Biogeosciences
Discussions

Open Access

Diagenesis and benthic fluxes of nutrients and metals during experimentally induced anoxia in the Gulf of Trieste (northern Adriatic Sea)

N. Koron[1], N. Ogrinc[2], E. Metzger[3], B. Riedel[4], and J. Faganeli[1]

[1]National Institute of Biology, Marine Biological Station, Fornače 41, 6330 Piran, Slovenia
[2]Jožef Stefan Institute, Department of Environmental Sciences, Jamova 39, 1000 Ljubljana, Slovenia
[3]LUNAM Université, Université d'Angers, UMR CNRS 6112 LPGN-BIAF-Laboratoire des Bio-Indicateurs Actuels et Fossiles, 2 Boulevard Lavoisier, 49045 Angers Cedex, France
[4]University of Vienna, Department of Limnology and Oceanography, Althanstrasse 14, 1090 Vienna, Austria

11729

Abstract

Sequential nutrient regeneration and organic matter (OM) degradation in surface sediments of the Gulf of Trieste (northern Adriatic Sea) were examined using in situ benthic chambers under normoxic, anoxic and reoxic conditions. Intensive NH_4^+ and PO_4^{3-} anoxic regeneration was subsequently slower in prolonged anoxia. NH_4^+ production was probably also a consequence of dissimilatory nitrate reduction to NH_4^+. The presence of anammox and laterally pumping of oxygenated water by benthic infauna explained the presence of NO_3^- in anoxia. Anoxic phases were characterized by enhanced dissolution of Si_{biog}, decreasing pore water Ca and Mg concentrations indicating carbonate precipitation and higher Fe and Mn concentrations as a result of reduction/respiration. Reoxygenation was characterized by enhanced bioturbation. Nitrification caused NH_4^+ decrease and P precipitated quickly as carbonate fluorapatite and $FePO_4$. In addition adsorption of P onto Fe-hydroxides could also occur since Fe (and Mn) reoxidized quickly. Increased Ca levels suggested enhanced carbonate dissolution. Diffusive fluxes at the sediment–water interface (SWI), calculated from pore water modelling using diffusion-reaction model, revealed high anoxic NH_4^+ effluxes and Ca (and Mg) influxes. PO_4^{3-} fluxes were very low and high NH_4^+/PO_4^{3-} flux ratios in anoxic and reoxic phases suggested an excess of benthic inorganic N. Nutrient budgets at the SWI showed intensive anoxic recycling of inorganic N but low P and Si cycling in all redox phases.

1 Introduction

The Gulf of Trieste is an example of shallow coastal marine environments that are characterized by relatively low organic matter (OM) contents in sediments (Ogrinc et al., 2005). The largest fraction of sedimentary OM originates from the pelagic production, which escapes degradation in the water column and settles on the sediment bed. The remainder originates from benthic primary production, which represents a significant

source of easily degradable OM in this environment due to the euphotic zone reaching the bottom (Kemp et al., 1999; Welker et al., 2001). The autochthonous (marine) origin of OM is confirmed by its $\delta^{13}C_{org}$ values (Faganeli et al., 1991; Ogrinc et al., 2005). The Gulf, becoming recently oligotrophic, experiences two phytoplankton blooms yearly occurring in spring and autumn (Mozetič et al., 2012). The first is a consequence of increased nutrient-rich fresh water inflow into the Gulf, whereas the autumn bloom follows disruption of the stratified summer water column, and thus releases of the trapped nutrients. Benthic microalgae exhibit summer peaks due to the highest release of nutrients from pore waters (Welker et al., 2002).

Vertical stratification of water masses in the gulf lead to O_2 depletion in the bottom water layers causing hypoxia and even anoxia (Kemp et al., 1999). Coastal hypoxia and anoxia are widespread and increasingly common events that can result in seasonal or even persistent "dead zones" (Diaz and Rosenberg, 2008), which are also known in the Gulf of Trieste (Faganeli et al., 1985; Stachowitsch, 1991; Riedel et al., 2008). These can influence the biogeochemical processes taking place in sediment by marine microorganisms and influenced by activities of benthic infauna. The latter include changes in sediment burrowing and reworking by benthic invertebrates (Aller, 1982). In sediments of the Gulf of Trieste, the most important macrofauna are sea urchins, brittle stars and polychaetes (Ogorelec et al., 1991; Stachowitsch et al., 2007). Their activities influence nutrient release and the redox cycling of elements at the sediment–water interface (SWI) (Hunter et al., 2012). With the occurrence of hypoxia or even anoxia, the activity of sediment infauna decreases limiting the sediment reworking and reoxidation of reduced chemical species originating from deeper sediment layers where anoxic OM mineralization takes place (Aller and Yingst, 1988; Hines et al., 1997). This leads to a migration of reductive layers upwards and enhances the importance of sulfate reduction in the topmost sediment layers. Due to the accumulation of toxic hydrogen sulfide, the mortality of benthic macrofauna increases and the decaying biomass acts as an additional source of "fresh" easily degradable OM.

