

# Nitrogen and Phosphorus in the Northern Adriatic Sea

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In the last two decades of the 21st century, a gradual decrease in nitrogen and phosphorus has been observed along the coastal area of the Northern Adriatic Sea. This depletion is attributed to reduced river flows. Studies conducted over the past four decades have indicated that the N/P ratio in the open sea is unlikely to undergo significant change. In fact, it tends to increase due to the unique characteristics of the Northern Adriatic Sea, which experiences slow water turnover and is influenced by strong winds. Additionally, the Northern Adriatic Sea receives a substantial amount of freshwater from rivers, accounting for about one-third of the total freshwater flow into the Mediterranean. These rivers carry nutrient loads that contribute to the high productivity and abundance of fish in this sea, making it one of the most productive areas in the Mediterranean. It has been observed that the cessation of anthropogenic phosphorus input, which has been regulated since the late 1980s with legislation limiting its use in detergents, has significantly affected the trophic chain.

Keywords: Northern Adriatic Sea ; eutrophication ; nitrogen ; phosphorus ; fishing resource ; freshwater ; long term research ; plankton

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## 1. Peculiarity of the Northern Adriatic Sea

The Northern Adriatic Sea is particularly vulnerable to nutrient pollution due to its unique characteristics, including shallow depths, limited water exchange, and the influence of river discharges. The Northern Adriatic Sea, covering an area of 19,000 km<sup>2</sup> with an average depth of 35 m, receives freshwater input from numerous rivers and streams, including the Po River (1500 m<sup>3</sup> s<sup>-1</sup>, [1]), which contributes more than 50% of the external nutrient input [2][3][4]. The Adriatic's salinity is lower than that of the Mediterranean because the Adriatic collects one-third of the freshwater flowing into the Mediterranean Sea [5].

The Po watershed is very large (75,000 km<sup>2</sup>, [1]) and includes highly developed Italian regions with a resident population of 16 million people [6][7]. This area is intensively cultivated with heavy use of natural and artificial fertilizers [8]. Being one of the most densely populated and agriculturally productive areas in Europe [9], the Po Valley significantly influences the nitrogen (N) and phosphorus (P) input to the Northern Adriatic Sea, affecting the productivity and trophic dynamics of the whole Mediterranean basin [10][11][12][13]. When these N and P inputs enter the sea, they fuel the growth of phytoplankton and macroalgae. However, when present in excessive amounts, they can lead to eutrophication. This process in the Adriatic Sea is significantly influenced by seasonal circulation patterns [14][15][16]. In winter, the anticlockwise superficial and deeper circulation along the western coasts brings in nutrient-rich waters from the Po River [5][17][18][19] and other rivers originating in the Apennines [20][21][22][23]. These colder and less saline waters flow close to the Italian coast throughout the water column.

In contrast, during the summer season, the hydrodynamic conditions change, resulting in weaker currents and a series of clockwise and anticlockwise gyres, as well as strong water column stratification, with colder waters from the previous winter near the bottom [12][24][25][26][27][28][29]. As a result, nutrient concentrations in the surface waters increase, creating favorable conditions for the growth of phytoplankton and macroalgae. Following the cyclonic circulation, the waters of the Mediterranean Sea flow into the Adriatic Sea from the eastern side of the Strait of Otranto while on the western side, they flow from the Adriatic to the Mediterranean Sea [30][31][32][33][34].

## 2. Influence of Climate Change in the Northern Mediterranean Area

Several authors have demonstrated the Mediterranean's particular sensitivity to the North Atlantic Oscillation (NAO). However, the influence of the NAO on the Mediterranean exhibits heterogeneity and distinct trends in two regions: the Northern Mediterranean (southern Europe) and Central/Northern Europe. These regions demonstrate contrasting patterns to the NAO trend [35][36][37][38][39]. An analysis of rainfall data collected in the Mediterranean spanning two centuries, namely the XIX and XX centuries, was conducted, and the trends over the Italian territory starting from the 1970s were analyzed. The findings revealed a negative trend in rainfall, particularly pronounced during the winter season. This

decrease in rainfall was more prominent in northern Italy compared to the southern regions. Moreover, the study documented an increase in the occurrence of more intense rainfall events during the analyzed period [36][38].

In recent decades, the fluvial loads of rivers in the Mediterranean Sea have undergone significant changes, particularly in the last two to three decades. These changes have had more pronounced and evident effects in the Mediterranean Sea due to two main factors: firstly, the constrained availability of water resources in the Mediterranean region, and secondly, the increased anthropic pressure, especially in coastal areas and the Po Valley. The construction and utilization of river dams have evolved rapidly since the 1950s [40], substantially altering the natural outflow of Mediterranean rivers. The widespread use of these dams for irrigation and various other purposes has led to profound modifications in the fluvial dynamics of the region's rivers. The second crucial factor contributing to these changes is the ongoing climatic shifts in the Mediterranean region. These changes have been extensively documented through the monitoring programs that have recorded variations since the latter part of the 20th century. Additionally, modeling processes have forecasted an increase in drought occurrences, primarily attributed to the rise in temperatures [41][42][43][44][45].

