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Carbon and nitrogen isotope composition of particulate organic matter in relation to mucilage formation in the northern Adriatic Sea

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ABSTRACT

Carbon and nitrogen stable isotope ratios of particulate organic matter (POM) were studied approximately weekly during spring and summer 2003 and 2004 in the Gulf of Trieste (northern Adriatic Sea) in order to track the temporal variations and differences between two years. In parallel, particulate organic carbon (POC) and particulate nitrogen (PN), phytoplankton biomass (chlorophyll *a*), and N and P nutrients were monitored. All studied parameters, especially N and P nutrients and chlorophyll *a*, showed higher concentrations and larger variability in spring 2004. As a consequence the macroaggregates were produced in late spring 2004. The C and N isotope composition of POM was not directly linked to phytoplankton biomass dynamics. The $\delta^{13}C_{POC}$ values covaried with temperature. In 2004, $\delta^{13}C_{POC}$ variations followed the $\delta^{15}N_{PN}$ values as well as the $\delta^{13}C_{DIC}$ values which were probably more dependent on the photosynthetic use of ^{12}C. Variations in $\delta^{15}N_{POM}$ values were most probably the consequence of variations in N nutrient sources used in phytoplankton assimilation. The significant correlation between $\delta^{15}N_{PN}$ values and nitrate concentrations in 2004 implies intense nitrate assimilation in the presence of higher nitrate concentration. This suggests nitrate as the key nutrient in the »new primary production«, later producing macroaggregates with a mean $\delta^{13}C$ and $\delta^{15}N$ values of −19‰ and 5‰, respectively. A low fractionation factor ε, <1‰, lower than that reported in other marine and lacustrine systems, was found probably to be a consequence of distinct phytoplankton species, i.e. several classes of autotrophic nanoflagellates, and specific growth conditions present in the Gulf of Trieste. The tentative use of C isotope composition of POM revealed a higher contribution of allochthonous organic matter in 2004 compared to 2003 due to higher riverine inflow.

1. Introduction

The study of the biogeochemistry of coastal seas, comprising about 20% of ocean area, is important because of their intense productivity and related biogeochemical C and N cycles (Walsh, 1991). They are at present affected by increasing eutrophication and climate changes (Meyers, 1997). The northern Adriatic Sea is an example of such a marine basin where phytoplankton blooms are mostly induced by the riverine nutrient input leading occasionally to mucilage appearances (Malone et al., 1999; Giani et al., 2005) composed predominantly of heteropolysaccharides and lipids (Kovac et al., 2008). Hence, knowledge of basic biogeochemical processes governing phytoplankton production and organic matter formation in this area could help to clarify the formation of macroaggregates.

Stable C and N isotopes are nowadays widely recognized as reliable indicators of marine microbial and biogeochemical processes (Altabet, 1996; Fry, 2007). Complete understanding of these processes can be achieved only through knowledge of the isotopic composition of the source matter and the corresponding fractionations in microbial transformations. These studies are difficult to perform under natural conditions because of the occurrence of different reactions and processes (Ostrom et al., 1997). Variations in ^{13}C in phytoplankton are mostly the result of species composition, temperature, light intensity, growth rate, membrane permeability, C fixation pathways and carbonate equilibrium (pCO_2) (Thompson and Calvert, 1995; Rau et al., 1997; Ostrom et al., 1997, Popp et al., 1998). According to Nakatsuka et al. (1992) the ^{13}C of blooming phytoplankton seems more dependent on the growth rate rather than on phytoplankton species and the ^{13}C composition of DIC. The ^{15}N isotopic signal allows us to decode the N microbial processes including assimilation, fixation, mineralization, nitrification and denitrification (Altabet, 1996; Ostrom et al., 1997). Phytoplankton ^{15}N composition primarily reflects isotopic discrimination during NO_3^- uptake (Nakatsuka et al., 1992) as well as N_2 fixation and N recycling including the zooplankton release (Pantoja et al., 2002). ^{13}C and ^{15}N enrichment through the marine food web of about 1–2‰ and 3–3.5‰, respectively, is usually observed (Ostrom and Fry, 1993). ^{13}C and ^{15}N primary isotope signals can be altered during heterotrophy and sediment burial (Jasper and Hayes, 1990; Sachs et al., 1999).

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The principal scope of this study was to investigate the temporal variability of the stable carbon and nitrogen isotope composition of particulate organic matter (POM) in the Gulf of Trieste (northern Adriatic Sea) in a year affected (2004) and not affected (2003) by mucilage formation. In order to better understand POM dynamics, the determination of particulate organic carbon (POC) and nitrogen (PN), chlorophyll *a*, dissolved inorganic carbon (DIC) and its ^{13}C isotopic composition, as well as nitrogen and phosphorus nutrients were made. Finally, this study aimed to determine the major mechanisms that influence the temporal variations of ^{13}C and ^{15}N in POM in the northern Adriatic Sea.