11731

The aim of this study was to simulate anoxia and reoxidation for variable amount of time in order to investigate the consequences of shifts in benthic biogeochemical processes using the changes of pore water composition of nutrients and metals encompassing oxic and anoxic conditions and subsequent recovery. Since the composition of pore water serves as a sensitive indicator of early diagenetic reactions (Berner, 1980), it was the primary focus of this research. This study was a part of a broader project entitled "Low dissolved oxygen events in the Northern Adriatic: in situ experimental insights into multi-level responses before, during and post-anoxia" with its main objectives being a behavior, mortality and regeneration of infauna community in extreme conditions. The recovery of deteriorated marine environment, which experiences severe anoxia events is usually slow. Sedimentary biogeochemical data were used also as a proxy for evaluating environmental status in such extreme conditions and as a tool for projection of environmental consequences induced by anoxia. The results also allow us to discuss the consequences of advanced remineralization in a relatively organic poor sedimentary environment.

2   Materials and methods

2.1   Study area

The study site was located 2.3 km off Piran (Slovenia) in the southern part of the Gulf of Trieste (northern Adriatic Sea) at the Marine Biological Station hydrographic buoy Vida (45°32.300′ N, 13°33.000′ E). This northernmost part of the Adriatic Sea is covering an area of 500 km^2 with a maximal depth of 25 m and is isolated from the rest of northern Adriatic by a shoal. The salinity of bottom waters ranges from 36 to 38.5 and bottom water temperatures range from 8 °C in winter and 20 °C in summer. A density gradient in late summer can result in bottom water layer hypoxia and even anoxia (Faganeli et al., 1985). Sediment in the southern part of the Gulf is composed mainly of silty sand that is high in biogenic carbonate, populated mostly by brittle stars, sponges and

11732

tunicates and actively bioturbated by polychaetes and bivalves (Ogorelec et al., 1991). The sedimentation rate, determined using ^{210}Pb, is approximately $1.2\,\mathrm{mm\,yr^{-1}}$ in the central part of the gulf increasing up to $3\,\mathrm{mm\,yr^{-1}}$ towards the shore (Ogorelec et al., 1991). The sediment surface is populated by microalgae composed mostly of diatoms (Welker et al., 2002).

2.2 Experimental design and sampling procedure

Benthic experiments, conducted from 2009 to 2011, included a simulation of different episodes of anoxia using benthic chambers with each simulation experiment consisting of three separate phases. The first phase, called normoxic, represented conditions that governed the environment at the time of sampling. This phase was followed by the anoxic phase, in which the system inside the benthic chamber slowly became anoxic due to benthic respiration and limited contact with outer environment. The anoxic phase was followed by the recovery phase, in which the benthic chamber was removed and the system was left to recover for at least 7 days. Various durations of anoxia were simulated throughout the project. In 2009, anoxia only 7 days in length was mimicked. In the following year a greater number of experiments were performed, with anoxia lasting 7 days, 1 month, 2 months and 10 months. The recovery phase in all, except the 10 months experiment, lasted 7 days, while in the last phase it lasted 3 months. Samplings of 1 yr anoxia and the 1 yr recovery phase were performed in 2011.

In an experiment conducted in 2010, with anoxia onset lasting 7 days, a benthic chamber called Experimental Anoxia Generating Unit (EAGU) were equipped with sensors for dissolved oxygen (O_2) and sulphide (H_2S) and cameras primarily used for studying the behavior and survival/mortality of benthic infauna since each group of organisms showed different tolerance on changing O_2 levels (Reider et al., 2013; Grego et al., 2013a,b; DeTroch et al., 2013; Langlet et al., 2013a,b). The other chambers used were simpler lacking sensors and cameras. They were however designed with special rubber-closed openings used for sample manipulations inside the chamber.