Grilli et al. [46] confirmed that during the first two decades of the 21st century, the river flows of the Po River have exhibited a continuous decrease, along with variable trends in flood events. Specifically, the average daily flow of the Po River was observed to be 12% lower in the period from 2006 to 2015 compared to the earlier period from 1971 to 2005. Notably, the annual mean flow of the Po River experienced significant changes due to the occurrence of persistent drought periods. Moreover, the frequency of flow rates higher than  $3000 \text{ m}^3 \text{ s}^{-1}$  declined between 2006 and 2015 (the latter period considered in the analysis), and such higher flow events were more concentrated in certain months, namely February, April, November, and December. In contrast, previous decades experienced a greater number of these events that were spread over a larger period throughout the year.

Different authors have reported significant changes in various aspects of marine ecosystems [47][48]. These changes include alterations in the composition of plankton communities, shifts in the distribution of macrobenthos, the introduction and spreading of non-indigenous species, changes in the total biomass of target demersal fishes, and fluctuations in the catches of small pelagic fish [49][50][51][52][53][54][55][56][57].

### **3. Nitrogen and Phosphorus Conditioning in the Sea**

The period of significant social changes, robust post-World War II industrial development, and the subsequent globalization of trade from the 1950s to the 1990s led to a substantial increase in the consumption of N and P for various purposes. Notably, N was extensively used as a fertilizer in agriculture, and its subsequent mineralization in surface and ground water, rather than industrial discharges into the atmosphere and urban wastewater, resulted in a substantial input of N watercourses eventually reaching the sea [8]. This pattern was also observed in the Northern Adriatic basin. As for P, its primary uses were prevalent in domestic environments and industry [8]. N and P are two elements that exhibit different behaviors once emitted into terrestrial and aquatic environments. The fate of P in the soil is primarily determined by chemical processes, such as adsorption/desorption and dissolution/precipitation. In contrast, the fate of N is primarily governed by biological processes including mineralization, nitrification, and denitrification [58].

Indeed, the extensive use of P and N during the latter half of the 20th century, along with the effects of climate change, has had significant implications for the Northern Adriatic Sea. The impact of climate change has become particularly evident in this region, starting from the end of the 20th century [36][59]. Notably, these changes are characterized by intense precipitation events, especially in spring and autumn, which significantly influence river outflows, leading to the transport of freshwater and suspended sediment into the sea [18][60][61]. As a consequence, these freshwater and sediment inputs carry pollutants, including N and P [19][23][62][63]. The combination of nutrient inputs from anthropogenic sources and climate-induced changes in hydrological patterns has contributed to alterations in nutrient concentrations and dynamics within the Northern Adriatic Sea.

In Italy, the total use of P in domestic detergents was prevented through Ministerial Decree n. 413 of 13 September 1988, which took effect from January 1989. Previously, from 1985 to 1988, there were other gradual measures implemented to reduce the use of P. Subsequently, in 2012, Europe adopted restrictive measures through Regulation 259/2012/EC, setting limitations for P of 0.5 g/dose in domestic laundry detergents and 0.3 g/dose in domestic dishwasher detergents. These regulatory measures have significantly contributed to the reduction of P inflow in surface watercourses up to the sea. As a result of this reduction, observable effects were recorded in the coastal strip with particular evidence in the Western North Adriatic Sea.

The predictions made by Caggiati & Ferrari <sup>[9]</sup> anticipated a decrease in P levels by the year 2020. Subsequent observations from the late 1990s to the 2000s showed a leveling off of P inputs into the sea, followed by a downward trend in the first two decades of the 21st century. However, the same trend was not observed for N. Despite the study by Caggiati & Ferrari <sup>[9]</sup> and subsequent works (e.g., <sup>[46]</sup>), N levels did not exhibit evident decreases, except in the strictly coastal strip around 3 km from the coast, where observations by Ricci et al. <sup>[23]</sup> demonstrated lower river flows and consequently reduced N and P loads. Over the years, the annual runoff of the Po River has exhibited significant fluctuations on a multi decadal time scale, with an overall decrease (–33% <sup>[64]</sup>) observed in all rivers of the Northern Adriatic when comparing recent discharges to those before the 1980s. Notably, during the dry years 2005–2007 (the last period of data analysis considered), the Northern Adriatic ecosystem experienced a considerable reduction in river water flows and nutrient loads compared to previous years characterized by medium-high regimes, as confirmed by Cozzi & Giani <sup>[64]</sup>.

The decreasing temporal trend of N and P levels observed in the Adriatic Sea is consistent with trends seen in other European seas that are characterized by shallow waters (continental shelf) and are strongly influenced by freshwater inputs. For example, similar trends have been observed in the coastal zone of Baltic Sea as well <sup>[65]</sup>.

The excess accumulation of N and P has significantly accelerated the expansion of eutrophication in these seas. In the Northern Adriatic Sea, the eutrophication phenomenon has been perceived as a pollutant due to the excessive proliferation of algae, which have degraded water quality, benthic habitats, and community structures <sup>[66][67][68]</sup>.

In particular, offshore of the Po Delta and along the western coast, the process of oxygen consumption (hypoxia/anoxia) was accentuated during the summer when waters are warm and calm, and stratification of the water column occurs. This leads to widespread and persistent oxygen deficiencies in bottom waters, resulting in the suffering of benthic communities <sup>[3][69][70][71][72]</sup>. Another important phenomenon that occurred concomitant with eutrophication was the excessive proliferation of mucilage, which was documented especially in the late 1980s and in the early 2000s <sup>[3][7][25][73][74][75][76][77][78]</sup>.

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