

## Diffusive fluxes of dissolved nutrients at the sediment/water interface in Makirina Bay (Central Dalmatia, Croatia)

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The biogeochemical cycles of nutrients in coastal regions exhibit some peculiarities compared to those in open ocean basins. Coastal areas are directly exposed to anthropogenic pollution. The productivity of biomass is higher and a significant part of primary production takes place within the sediment; however, a high sedimentation rate increases the preservation rate of organic carbon in the sediment. The coastal situation is furthermore specific because of terrigenous input of sedimentary organic matter that is less enriched in N and P than marine detritus, suggesting that coastal zones are a more efficient sink for carbon than for other nutrients. However, the organic-rich coastal sediment is also an important source of dissolved carbon, at least for the bottom water mass. The aim of our work was to quantify the diffusive benthic fluxes of dissolved inorganic carbon (DIC), nitrogen, phosphorus, and sulphur at the sediment/water interface in a shallow coastal area, as well as to estimate the source of DIC efflux from the sediment using isotope techniques.

### Site description

Makirina represents the southernmost part of the Bay of Pirovac in the ibenik aquatorium (Central Dalmatia, Croatia). Its dimensions are approx. 1250x300 m with water depth between 0.1 and 4.5 m. In the Southern part of Makirina, which was investigated in this study, the depth is between 0.2 and 0.5 m. In the case of an extremely low tide (a few times per year), complete withdrawal of the water mass can take place. The carbonate bottom of the bay is covered by a layer of clayey silt (up to 2 m thick) with typical characteristics of peloid mud covered by sea grasses and algae such as *Posidonia oceanica*, *P. mediterranea*, *Zoster marina*, *Acetabularia mediterranea*, and *Codium bursa*. Phase analysis of the surficial segment (0–35

cm) of the recent sediment revealed that terrigenous non-carbonate minerals represent as much as 60% of the total inorganic fraction. Among the carbonates dolomite prevails over amorphous CaCO<sub>3</sub>, calcite and aragonite of mostly authigenic origin. The presence of framboidal pyrite indicates the existence of micro-environments with strongly reducing conditions even in the uppermost part of the sediment column (0–1 cm) in spite of intensive bioturbation and irrigation due to macrobenthic organisms.

### Materials and methods

Sediment cores were collected manually in July 1997 in the shallow part of the bay (water depth <30 cm) with a Plexiglas tube of inner diameter 36 mm. Sediment cores were cut into 2–4 cm thick sections and pore water was squeezed from the sediment in an inert atmosphere under a nitrogen pressure of 0.4 MPa and filtered through a 0.45 µm membrane filter. The pH was measured immediately after collecting the pore water samples. Successive samples were collected for total alkalinity (2 ml), metal cation analysis (5 ml), nutrient (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) analyses (5 ml) and δ<sup>13</sup>C-DIC (3 ml). The latter sample was preserved with HgCl<sub>2</sub> to suppress the microbial activity during storage. Pore waters for analyses of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> were refrigerated. For metal analysis ultra-pure HNO<sub>3</sub> was added. Total alkalinity was determined by the Gran titration method. The concentration of DIC was calculated from pH and total alkalinity. Nitrate, nitrite, ammonia and phosphate concentrations were determined using standard colorimetric procedures. Sulphate was determined turbidimetrically. The precision of all anion analyses was better than ±2%. Concentrations of Ca<sup>2+</sup> (± 2%), Mg<sup>2+</sup> (± 1%) and Fe<sub>tot</sub> (± 3%) in pore water were measured

by flame AAS (Varian AA5). The stable isotope composition of DIC was determined by mass spectrometry on  $\text{CO}_2$  extracted from water samples with 100%  $\text{H}_3\text{PO}_4$  in evacuated ampoules. Results are reported in permil (‰) as deviation from the Vienna PDB standard (VPDB). The concentration of organic carbon in the sediment was determined on a LECO IR-212 Organic Carbon Determinator, total sulphur was measured using a LECO SC-132 Sulphur Determinator and total nitrogen using a LECO CHN-600 Elemental Analyser.