11733

All benthic chamber deployments and sediment core samplings were performed by SCUBA divers after careful and thorough planning of correct positioning of all utensils. Firstly, before the deployment of chambers, 4 cores (normoxic) were sampled using Plexiglass tubes (6 cm i.d., 12 cm length) and sealed with rubber stoppers underwater. The chambers were pushed approximately 2 cm into the sediment and carefully sealed to avoid any leakage of ambient water into or experimental water out of the chambers. In the experiment using EAGU, O_2 and H_2S sensors were used to monitor the evolution of anoxia inside the chamber (Riedel et al., 2013). After the elapsed time set by the experiment outline SCUBA divers again performed core sampling. After sampling, the benthic chamber was carefully removed to avoid any further disturbance of the sediment. The area previously covered by the benthic chamber and anoxic water column became exposed to ambient seawater and the recovery period began. The sampling of the "recovery" sediments was performed after 7 days, following same sampling protocol as before. The sampling procedure was the same in every experiment, except with 2 months anoxia, which lacked the recovery phase. Recovery cores of 7 days and 1 month anoxia experiment were sampled after a 7 day period, whereas in the 1 yr experiment they were collected after 3 months period.

After each campaign, all samples were carefully transported to the lab where the cores were extruded and sectioned into 0.5 cm thick slices for the upper 2 cm, and 1 cm slices for next 5 cm. All core sample manipulations, including pore water, were performed in an N_2-filled glove bag or box. Core slices were put into sterile 50 mL centrifuge tubes (Corning Inc.) to allow the pore water extraction. This was performed by centrifugation at 3500 rpm for 20 min at in situ temperature measured at the sea bottom at the time of sampling. Pore waters from matching depths were filtered through 0.2 µm Millipore-HA filters in an inert atmosphere and combined three or four cores to obtain enough sample for all required analyses. Where necessary pore waters were acidified and refrigerated until analyses. Sediments devoid of pore waters (solid phase) were kept frozen until analyses.

11734

2.3 Analyses

2.3.1 Solid phase

Sediment samples for C_{org} and N_{tot} analyses were freeze-dried, ground in an agate mortar and sieved through 200 μm mesh to remove coarse shell debris. C_{org} was determined in sediments acidified with 1 M HCl to quantitatively remove carbonates (Hedges and Stern, 1984), whereas N_{tot} was determined in non-acidified samples using a CHN analyzer (Elementar varioMICRO CUBE; Elementar Analysensysteme GmbH, Hanau, Germany). Total P was analyzed by extraction with 1 M HCl after ignition and P_{org} was calculated from the difference in P contents of 1 M HCl extracts before and after ignition of the samples (Aspila et al., 1976), whereas Si_{biog} was extracted with Na_2CO_3 (DeMaster, 1981) and dissolved $Si(OH)_4$ determined colorimetrically (Grasshoff et al., 1999).

A small sediment core was also sampled to determine the porosity of sediments at the experimental site according to Čermelj et al. (1997).

2.3.2 Pore waters

Nutrient concentrations in pore waters were determined using standard analytical methods (Grasshoff et al., 1999). Detection limits for nutrients were: 0.5 μmol L^{-1} for $NO_3^- + NO_2^-$, 0.4 μmol L^{-1} for NH_4^+ and 0.01 μmol L^{-1} for PO_4^{3-}. Concentrations of Si, Fe, Mn, Ca and Mg in filtered and acidified samples were determined using ICP-OES (Perkin-Elmer Optima 5300 DV). NASS-6 certified reference material was used for quality control. All samples were available in only one replicate, so the reproducibility of the method was determined based on multiple measurements of the standard solutions and reference material, whereas limit of detection and limit of quantification were determined based on three and ten standard deviations of the blank samples measurements, respectively. The method detection limit (MDL) for ICP-OES was cal-

culated based on the t-statistics calculated at two different confidence intervals (99 % and 95 %) multiplied by average standard deviation in mgL^{-1}.

2.3.3 Pore water and benthic flux modelling

The fluxes of PO_4^{3-}, NH_4^+, dissolved silicon (dSi), Ca, Mg, Mn and Fe across the sediment–water interface (SWI) were determined using Fick's first law of diffusion and advection (Lerman, 1979):

$$F_{z=0} = -\phi D_s \left(\frac{\partial C}{\partial z}\right) + \phi \omega C|_{z=0} \tag{1}$$

where F is the rate of flux [mol m^{-2} s^{-1}], Φ is sediment porosity, D_s is the effective diffusion coefficient [m^{-2} yr^{-1}], C/z is the concentration gradient across the SWI [mol dm^{-4}], sedimentation rate [cm s^{-1}]. The measured Φ was 0.55, while D_s were corrected for temperature and average porosity (Lerman, 1979). C/z was estimated from a profile of concentrations plotted against depth using the diffusion-reaction model for PO_4^{3-}, NH_4^+ and dSi, while Ca, Mg, Mn and Fe depth profiles were described by a curve fitting routine of a polynomial function.

