Diel metabolism and nutrient cycling in the northern Adriatic lagoonary sediments

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Abstract: Metabolism and nutrient fluxes were studied in the Lagoon of Grado (Gulf of Trieste, N Adriatic) using in situ deployed clear benthic chambers. It was found that there were several processes influencing the biogeochemistry of this environment including various microbial processes, degradation of organic matter, carbonate dissolution and precipitation and exchange between pore water and overlaying water.

Key words: lagoon, incubation experiment, nutrient fluxes, metabolism

Introduction

Lagoonary systems, areas of great economic importance and subjected to pollution, are characterized by intense benthic primary production. The aim of this study is to present the metabolism and nutrient fluxes found in the Lagoon of Grado (The Gulf of Trieste, N Adriatic) using in situ deployed light benthic chambers. Field experiments were performed in June and September/October 2003, and March 2004 at stations Artalina (ART) at depth of 1.5-1.8 m and Barbana (BAR) at depth of 0.5-1.5 m. The surficial sediments are composed of sand (10%) and pellites (90%) and are bioturbated mainly by polychaetes. The carbonate content averages about 50%. The sediment is inhabited by extensive beds of marine diatoms and at station BAR also by some patches of macroalgae *Gracilaria*. The chamber consists of a 30x50x30 cm Plexiglass box, which is open at the bottom, with valves on the lid for sampling and a flexible polyethylene bag to compensate for the volume removed during sampling. Attached to the inside of the chamber lid is a stirring mechanism coupled to a motor driven at a speed of 50 rpm. After 2, 3 and 12 hours samples were collected by divers. In addition, virtually undisturbed sediment cores were collected by divers inserting a Plexiglass tube (12.5 cm i.d.) directly into the sediment. The sediment was extruded and sectioned into 1 and 2 cm intervals in a N_2-filled glove bag, and pore water extracted by centrifugation. The water and pore water samples, except for oxygen, were filtered through 0.45 mm Millipore HA membrane filters. Diel fluxes of solutes across the sediment-water interface were evaluated from the significant differences between extremes and by integrating the area under rate of chang-

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ing diel curves. Nitrate, ammonium, phosphate, dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were determined using standard procedures (GRASSHOFF ET AL., 1983). Oxygen was determined by the Winkler method (GRASSHOFF ET AL., 1983). Alkalinity was measured by titration with HCl, and dissolved inorganic carbon (DIC) using a Shimadzu TOC 5000A analyzer. The HCl acidified samples were analyzed for dissolved organic carbon (DOC) using a high temperature catalytic oxidation (Shimadzu TOC 5000A) analyzer. The isotopic composition of DIC ($\delta^{13}C_{DIC}$) was analyzed in CO_2 liberated from water samples after acidification, using a Europa 20-20 mass spectrometer.

RESULTS AND DISCUSSION

Pore waters and solid phase

A general increase in concentrations with sediment depth were observed for DIC, NH_4, and PO_4^{3-}, while for DOC, DON and DOP an irregular depth pattern was observed. The inorganic N/P ratios were mostly >20 (atomic). Steep near-surface gradients were observed for all solutes. Higher concentrations of DIC, NH_4^+, PO_4^{3-}, DON and DOP, and DOC in autumn were observed at station ART compared to station BAR. The $d^{13}C_{DIC}$ values show a decreasing trend with depth and lower values were always found at station ART influenced by more pronounced degradation of organic matter. Sedimentary C_{org} levels were also higher at station ART (2.7-1.8 %) compared to BAR (approx. 1.2 %).

Benthic processes

Substantial diel patterns of dissolved O_2, DIC, NH_4^+, NO_3^-, PO_4^{3-}, DOC, DON and DOP were observed during the series of measurements at both stations except in September at station ART where a temporal decrease of O_2 and an increase of DIC and NH_4^+ concentrations appeared. Normally, inverse correlations appeared between diel O_2 and DIC changes. An inverse correlation was also observed between diel fluctuations of NH_4^+ concentrations and O_2 fluctuations. The lowest NH_4^+ concentrations appeared during the photoperiod despite the fact that benthic micro- and macroalgae may show a reduced but still substantial uptake of ammonia at night (NIXON ET AL., 1976). Ammonia is suggested to be an active inorganic nutrient in N as-

Table 1. Apparent daytime benthic community production during incubation experiments at stations Artalina (ART) and Barbana (BAR).

