

Sensitivity of the Mediterranean Ecosystem to Nutrient Deposition—Data Analysis Report

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Synopsis: This analysis complements the paper Sensitivity of the Mediterranean Ecosystem to Nutrient Deposition: An Interdisciplinary Review, through the cited dataset in <https://hdl.handle.net/20.500.14083/27684>, with data analyzes and, through the cited excerpts of the final presentation in <https://hdl.handle.net/20.500.14083/41643>, with the uploaded supplementary material. Both originate from the same authors and refer to the publications cited there. This complementary analysis shows an increase in nutrient ratios compared to the initial conditions in the 1980s and a shift in the composition of organic matter in favor of nitrogen compared to phosphorus.

Keywords: Mediterranean Sea; Aerology; Biogeochemistry; Top-Down Control; Nutrient-Depleted Waters

1. Background

In the Mediterranean region, the average material fluxes in the upper layers go in the opposite direction. Consequently, the fluxes caused by advection, mixing and sinking of organic matter ^[1] strongly influence the horizontal spatial distribution and play an important role in the development of a negative trophic gradient from the Western Mediterranean to the Eastern Mediterranean. In an oceanic framework with eight different cruises in comparison, two important Mediterranean sites, both in the northwestern Mediterranean, are analyzed.

In order to obtain a quantitative behavior of total nitrogen and phosphorus concentrations, the mass fluxes between the basins of the Mediterranean are considered as transport processes at the first trophic levels.

In this description with concentration variables, zooplankton and phytoplankton are considered as extended compartments providing secondary and primary productivity, and nitrogen and phosphorus are considered in all their forms: oxidized and reduced dissolved inorganic nutrients and organic matter.

The two surface layers are connected by horizontal fluxes that give the net inflow of Modified Atlantic Water to the western and eastern basins, while the deeper layers are connected by the opposite fluxes of Levantine Intermediate Water.

The results are anchored both in the synthetic paper ^[1] and in the unabridged and revised version of the ECHYM ecomodel ^[5] with the aerological references dated to before 2007. The neighboring approaches are currently being explored to improve the analysis of the processes towards the scales that enable and resolve the recurrent eddies ^[2].

The pure trophodynamics of total nitrogen and phosphorus achieves almost complete homogeneity of nitrogen and phosphorus concentrations in all layers, both at the surface and at depth after the required time on the order of the spin-up time of the hydrodynamics in the basins.

The aim of this complementary analysis is to compare the relative availability of dissolved inorganic nutrients and organic matter stock formation with the results of recent cruises and historical data.

In addition, this analysis is able to track the dynamics and remineralization of organic carbon to understand the accumulation and reuse of this nutrient by marine organisms and the change in seawater acidity ^[3,4].

In the next sections, the areology and the biology are described after defining the atmospheric inputs by fluxes through the basins.

This is followed by the analysis in both a general and a specific framework, with particular attention to the differences between the purely trophodynamic case, i.e. nutrient ratios, and the biogenic flux response. This is followed by a comparison with real data from the basin.

The summary considers the results of the model in relation to the biogeochemistry of the Mediterranean Sea and the potential applications of this framework in view of the complemented paper ^[5], which finally provides a review of the topic, a new analysis based on the publicly available data and the prospect of new applications in different oceanic ecosystems.

2. Aerology

The solution of a large-scale circulation problem in environmental applications depends both on general considerations arising from general knowledge in the ecological domain and on the detailed physical conditions of the basin to be analyzed. Here we choose an oceanic approach. Based on the general considerations, the adjustment of the vertical fluxes within the basin is tested.

The analysis of the non-linearities resulting from the interactions between the physical dynamics and the biochemical processes is also investigated in an oceanic framework.

Therefore, a three-dimensional approach is preferable if the vertical dynamics are to be fully resolved. Let us enumerate the two main processes that should be improved according to the complemented paper: the evaporation effects and the mesoscale dynamics.