The diffusion–advection–reaction model included the degradation of OM via first-order kinetics, equilibrium adsorption from pore water onto sediment particles and dissolution precipitation reactions using the following equation (Lerman, 1979):

$$\frac{\partial C}{\partial t} = 0 = D\frac{\partial^2 C}{\partial z^2} - \omega \frac{\partial C}{\partial z} - kC + J + R_0 \exp^{(-\beta z)} \tag{2}$$

where k is the reaction rate constant, J is the rate of reaction, R_0 is the production rate at the SWI [mol dm^{-3} s^{-1}], is the depth attenuation constant [cm^{-1}]. The change of PO_4^{3-}, NH_4^+ and dSi with depth and time in the model was described for every species separately depending on the processes influencing their distribution: decomposition of OM to NH_4^+ and PO_4^{3-}; equilibrium adsorption for NH_4^+, PO_4^{3-} following a simple linear

isotherm; precipitation of PO_4^{3-} to form authigenic minerals and dissolution of biogenic silica assuming first-order reaction. Thus, the change of nutrient concentrations with depth can be described by the following steady-state differential equations.

For NH_4^+:

$$\frac{\partial C}{\partial t} = 0 = \frac{D_s}{1 + K_N}\frac{\partial^2 C}{\partial z^2} - \omega(1 + K_N)\frac{\partial C}{\partial z} + R_0 \exp^{(-\beta z)} \tag{3}$$

where K_N is the equilibrium adsorption constant for NH_4^+.

For PO_4^{3-}:

$$\frac{\partial C}{\partial t} = 0 = \frac{D_s}{1 + K_P}\frac{\partial^2 C}{\partial z^2} - \omega(1 + K_P)\frac{\partial C}{\partial z} - \frac{k_m(C - C_{eq})}{1 + K_P} + R_0 \exp^{(-\beta z)} \tag{4}$$

where K_P is the equilibrium adsorption constant for PO_4^{3-}, C_{eq} concentration at saturation with the authigenic precipitate dependent on T and k_m authigenic mineral precipitation rate constant.

For dSi:

$$\frac{\partial C}{\partial t} = 0 = D_s\frac{\partial^2 C}{\partial z^2} - \omega\frac{\partial C}{\partial z} + k_m(C_\infty - C) \tag{5}$$

where k_m is the rate constant for Si dissolution and C_∞ is asymptotic concentration at $z \to \infty$. The equations were solved using the following boundary conditions at:

at $z = 0 : C = C_{z=0}$

at $z \to \infty : C \to C_\infty$ for NH_4^+ and dSi and $C \to C_{eq}$ for PO_4^{3-}.

The parameters used in the diffusion-advection-reaction model together with the model output data are collected in Table 1.

3 Results

3.1 Solid phase

Results on C_{org}, N_{tot} P_{tot}, P_{inorg}, P_{org} and Si_{biog} results and C_{org}/N_{tot} and C_{org}/P_{org} ratios (molar) in the sediment solid phase during anoxia are presented in Fig. 1. Our C_{org}, N_{tot}, P_{tot}, P_{inorg}, P_{org} and Si_{biog} results (Fig. 1) from normoxic phase agreed with previously reported values from surficial sediment at this study site (Čermelj et al., 1997; Ogrinc et al., 2005). Little vertical variation of concentrations in all measured parameters was observed except those of P_{tot} and Si_{biog}, which decreased with depth. The C_{org}/N_{tot} ratios (molar) ranged from 6 to 12 and C_{org}/P_{org} ratios (molar) averaged about 200 both roughly corroborating with the values typical for OM of marine origin (Ogrinc et al., 2005).

