaches a different state with DIN:DIP in the surface seawater close to the Redfield ratio (16:1). This result suggests that atmospheric deposition alone could explain the unusually high N:P ratio observed in the basin. A further increase of anthropogenic DIN atmospheric deposition in the near future leads to an increase by 4%–9% in the DIN:DIP ratio in the surface seawater. The here-calculated importance of the atmospheric deposition for the oceanic nutrient budget in the eastern Mediterranean Sea is also supported by the observed depletion of $^{15}\text{N}$ and enrichment of $^{18}\text{O}$ of the mixed-layer reactive N, recently reported for the region (Emeis et al. 2010; Mara et al. 2009).

These changes in the DIN:DIP content in the seawater affect the fluxes and biomass stocks. In particular, from the end of the springtime phytoplankton bloom through the rest of the year, because of the stratification of the seawater column, external sources of nutrients (mainly atmospheric deposition of DIN and DIP) and recycling of nutrients support marine primary production in the eastern Mediterranean. Figure 4a shows the overall results of the present-day simulation for the pelagic community after integration of the C fluxes and biomass stocks in the upper 100 m of the water column over the year. Heterotrophic organisms take most of their C (>90%) from the small autotrophic organisms (picoflagellates and flagellates), followed by the larger ones (dinoflagellates and diatoms). Bacteria that act as phyto competitors in dissolved nutrients uptake and as detritus consumers provide more than 40% of C to their predators while the remaining 60% comes from phytoplankton. The carbon budget demonstrates the complex

![Figure 3: Monthly variation of the DIN:DIP ratio integrated into the upper-200-m seawater column, as computed by the 50-yr simulations for the past (1860; black), the present day (green), and the future (2030; red).](image)

![Figure 4: (a) Mean annual carbon fluxes (mg C m$^{-2}$ yr$^{-1}$) and biomass stocks (mg C m$^{-2}$), within the planktonic community, integrated into the upper-100-m seawater column, as computed for the present-day simulation, and fractional changes (%) of the mean annual carbon fluxes and biomass stocks in the pelagic community in (b) the past (1860) and (c) the future (2030) compared with the present-day simulation.](image)
The uncertainty in these model results associated with the year-to-year variability of the atmospheric deposition fluxes has been evaluated by the sensitivity simulations summarized in Table S1 in the supplementary material. The largest uncertainties have been computed for the carbon fluxes from phytoplankton to zooplankton (−12% to +10.5%) and for the zooplankton biomass (−17.6% to +15%), while bacteria show the smallest sensitivity to the changes in the atmospheric deposition fluxes (−0.6% to +0.5%).

To investigate how the marine ecosystem functioning in the east Mediterranean has changed and will change as a result of human-driven atmospheric emissions, the present-day simulation is compared to the simulation for 1860 with reduced DIN and DIP atmospheric deposition and for 2030 with increased DIN atmospheric deposition but no change in DIP deposition (section 2b). Figures 4b and 4c show the fractional changes of the annual-mean C fluxes and biomass stocks in the pelagic community.

According to our calculations, anthropogenic DIN and DIP entering the atmosphere have enhanced the phytoplankton biomass by 16% and the bacterial biomass by 5% in the upper 100 m of the seawater column over the past 1.5 centuries (1860; Fig. 4b). Zooplankton biomass has also been calculated to increase since 1860, with a higher increase in microzooplankton (28%), followed by mesozooplankton (8%) and heterotrophic flagellates (4%).

Small fractional changes in carbon fluxes and biomass stocks are projected for the future (2030; Fig. 4c) compared to the present-day simulation. For this simulation relatively small changes are expected compared to those driven by the observed variability of the present-day atmospheric deposition (Fig. 2a and 2b) because marine primary production in the eastern Mediterranean Sea is primarily P limited (Thingstad et al. 2005) and no change in DIP deposition has been considered.

These results request further modeling investigation in view of the projected global warming associated with anthropogenic emissions. Vertical mixing in the Mediterranean Sea is an important mechanism for the fertilization of the surface waters during the mixing period of the water column. Under global warming, a higher surface temperature would result in a stronger stratification of the water column (Barale et al. 2008), thus increasing the importance of the external sources of nutrients like atmospheric deposition. However, thermal instability in the atmosphere occasionally induced by air pollution could lead to strong convective events in the atmosphere that could also increase the vertical mixing in the water column bringing limiting nutrients like P to support the phytoplankton growth.

4. Conclusions

In the present study, a one-dimensional marine physical–biogeochemical model has been used to assess the impact of anthropogenic-originated DIN and DIP atmospheric deposition on the eastern Mediterranean marine ecosystem based on atmospheric deposition fluxes observations and estimates of their changes over the past 1.5 centuries and in the future.

In the upper 200 m of the water column the DIN: DIP ratio has been calculated to have increased by up to 45% as a result of human activities over the past 1.5 centuries. Thus, human-driven atmospheric deposition of DIN and DIP was found to be able to explain and maintain the anomalous high N:P ratio measured in the east Mediterranean seawater. Over the same period, anthropogenic DIN and DIP atmospheric deposition has been calculated to increase the total year-round phytoplanktonic, zooplanktonic, and bacteria biomasses by 16%, 9%, and 3%, respectively. These changes are significant for phytoplankton and bacteria biomass since they are higher than the uncertainty of models results associated with the observed year-to-year variability in atmospheric deposition fluxes (−6% to +5% and −0.6% to +0.5%, respectively; Table S1). However, the computed changes in zooplanktonic biomass are not significant since they are within the range of uncertainty provided in Table S1 (−17.6% to +12%).

In the present-day simulation, more than 40% of the C is recycled through bacteria, confirming the complex microbial food-web character of the ecosystem.

The projected increase in DIN atmospheric deposition accompanied by no change in DIP atmospheric deposition has been calculated to cause only small changes in carbon fluxes and planktonic biomass stocks due to the P-limited behavior of the eastern Mediterranean marine ecosystem. However, these changes do not account for the marine ecosystem dynamics variability in the region, in particular that related to climate change and deserving investigation in the future.

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