For the first effects, a comparison of the impact of different vertical mixing parameters on the variability of the lower trophic levels in the Mediterranean pelagic ecosystem was performed, using a three-dimensional coupled ecological-hydrodynamic model as a testbed. The hydrodynamic influences are determined by a

primitive equation model, while the ecological dynamics are described by an aggregate model based on inorganic nitrogen, phytoplankton and detritus.

Comparison of the present A-Physics closure scheme with more complex parameterizations based on the Richardson number revealed a better developed mixed surface layer together with a sharper vertical density gradient as the most striking feature exhibited by the latter compared to the A-Physics results. The cyclonic and anticyclonic patterns are enhanced by the altered thermohaline structure of the ocean. This has a direct impact on the advection of tracers on a large scale and also improves tracer trapping by synoptic eddies. The intensification of cyclonic patterns leads to a stronger upwelling in the eddy core with a more effective nutrient input from deep layers into the euphotic zone. It is therefore shown that different choices for the scheme of turbulent closures lead to a potentially different space-time evolution of the biochemical variables. It is shown that the third-order closures are not feasible due to the instability of the ecological submodel and the inability of this parameterization to deal with climatological constraints.

The models proposed so far for the Mediterranean Sea at the basin scales are of two types: trophodynamic models capable of resolving the spatial resolution of the physical processes in the subbasins acting on the distribution of nutrients, especially inorganic fractions; flux production models that take into account the classes of microzooplankton that act on the picoplankton and close the ecosystem with the mesozooplankton that graze the phytoplankton, seagrasses and smaller classes of zooplankton.

The feasibility of three-dimensional modeling of the entire Mediterranean Sea is demonstrated by the results of the trophodynamic model using simulations of surface chlorophyll. The model takes into account the nutrient distribution as a limiting factor, the phytoplankton compartment and the recycling detritus. The introduction of zooplankton that graze the phytoplankton, does not change the distribution pattern very much and can therefore be considered as a controlling factor that is generally relatively less important for phytoplankton growth in the bottom-up control and

sometimes in the top-down control than in eutrophic or mesotrophic systems. However, the choice of a single limiting nutrient may not be sufficient to define the geochemical provinces in the Mediterranean Sea. The results of the trophodynamic model are illustrated by the simulations of chlorophyll and nutrient conservation at the surface within the chosen B-grid discretization, as can be seen in **Figure 2** of the complemented paper ^[5], where five powers of ten online are read exponentiated on page 33.

The described multinutrient and size-fractionated phytoplankton is proposed here as a model for flux producers. The ECHYM model limits the number of biologically active variables and contains the most important processes related to the biological energy flow in the Mediterranean ecosystem. The microbial food chain is bypassed by a classical first-order kinetics of recycling compartments with a dynamic composition in terms of phosphorus and nitrogenous and carbonaceous organic matter. The motivation for this choice is the known interaction in the Mediterranean region between the microbial and the classical chain based on the comprehensive datasets systematically collected and studied within the Mediterranean Targeted Project 1993–1999 and the historical data collected in parallel in 2002 ^[21].

Although the spatial distribution of data in the Mediterranean is sparse, the of phosphate and nitrate concentrations confirm the general oligotrophic nature of the deeper layers of the Mediterranean compared to the global ocean.

The inflows from the rivers are included, taking into account their imbalance after the damming of the Nile.

The measured value of dissolved plus particulate organic nutrients, i.e. total organic matter, is used as the inflow from the Atlantic. The Po and Rhone rivers are considered implicitly and explicitly, respectively; the atmospheric inputs of phosphorus and nitrogen all contribute to the dissolved inorganic nutrient compartments and come from two specific assessments.

The three atmospheric inputs are: No Inputs, NIRUN, where atmospheric deposition is zero; Geochemical Averages, GARUN, where these geochemical estimates are fully incorporated into the marine inorganic nutrients; and Atmospheric Values, AVRUN, where these experimental averages are also incorporated into the inorganic nutrients. The atmospheric inputs are continuous and pass immediately into the inorganic phase. They are evenly distributed over the year and load the 10 m thick sea surface layer with the same amounts of nutrients in every 2400-s time step.

