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Impact of different forcing factors on N:P balance in a semi-enclosed bay: The Gulf of Trieste (North Adriatic Sea)

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ABSTRACT

The availability and partition of nitrogen (N) and phosphorus (P) in inorganic and organic compartments, as well as their stoichiometric ratio, are influenced by both physical and biological forcing factors. On this basis, the temporal and spatial dynamics in N:P atomic ratios in different compartments may provide information on the functioning of marine ecosystems. Here we explore the relative importance of water temperature, river inputs, wind mixing, stratification, ingression of nutrient-depleted Eastern Adriatic Current and phytoplankton biomass on concentrations and ratios between nitrogen and phosphorus in a semi-enclosed bay (the Gulf of Trieste), using data from monitoring programs carried out during 8 years. Water samples are first classified in 6 water types based on N:P ratios in different components, and then relationships between water type space–time distribution and a set of forcing factors is sought. Results show that the gulf is characterised by relatively stable N:P ratios in all compartments (about 23–26), always exceeding the classical Redfield ratio. In the surface layer, however, nitrogen and phosphorus dynamics are decoupled because of river input and plankton productivity, and a significant spatial and temporal variability is observed in terms of stoichiometric balance, nutrient concentrations and partition among the different pools. Deviations from stable N:P ratios follow a seasonal evolution. In spring, continental inputs alter inorganic nutrient compartments (N:P up to 115); later on, during the seasonal succession of biological processes (e.g. late spring phytoplankton blooms, summer increase in microbial activities and autumn phytoplankton blooms), a change is also seen in the organic dissolved and particulate pools. Multivariate statistical analysis suggests that, among the considered forcing factors, the most relevant in modulating the N:P stoichiometry in the Gulf of Trieste are river inputs and ingression of the Eastern Adriatic Current (acting in opposite directions) along with phytoplankton dynamics. During the whole period, besides variations in N:P stoichiometry, in the Gulf of Trieste dissolved organic matter represents the largest pool of N and P, which can provide a source of nutrients for the planktonic community alternative to inorganic nutrient.

1. Introduction

In regions of freshwater influence, continental nutrient inputs undergo profound transformations due to particle formation, deposition or dissolution through physical, chemical and biological processes. Alterations in the partitions between dissolved and particulate phases and between inorganic and organic pools, and the ratio between nitrogen (N) and phosphorus (P) availability, may severely influence primary production and microbial metabolism. In either N- or P-limited ecosystems, the role of dissolved organic N and P pools may be crucial in sustaining autotrophic production through microbial-mediated recycling processes (Ivančić et al., 2009; Labry et al., 2002; Põder et al., 2003; Stepanauskas et al., 2002), and the particulate compartment may have the ability to "buffer" inorganic matter availability, especially phosphorus concentrations (Conley et al., 1995). In particular, as far as phosphorus is concerned, dissolved inorganic phosphorus (DIP) concentration in turbid estuaries has been shown to be strongly influenced by suspended sediment because it may initially be absorbed onto particles in freshwater and then released as DIP after mixing with

Abbreviations: DIN, dissolved inorganic nitrogen; DIP, dissolved inorganic phosphorus; DON, dissolved organic nitrogen; DOP, dissolved organic phosphorus; EAC, Eastern Adriatic Current; N, nitrogen; NH_4, ammonium; NO_2, nitrite; NO_3, nitrate; P, phosphorus; PN, particulate nitrogen; PO_4, orthophosphate; PP, particulate phosphorus; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus; TN, total nitrogen; TP, total phosphorus

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seawater (Deborde et al., 2007; Fang, 2000; Gardolinski et al., 2004). In the Adriatic Sea, in the northernmost part of which lies the Gulf of Trieste, there is a large excess of nitrogen over phosphorus (Socal et al., 1999; Tedesco et al., 2007; Solidoro et al., 2009) due to the strong imbalance produced by the rivers (Lipizer et al., 1999; Milan et al., 2003; Solidoro et al., 2009). In this area, on the basis of the high N:P ratio in the seawater column and of bioassay studies (Chiaudani and Vighi, 1982; Degobbis, 1990; Graneli et al., 1999; Pojed and Kverder, 1977), phosphorus is regarded as the limiting nutrient for primary productivity. In fact, after enforcement of environmental regulation banning phosphorus use in detergents, a reversal in eutrophication trends and a decline in chlorophyll-*a* concentration has been observed all over the basin (Mozetič et al., 2010). Accumulation of dissolved organic matter, possibly due to severe phosphorus limitation of bacterial efficiency (Thingstad et al., 1997; Thingstad and Rassoulzadegan, 1995) may greatly affect the marine environment, favouring seasonal bottom oxygen depletion (Malej and Malačič, 1995; Orel et al., 1993) and formation of mucilaginous aggregates (Degobbis et al., 2000; Fonda Umani et al., 2007; Precali et al., 2005). The occurrence of these phenomena seems to be associated with an excess of organic matter, with uncoupling between nitrogen and phosphorus in both inorganic and organic compartments (Danovaro et al., 2005; Degobbis et al., 2005; Graneli et al., 1999; Lipizer et al., 1997; 1999; Obernosterer and Herndl, 1995) and with phosphorus limitation of biological processes (Graneli et al., 1999; Socal et al., 1999; Zoppini et al., 2005).