Date	Station	Temperature (°C)	Production (mM O_2 $m^{-2}d^{-1}$)	Production (mM C $m^{-2}d^{-1}$)
June	ART	26-30	8	13
2003	BAR	26-29	40	35
Sept	ART	20-23	12	55*
2003	BAR	18-19	13	75**
March	ART	2-4	17	28
2004	BAR	4-9	29	16

* C_{org} mineralization; ** carbonate dissolution

similation processes and supported high biomass in the lagoon indicating a highly efficient recycling of N within the lagoon community. Generally, the high inorganic N/P ratios observed suggest that an excess of N was present and that the whole lagoon ecosystem is most probably P-limited. Nutrient regeneration at the sediment-water interface and in surficial sediment is the primary source of nutrients available for assimilation processes, especially in the warmer period of the year (June, September) when the natu-

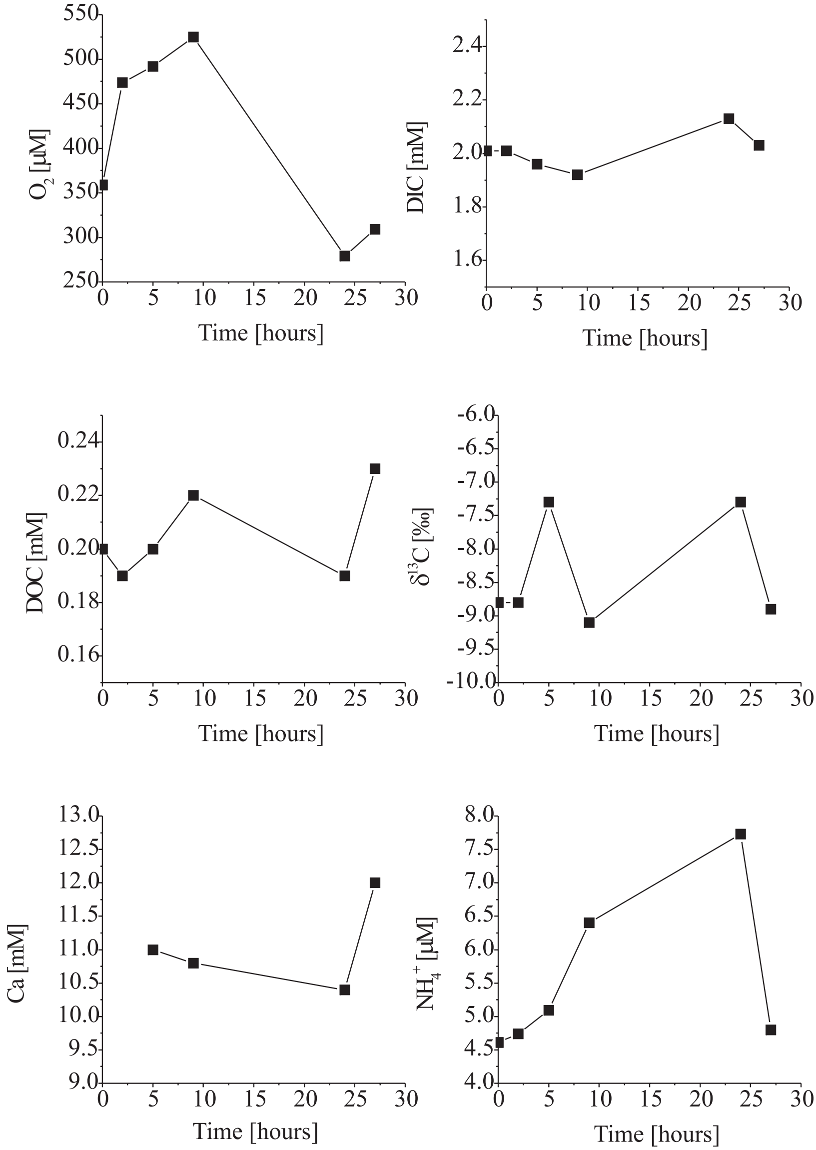

Figure 1. Example of the diel cycle of O_2, DIC, DOC, $\delta^{13}C_{DIC}$, Ca, NH_4^+ concentrations at station BAR in June 2003.

ral nutrient input from fresh water inflows is limited. The NO_3^-, PO_4^{3-}, DOC, DON and DOP variations were apparently not related to changes of O_2 and DIC. The decoupling between O_2-DIC concentrations and the nutrient results indicate that the benthic primary producers are capable of storing nutrients or that other un-measured nutrient pools are supporting primary production.

The apparent community production measured from DIC concentration differences were higher than the O_2-based production estimations (Table 1) in September probably due to intense mineralization, decoded by lower $\delta^{13}C_{DIC}$ values averaging –6.7 ± 0.3 ‰, at station ART and carbonate dissolution, $\delta^{13}C_{DIC}$ values approaching 0 ‰, at station BAR. This trend was also confirmed by pore water $\delta^{13}C_{DIC}$ values. In June at station BAR, the DIC mostly originated from C_{org} mineralization while in other periods both the carbonate dissolution and C_{org} mineralization were important. However, no attempt was made to differentiate between micro- and macroalgae production at BAR and we consider the benthic microalgae as the most important primary producer.

In conclusion, the Grado lagoonary system is characterized by the coupling of metabolism and mineralization. This lagoon environment accumulates rather high nutrient concentrations through benthic micro- and also macroalgae assimilation and decomposition. These benthic biogeochemical processes are probably also important for trace metal cycling, especially Hg mobilization and sequestration in the studied area.

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