The simulations of this numerical sensitivity experiment begin after the start of the hydrodynamics, which spans four years separately, with the realistic nitrogen and phosphorus initial conditions recorded by cruises in the 1980s and the introduction of relaxation in the Strait of Gibraltar, the Adriatic and the Aegean Sea and river loadings. The three biogeochemical numerical trends each span six years.

3. Biology

The Mediterranean Sea can be divided into two upper layers, representing the euphotic zones of the western and eastern Mediterranean and the two aphotic parts of the western and eastern basins. The opposite average fluxes are the inflow from the Atlantic into the western upper layer and the corresponding outflow of the Levantine Intermediate Water from the western basin into the Atlantic.

The estimates agree well with the most recent estimates of these fluxes, which are based on current measurement data as well as two-layer models, budgets and salt fluxes. The multi-year mean value obtained from recent observations converges with the value obtained from the two-layer models. A refined estimate may be relevant for the eastern basin, and it is suggested that in addition to the high-frequency forcing, surface salinity should also be slowed down. Possibly this should be done using sensitivity experiments for the different precipitation values in conjunction with numerical schemes for the external modes at the free-surface.

For this study, the fluxes are taken symbolically to obtain the general characteristics of the ecological system, and then specialized only for the applications of biogeochemical fluxes.

The fluxes along the Strait of Sicily are also represented. The Modified Atlantic Water flows into the Eastern Mediterranean, while the countercurrent of the Levantine Intermediate Water flows westward in the lower layer. In this case, estimates are available as analysis and assessment of salinity and water balance. The estimates for these two flows are close to each other.

For the vertical fluxes, convection, upwelling and downwelling as well as vertical mixing are the processes to be parameterized. The estimates are determined on the basis of the oxygen budget due to remineralization processes.

The chemical processes are tracked using an aggregate description that takes into account: dissolved inorganic nitrogen, both oxidized and reduced, dissolved inorganic phosphorus, total organic nitrogen, both dissolved and particulate, total organic phosphorus, both dissolved and particulate, and total organic carbon, both dissolved and particulate.

The different fractions of dissolved nutrients determine the growth of phytoplankton in two size fractions by nutrient uptake and zooplankton by phytoplankton grazing. The parameterization is the classical concentration parameterization and does not differ by the presence or absence of species in the western or eastern basin.

The measurements of the Chl:C ratio show a high variability in the different marine ecosystems: in the Eastern Mediterranean, cells are exposed to a decrease in the Chl:C ratio, and the availability of light over a longer period of time and at greater depths also leads to a decrease in the Chl:C ratio. The interaction of these two factors means that conditions in the nutrient-poor eastern basin are significantly worse than in the western basin. This environmental behavior is confirmed by measurements in phytoplankton cultures ^[6], with the lowest values at low nutrient levels and high PAR

being around 0.003. Our working value of 0.0067 is representative of measurements in the Aegean Sea and lies between the higher Chl:C ratios in the Western Mediterranean and the very low ones in the far eastern oligotrophic regions.

The monthly chlorophyll maps and vertical sections can be followed here as in the uploaded supplement to show the seasonal evolution of chlorophyll. These excerpts from the final presentation form the basis for both the complemented paper and this complementary analysis, in which we examine the effects of atmospheric deposition on the intermediate layers. Seasonal variability at the surface also includes monthly variability in the eastern 34°N and western 6°W transects (**Final Presentation**).

Organic matter in the form of carbon, nitrogen and phosphorus components is ultimately responsible for the export of organic matter from the euphotic zone.

The three shifts in the nutrient components of organic matter are: The grazing of phytoplankton by the 1:12:48 nutrient rates of herbivores, driving uptake at higher trophic levels ^[7]; The sloppy feeding of organic carbon and nitrogen and the release feeding of dissolved inorganic nitrogen, making nutrients available to the ecosystem in various forms; The 1:2:4 rate ratios of remineralization of orgc nutrient, each increasing from carbon and nitrogen to phosphorus, while the overall velocity of organic matter sink remains the same for all components, i.e. 5 m d⁻¹.