## Results and discussion

The concentration of organic carbon and total nitrogen in the sediment is relatively high (up to 5 and 2%, respectively) which is favourable for the development of anoxic conditions that promote preservation of organic matter in the sediment. The C:N ratio is extremely low ( $1.5 < \text{C/N} < 4.5$ ) which is very untypical for marine sediments, as well as for terrestrial organic litter (20 or more, Ulrich and Bredemeier, 1993). In spite of the high nitrogen concentration in the sedimentary organic matter, the concentration of dissolved nitrogen in the pore water did not exceed 0.2 mM/l, indicating that the release of nitrogen as a consequence of the decomposition of sedimentary organic matter into the pore water is rather small, or that the dissolved nitrogen species are consumed by some other processes. The high concentration of sedimentary organic matter enables formation of anoxic microenvironments where anaerobic decomposition of organic detritus close to the sediment/water interface, including intensive bacteria-mediated methanogenesis, can take place. At the same time, the bottom of Makirina Bay is mostly covered by sea-grasses. Assuming both circumstances, nitrogen or ammonia fixation by the bacterial population and plants can form a possible explanation. This process was found in numerous and varied coastal environments and has to be quantitatively taken into account, especially in saltmarsh and sea-grass ecosystems (Capone, 1988). Nevertheless, the most plausible explanation for the extremely high nitrogen accumulation in the sediment could be the fertilization of fields and vineyards located close to the edges of Makirina Bay.

The pH,  $\text{Mg}^{2+}$ ,  $\text{Fe}_{\text{tot}}$ ,  $\text{Mn}_{\text{tot}}$ , and  $\text{SO}_3^{2-}$  concentrations in pore water decrease with depth, whereas total alkalinity, DIC and  $\text{Ca}^{2+}$  increase as expected for environments where anaerobic processes of decomposition of sedimentary organic matter take place. The observed increase of  $\delta^{13}\text{C-DIC}$  with depth is typical for methanogenic environments. Consumption of

sulphate, iron and manganese is due to precipitation of authigenic mineral phases such as framboidal pyrite which was found in the uppermost segment of the sediment (0–1 cm). The concentration depth profile of nitrate and ammonia is more irregular because of processes discussed above. A concentration increase in the upper part of the sediment column is typical of environments where intensive decomposition of sedimentary organic matter takes place, whereas the decrease below 10 cm can be attributed to secondary assimilation processes.

The concentration profiles of solutes in the pore water were described using a one-dimensional model adapted to porous sediments in the form of the general diagenetic equation by Berner (1980), where advection was taken to be unimportant relative to diffusion over the entire depth interval and enhanced transport due to irrigation was not included either. The same approach was used to determine the reaction rates in similar terrigenous sediments by Aller (1980). If the sediment solute distribution is assumed to be controlled by a one-dimensional vertical transport and reaction processes, the diffusive flux of a constituent across the sediment/water interface,  $J_{\text{diff}}$  [ $\text{mmol m}^{-2} \text{day}^{-1}$ ], can be calculated by Fick's first law and is independent of transport in the steady state. Values obtained were  $9.81 \text{ mmol m}^{-2} \text{day}^{-1}$  for DIC,  $-0.58 \text{ mmol m}^{-2} \text{day}^{-1}$  for  $\text{NH}_4^+$ ,  $-0.28 \text{ mmol m}^{-2} \text{day}^{-1}$  for  $\text{NO}_3^-$ , and  $0.002 \text{ mmol m}^{-2} \text{day}^{-1}$  for  $\text{PO}_4^{3-}$ . The primary source of the dissolved inorganic carbon in pore water, i.e. the main process governing its formation, was resolved using a plot of the DIC concentrations vs its isotopic composition,  $\delta^{13}\text{C-DIC}$ . The positive correlation between  $\delta^{13}\text{C}_{\text{DIC}}$  values and DIC concentrations below a depth of 2.5 cm in the sediment indicates prevailing methane production in the absence of methane oxidation (LaZerte, 1981; Herczeg, 1988).

## Conclusion

A strong anthropogenic influence on the environmental conditions in the Bay was observed, resulting in an extremely low C/N ratio in the sedimentary organic matter. In spite of the extremely high N concentration in the sediment, the observed benthic flux of dissolved nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) was negative, indicating strong assimilation of dissolved nitrogen in the sediment. In spite of intensive macrobenthic activity, anaerobic degradation of sedimentary organic matter takes place even in the uppermost layer (0–1 cm) of the sediment with methanogenesis as the predominant source of dissolved inorganic carbon.