The Gulf of Trieste is a shallow, semi-enclosed bay, influenced by external inputs of different origins, including rivers (Isonzo–Soča), urban wastes from Trieste and Monfalcone, karsic groundwaters and ingression of the Eastern Adriatic Current (EAC). The different inputs are characterised by distinct concentrations, partitions and ratios between N and P in the different pools (Burba et al., 1992; Cozzi et al., 2008). It is believed that physical (general circulation, seasonal temperature cycle, river inputs, vertical stratification, wind mixing) and biological (autotrophic and heterotrophic processes of production, consumption and remineralisation) forcing factors interact on nutrient pools (Solidoro et al., 2007), modifying the partition among the dissolved–particulate and inorganic–organic compartments and also the stoichiometric ratio. Modification of stoichiometric composition during flows of matter through different ecosystem components implies a selective utilisation, so altered N:P values possibly represent a trackable signal of mass transfer from the dissolved inorganic to the dissolved and particulate organic pools through biological activity. On this basis, an analysis of the temporal evolution of N:P ratios in the different compartments, associated with the study of the variability of several forcing factors, might contribute to the understanding of the functioning of the system.

The aim of this study is to explore and possibly disentangle the relative importance of several physical and biological forcing factors on temporal and spatial variability of N and P stoichiometry and partition in this coastal area. The analysis is based on *a posteriori* elaboration of data collected during an 8 years monitoring programme. Data were collected on a monthly basis in a network of fixed sampling stations. However, given high space–time variability of most ecological processes in this highly dynamic environment, we chose to look for a dynamic representation of the system, obtained by grouping together samples with similar properties, and therefore probably representing a water mass characterised by similar biogeochemical conditions and driving processes, even if observed in different time and space (Solidoro et al., 2007), and then looking for correlations between space–time distribution of this biogeochemical condition and external forcing factors.

In this paper, the classification of samples in water typology classes was based on differences and similarities among N:P ratios in the dissolved and particulate, organic and inorganic phases. The classification enabled recognition of similar and regular patterns in the modification in N:P stoichiometry, i.e. conditions mainly associated with a particular area and a particular period. These first results were then combined with information on the relative importance of several forcing factors (temperature, wind, river, stratification, seawater ingression from south and autotrophic biomass) in different areas, and the outcome allowed to assess the roles of internal processes and external inputs in shaping N:P stoichiometry in the water masses of the Gulf of Trieste.

2. Materials and methods

2.1. The area

The Gulf of Trieste is a semi-enclosed basin, located in the northernmost part of the Adriatic Sea, with a maximum depth of 25 m (Mozetič et al., 2002). The area is strongly affected by the freshwater inputs from the Isonzo River in the shallow northwestern coast (Malej et al., 1995; Stravisi, 1983) and from several submarine freshwater springs along the eastern karsic coast, characterised by short-term variability. The general circulation is usually cyclonic, but local atmospheric forcing (winds) and river plumes can strongly modify this overall scheme, especially in the surface layer (Malačič and Petelin, 2001; Malačič, 2003; Stravisi, 1983). The peculiar tidal regime of the area (Malačič et al., 2000), the alternation between winter mixing and summer stratification processes of the water column, the strong north-easterly winds (Bora), which can modify the vertical structure in a few hours (Querin et al., 2007) and the variable freshwater contributions together result in a very large inter-annual, seasonal and short-term variability in the hydrological and trophic conditions of the basin.

2.2. Sampling and analytical protocols

The data were collected in the framework of INTERREG II, INTERREG III Italia–Slovenia and Ecomadr research and monitoring projects.

Data discussed here refer to the period January 1999–December 2006 and derive from five stations (C1, T3, T11, T24 and T25) visited monthly since January 1999 (Fig. 1) and four additional stations (T8, T22, T23 and T26) included after June 2002; furthermore, station C1 was monitored on a weekly basis during the period May 2002–August 2005. In each station discrete samples for chemical analyses were collected with Niskin bottles at three depths (in the surface, intermediate and bottom layers) and at 0, 5, 10 and 15 m at station C1. Samples for dissolved organic and inorganic components were filtered onboard (pre-combusted Whatman GF/F filters, 450 °C for 4 h), collected in acid washed polyethylene vials rinsed with seawater and immediately frozen (−20 °C) until laboratory analysis. The dissolved inorganic nutrients orthophosphate ($P–PO_4$), ammonium ($N–NH_4$), nitrite ($N–NO_2$) and nitrate ($N–NO_3$) were analysed colorimetrically with a segmented flow autoanalyzer according to Grasshoff (1983). Total dissolved phosphorus (TDP) and nitrogen (TDN) were determined as $P–PO_4$ and $N–NO_3$, respectively, after UV decomposition of organic matter with addition of hydrogen peroxide to ensure oxidation (Armstrong et al., 1966; Golimowski and Golimowska, 1996). Dissolved organic phosphorus (DOP) and nitrogen (DON) were calculated as the difference between TDP and $P–PO_4$ and between TDN and dissolved inorganic nitrogen (DIN; $= N–NO_2 + N–NO_3 + N–NH_4$), respectively. The detection limit for phosphate, ammonium and nitrite+nitrate were 0.02, 0.04 and