The remineralization rate for phosphorus is $2.36 \cdot 10^{-6} \text{ s}^{-1}$, while the remineralization rates for nitrogen and carbon are $1.18 \cdot 10^{-6} \text{ s}^{-1}$ and $0.59 \cdot 10^{-6} \text{ s}^{-1}$, respectively; all three organic components start with zero values in the six-year simulations.

4. Analysis

Based on the previously determined average values, which are given in the dataset <https://hdl.handle.net/20.500.14083/27684>, the results for the entire Mediterranean Sea as well as the western and eastern basins, the biogenic values and the aphotic and abyssal parts are analyzed.

Table 1C. Ratio of dissolved inorganic nitrogen to dissolved inorganic phosphorus for the first three years of the spin-up and for the last three years, from the fourth to the sixth year, of the studied evolution of the NIRUN without any atmospheric input.

NIRUN Dissolved Inorganic Nitrogen To Dissolved Inorganic Phosphorus Ratio	First Three-Year Averages – Spin-up	Fourth–Sixth Year Averages – Work
Mediterranean Sea	21.78	22.0
Western Mediterranean	20.17	20.52
Eastern Mediterranean	23.58	23.62

The resulting average ratios (**Table 1C**) of the first three years are lower than the average ratios of the second three-year simulations, i.e. the average values from the fourth to the sixth year of all simulations given in the work ^[1, 5] and in the dataset cited in the complemented paper ^[5], <https://hdl.handle.net/20.500.14083/27684>.

The ratios are maintained and even increased both in general and within each basin, but with a stronger increase in the western basin with respect to the three-year averages of the spin-up simulations, starting from the concentrations measured in the basins during selected cruises in the 1980s. With a very small increase, the Eastern Mediterranean shows that the ecosystem in this undisturbed situation is very close to a consistent equilibrium, which in this case is also based on the experimental concentrations of the 1980s.

Organic matter behaves similarly in the Western Mediterranean and the Eastern Mediterranean (**Table 2C**). This analogy is reflected in the average total values for the Mediterranean. The ratio for the western basin is higher than 12, more than five points higher than the dissolved inorganic nutrient ratio of Redfield, Ketchum and Richards ^[8], i.e. 6.625. The strong presence of carbon in the concentration of organic matter, understood here as the sum of dissolved organic nutrients and particulate organic matter, relative to size-fractionated phytoplankton is to be expected since the remineralization rate of nitrogen is twice as high as that of carbon.

Table 2C. Organic matter content for carbon, nitrogen and phosphorus with their ratios in the studied case without atmospheric inputs, the last three years from the fourth to the sixth year; all organic components start with zero values in the spin-up simulations.

NIRUN Fourth–Sixth Years	Total Organic Carbon	Total Organic Nitrogen	Total Organic Phosphorus	Organic C:N Ratio	Organic C:P Ratio
Mediterranean Sea	$1.08 \cdot 10^{18} \mu\text{mol dm}^{-3}$	$8.66 \cdot 10^{16} \mu\text{mol dm}^{-3}$	$2.76 \cdot 10^{15} \mu\text{mol dm}^{-3}$	12.43	389.79
Western Mediterranean	$5.43 \cdot 10^{17} \mu\text{mol dm}^{-3}$	$4.43 \cdot 10^{16} \mu\text{mol dm}^{-3}$	$1.41 \cdot 10^{15} \mu\text{mol dm}^{-3}$	12.27	383.91
Eastern Mediterranean	$5.33 \cdot 10^{17} \mu\text{mol dm}^{-3}$	$4.23 \cdot 10^{16} \mu\text{mol dm}^{-3}$	$1.35 \cdot 10^{15} \mu\text{mol dm}^{-3}$	12.61	395.97

Another remarkable outcome of this complementary analysis is that the whole Mediterranean Sea as well as its major basins, the Western Mediterranean and Eastern Mediterranean, develop approximately a natural equilibrium in terms of organic matter C:N ratio, e.g. 12 in the bacteria, which are not explicitly included as a functional and predictive compartment in the model. This appears to be consistent with the situations described on the BOUM cruises ^[9], which give a C:N ratios of about 12 for dissolved organic nutrients and about 13 for particulate organic matter, with much phosphorus in the surface organic matter and less in the bottom organic matter. This ratio is also confirmed by measurements throughout the Ionian Sea ^[10] above 34°N on the last cruise and our eastern transect.