2. Materials and methods

2.1. Study area

The Gulf of Trieste is a shallow marine basin in the northernmost part of the Adriatic Sea (Fig. 1). The Gulf is approximately 500 km^2 in area with a maximum depth of 25 m and is partially isolated from the rest of the northern Adriatic Sea by a shoal extending SE–NW, from the Istrian peninsula to the Grado lagoon. The main freshwater inflow is from the Isonzo (Soca) River in the north with an average flow of about 200 $m^3\ s^{-1}$ exhibiting spring and autumn floods governing by snowmelt and rain, respectively (Fig. 2). The salinity of surface waters in the gulf ranges roughly between 30 (in spring) and 38 psu (Fig. 2), and surface water temperatures (Fig. 2) vary normally from 8 °C (February) to 26 °C (August). Vertical temperature and salinity gradients in late summer result in bottom water O_2 depletion and occasionally hypoxia and anoxia.

2.2. Samples

Sea water samples were taken weekly to biweekly from March to November 2003, and from February to September 2004 from the surface layer (0.3 m depth) at a sampling point F (45° 31.46' N, 13°33.72' E) in the southeastern part of the Gulf of Trieste (Fig. 1) using Niskin samplers. 5 L of water sample were filtered through precombusted Whatman GF/F filters (nominal pore size 0.7 µm), washed with small volume of distilled water, freeze dried, weighed and used for POC, PN, $^{13}C_{POC}$ and $^{15}N_{PN}$ analysis. 20 ml of water sample was filtered through Millipore membrane filter (nominal pore size 0.22 µm) for chlorophyll *a* determination. 0.5 L of unfiltered seawater sample was used for nutrient analysis.

Macroaggregates were collected in June 2004 at the sea surface using polyethylene bottles. Macroaggregates were centrifuged at 10,000 rpm for 15 min at ambient (20 °C) temperature. The sediment was rinsed with small volume of distilled water to remove salt and then freeze-dried to dryness. Supernatant was first filtered through a 0.2 µm filter and then ultrafiltered using a Vivascience (Sartorius) ultrafiltration system with 30,000, 10,000 and 5000 Da cutoff membranes. Three fractions with nominal molecular weights 30,000–10,000 (VF1), 10,000–5000 (VF2) and <5000 (VF3) were isolated. All ultrafiltered fractions were subsequently freeze dried.

2.3. Cultures

Cultures of *Scrippsiella trochoidea* (SCR), *Prorocentrum minimum* (PMNK), *Thalassiosira pseudonana* (THPN), and *Skeletonema costatum* (SKE), isolated from the Gulf of Trieste, were obtained from Department of Biological Oceanography, National Institute of Oceanography and Applied Geophysics Trieste (Italy). They were grown in f/2 medium (Guillard, 1975) and maintained at room temperature during a 12-hour light–dark cycle under 20 W fluorescent lamps. Cultures were not axenic. They were harvested at the stationary phase of growth, filtered through precombusted Whatman GF/F filters and freeze-dried.

2.4. Analyses

Nutrients, including nitrate (NO_3^-), ammonium (NH_4^+) and phosphate (PO_4^{3-}) were measured using standard colorimetric methods (Grasshoff et al., 1983). The precision of measurement was ±5%.

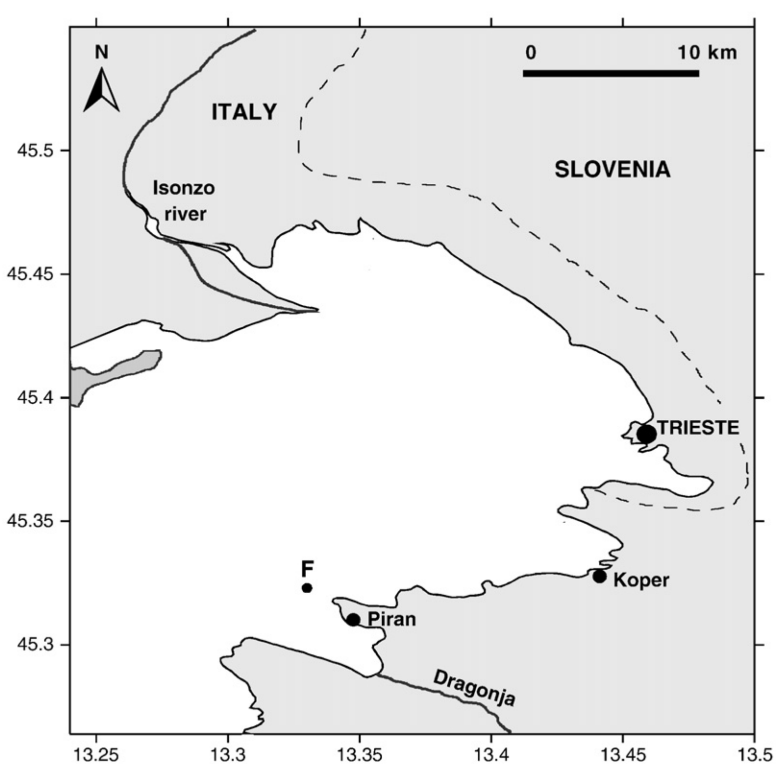

Fig. 1. Location of study site F in the Gulf of Trieste (northern Adriatic Sea).