This balance of about 12 is maintained by the bacteria along the water column through the heterotrophic uptake of dissolved inorganic carbon and nitrogen, while dissolved organic phosphorus accounts for about 20% of the bacteria requirements, which must take it up via the available phosphate or recycle it themselves much faster than the other inorganic nutrients. Atmospheric inputs maintain these ratios, increasing somewhat in the western basin and decreasing somewhat in the eastern basin, but less than 5%.

On the other hand, the ratio of carbon to phosphorus is about three times higher than the ratio in size-fractionated phytoplankton, i.e. 106. This situation seems to be

consistent with the remineralization rate of carbon in organic matter, which is 1:4 or four times lower than that of the phosphorus component in organic matter, as explicitly mentioned earlier. Otherwise, the equilibrium ratio is much higher than the C:P ratio of Redfield, Ketchum and Richards [8].

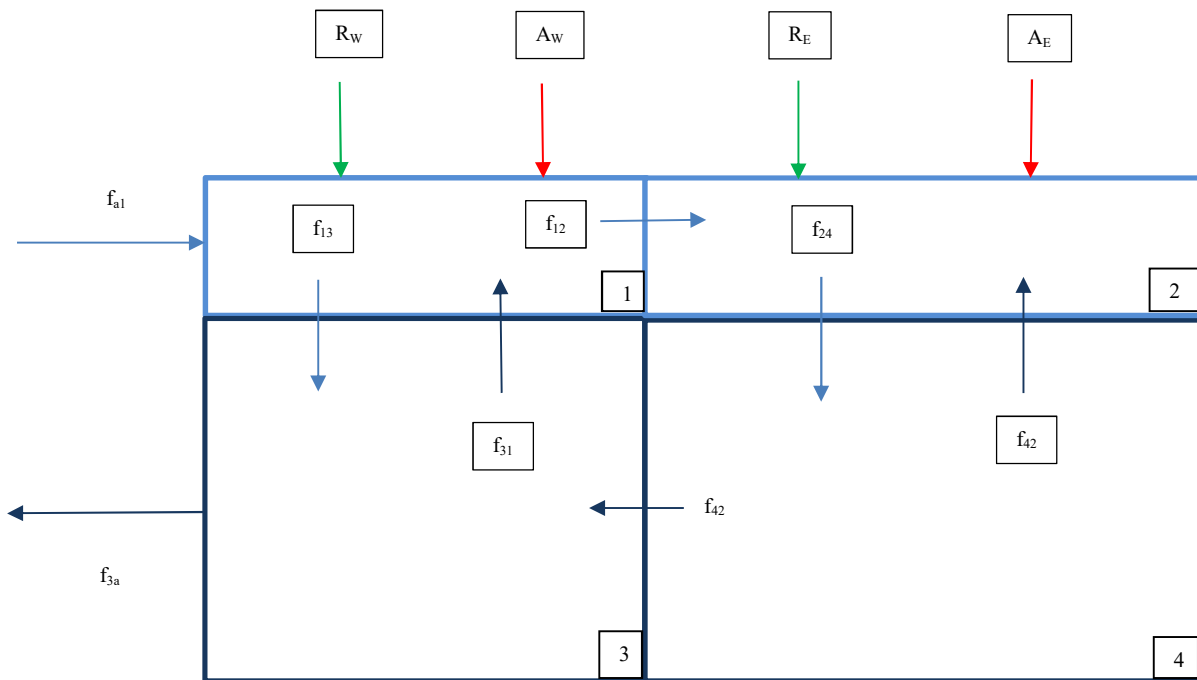


Plate 1C. Definitions of the boxes and fluxes: Boxes 1 and 2 are the western and eastern surface layers at about 100 m depth; Boxes 3 and 4 are the western and eastern deeper layers at about 1000 m depth; these depths, which are not included in the asymptotic concentration values, must be compared with the average Mediterranean depth of 1500 m and take into account the respective blue fluxes between the Atlantic and the Mediterranean and the green and red fluxes for terrestrial loads and atmospheric inputs, respectively.

If you arrange the four boxes from west to east and from the surface downwards (**Plate 1C**), you obtain the constitutive equations [11].

In general, the equilibria of the systems are as follows [12]: Σ and L are the matrices of the total concentrations in each box and the loads for the boxes, respectively, and F is the matrix of the water fluxes between the boxes.

The definition of the volumes and the parameterization of the biological fluxes, which are much larger than the vertical terms of the turbulent diffusivity, allow the solution of the ecosystem in quasi-stationary evolution, with a large-scale homogeneity in decadal evolutions of the order of the residence times of the nutrients in the basins. The former do not affect the asymptotic concentration values at all.

The deep asymptotic concentrations in the Eastern Mediterranean do not depend on the biogenic fluxes in this basin, but only on the western ones and on the inflows and outflows from the Strait of Gibraltar and the Strait of Sicily.

These solutions show that the concentrations of the deep layer in the Western Mediterranean do not depend on the fluxes in this basin, except for the exchange of outflows towards the Strait of Gibraltar and terrestrial and atmospheric inputs, not only in the western but also in the eastern area.

The equilibrium concentration Σ_2 of nitrogen and phosphorus in the deeper layer of the Western Mediterranean Sea is indeed

$$\Sigma_2 = \frac{L_1 + L_2}{f_{3i}}$$

where L_1 and L_2 comprise the inputs from the rivers ^[12]. If we take into account the atmospheric inputs, which are consistent but lower than the river loads, the final ratio of nitrogen to phosphate eventually changes to

$$\Delta \left(\frac{N}{P} \right) = \frac{N}{P} + \left(\frac{\Delta N}{N} - \frac{\Delta P}{P} \right)$$

Where ΔN and ΔP are the atmospheric inputs of nitrogen and phosphorus into the Mediterranean Sea. Similar linear formulas apply to the deeper layers of the Eastern Mediterranean, but mediated by the coefficients $f_{12}(f_{31}+f_{3a})$ and $f_{12}f_{13}+f_{12}f_{3a}+f_{13}f_{3a}$, which represent the composition of water and biogenic fluxes within and between the eastern basin, the western basin and the Atlantic Ocean. The concentrations in the Eastern Mediterranean do not depend on the rivers in this basin, but only on the western rivers and the inflows and outflows through the Strait of Gibraltar and the Strait of Sicily.

5. Summary

This complementary analysis shows an increase in nutrient ratios compared to baseline conditions in the 1980s and a shift in the composition of organic matter in favor of nitrogen compared to phosphorus.

The outcomes show an increase in all ratios, even compared to the high ratios resulting from the baseline conditions established by the cruise data in the 1980s. The responses accounting for biogenic fluxes show not only the accumulation of total nitrogen and phosphorus in the bottom layer, but also that these fluxes, together with the inverse estuarine circulation of the Mediterranean Sea, generate and maintain the respective and spatial trophic gradients of dissolved inorganic nitrogen and phosphorus. Organic carbon is tracked and provides average values that agree well with experimental estimates. The trophic model conditions are identical for both uptake and grazing processes in the Western Mediterranean and Eastern Mediterranean.

This analysis complements the paper Sensitivity of the Mediterranean Ecosystem to Nutrient Deposition: An Interdisciplinary Review in Research in Ecology by <https://hdl.handle.net/20.500.14083/27684>, uploading the analyzed dataset, and <https://hdl.handle.net/20.500.14083/41643>, uploading of the supplemented excerpts from the final presentation. The complemented paper consists of a review of

validation by chlorophyll, zooplankton function, and oceanic outlooks; the draft of the paper was published on September 19, 2024 for Trieste Next 2024.

Both this analysis and the paper are the consequent continuations of the work on atmospheric deposition described in both the 2007 synthetic paper and the 2022 unabridged and revised version of Chlorophyll Signatures and Nutrient Cycles in the Mediterranean Sea.

Credits: We incorporate here all the acknowledgments and explanations of the complemented paper that we add: on page 44, read *Cryptomonas ovata*; on page 45, read E., et al., 2006; and also thank the staff of Research in Ecology for their great efforts to improve both the revision and the editing of the complemented paper. The recurrent references in this complementary analysis, made at the Istituto Nazionale di Oceanografia e di Geofisica Sperimentale – OGS, are cited with the number in brackets with dashes and the new references follow below:

[1] Copin-Montegut, C., Copin-Montegut, G., 1983. Stoichiometry of carbon, nitrogen, and phosphorus in marine particulate matter. *Deep-Sea Research*. 30(A1), 31–46.

[2] Crispi, G., Pacciaroni, M., Viezzoli, D., 2006. Simulating biomass assimilation in a Mediterranean ecosystem model using SOFA: setup and identical twin experiments. *Ocean Science*. 2(2), 123–136. DOI: <https://doi.org/10.5194/os-2-123-2006>

[3] Touratier, F., Guglielmi, V., Goyet, C., et al., 2012. Distributions of the carbonate system properties, anthropogenic CO₂, and acidification during the 2008 BOUM cruise (Mediterranean Sea). *Biogeosciences Discussions*. 9, 2709–2753. DOI: <https://doi.org/10.5194/bgd-9-2709-2012>

[4] Álvarez, M., Sanleón-Bartolomé, H., Tanhua, T., et al., 2014. The CO₂ system in the Mediterranean Sea: a basin wide perspective. *Ocean Science*. 10(1), 69–92.

DOI: <https://doi.org/10.5194/os-10-69-2014>

[5] Crispi, G., Pacciaroni, M., 2025. Sensitivity of the Mediterranean Ecosystem to Nutrient Deposition: An Interdisciplinary Review. *Research in Ecology*. 7(1), 30–45.

DOI: <https://doi.org/10.30564/re.v7i1.8149>

[6] Falkowski, P.G., Dubinsky, Z., Wyman, K., 1985. Growth-irradiance relationships in phytoplankton. *Limnology and Oceanography*. 30(2), 311–321.

[7] Bougis, P., 1974. *Écologie du Plancton Marin, Tome II Le Zooplancton*. Masson et C^{ie} Éditeurs, Paris, FR. Collection D'Écologie(3), 126–154.

[8] Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of sea-water. In: Hill, M.N. (ed.), *The Composition of Sea-Water: Comparative and Descriptive Oceanography*. Interscience Publishers - Wiley, New York, NY US. *The Sea*, Vol. 2, 26–77.

[9] Pujo-Pay, M., Conan, P., Oriol, L., et al., 2011. Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea. *Biogeosciences*. 8(4), 883–899.

DOI: <https://doi.org/10.5194/bg-8-883-2011>

[10] Rabitti, S., Bianchi, F., Boldrin A., et al., 1994. Particulate matter and phytoplankton in the Ionian Sea. *Oceanologica Acta*. 17(3), 297–307.

[11] Crise, A., Crispi, G., Mosetti, R., 1995. Horizontal and vertical exchange of nitrogen in the Mediterranean Sea. *Annales Geophysicae*. Abstracts of the XX EGS General Assembly, Hamburg 3–7 April 1995. European Geophysical Society - Springer, Katlenburg-Lindau, DE. 13(SII), C224.

[12] Crispi, G., Mosetti, R., Solidoro, C., et al., 2001. Nutrients cycling in Mediterranean basins: the role of the biological pump in the trophic regime. *Ecological Modelling*. 138(1–3), 101–114.