During the 1 month and 2 months anoxic phases the C_{org}/N_{tot} ratios rose to values from 12 to 15 and 11 to 21, respectively, due to the dropping of N_{tot} levels. Interestingly, the results of 1 yr anoxia showed relatively high values of N_{tot}, comparable to those in normoxia, with C_{org} values being higher than in all short-term experiments. Only changes in the pool of P_{org} were observed and the degradation of P_{org} was most noticeable in the 2 months anoxia experiment reflecting in higher C_{org}/P_{org} ratios. Si_{biog} levels increased in the 7 days anoxia but were somewhat lower in the longer anoxic conditions. In the recovery phases, the C_{org} and P_{tot} and P_{org} values remained approximately unchanged in 7 days recovery but were higher in 1 month recovery. Conversely, N_{tot} values in both phases were much lower than in normoxia.

3.2 Nutrients

Concentrations of NH_4^+ and PO_4^{3-}, during normoxia (Fig. 2), were low and relatively constant throughout the whole sediment core, reaching values between 20 and 115 μmol L^{-1} for NH_4^+ and 2 and 40 μmol L^{-1} for PO_4^{3-}, respectively. Concentrations in overlaying water were lower, around 1 μmol L^{-1} for NH_4^+ and 0.1 μmol L^{-1} for PO_4^{3-}.

Pore water NO_3^- concentrations (not presented) in the normoxic phase ranged from 5 to 35 $\mu mol\,L^{-1}$, whereas the concentration in overlaying water was around 0.1 $\mu mol\,L^{-1}$. The profile of dSi showed lower concentrations at SWI and uniform levels at about 100 $\mu mol\,L^{-1}$ at all analyzed depths. Normoxic pore water profiles are comparable to those previously reported for the same sampling point (Čermelj et al., 1997; Ogrinc and Faganeli, 2006; Faganeli and Ogrinc, 2009).

Pore water profiles of NH_4^+, PO_4^{3-} and dSi during anoxia are presented in Fig. 2. Concentrations of NH_4^+ in the 7 days anoxia experiment were much higher compared to normoxic concentrations (Fig. 2) and ranged from 100 to 200 $\mu mol\,L^{-1}$ showing two distinct peaks at depths between 1.5 and 2 cm and between 4 and 5 cm, respectively. In 1 month anoxia, the concentrations of NH_4^+ were even higher reaching maximum values of 700 $\mu mol\,L^{-1}$. There was a noticeable increase in concentrations at the depths between 0.5 and 4 cm. In the 2 months and 1 yr anoxia experiment, the concentrations of NH_4^+ dropped and stabilized around 300 $\mu mol\,L^{-1}$ and 200 $\mu mol\,L^{-1}$, respectively. Concentrations of NO_3^- (not presented) in the 7 days and 1 month anoxia experiments did not change much and were comparable to those in normoxic conditions, ranging from 10 to 40 $\mu mol\,L^{-1}$, with peaks overlapping those of NH_4^+ profiles. In the 2 months and 1 yr anoxia experiments, its concentrations rose reaching values up to 100 $\mu mol\,L^{-1}$. The 7 days anoxia PO_4^{3-} profile was similar to NH_4^+ profile. Concentrations rose only in two active layers reaching values of 20 and 40 $\mu mol\,L^{-1}$, respectively. In the PO_4^{3-} depth profiles in the 1 month, 2 months and 1 yr anoxia experiments, the concentrations remained nearly constant throughout the sediment cores. Concentrations ranged from 0.5 to 9 $\mu mol\,L^{-1}$, and therefore, did not exceed the values observed in the normoxia or 7 days anoxia experiments. Concentrations of dSi during all anoxia experiments (Fig. 2) increased to levels > 200 $\mu mol\,L^{-1}$. High pore water dSi levels, around 150 $\mu mol\,L^{-1}$, also remained during reoxidation phases. Observed irregular ("disrupted") depth profiles of NH_4^+ after 1 month recovery and PO_4^{3-} and dSi observed after 1 yr of recovery indicate the importance of enhanced bioturbation.

11739

3.3 Metals

Vertical pore water profiles of Ca and Mg concentrations (Fig. 3) showed lower values in anoxic phases, particularly for Mg during 7 days and 1 month anoxia. In 1 month and 1 yr recovery experiments, pore water Ca concentrations increased to higher values than observed in normoxia while Mg concentrations reached levels approximately those encountered in normoxia. Changing of dissolved Fe and Mn (Fe(II) and Mn(II)) concentrations during anoxia experiments are shown in Fig. 3. In 7 days anoxia, there was a notable increase of Fe and Mn concentrations in pore waters compared to values under normoxic conditions. Concentrations increased from values of less than 5 $\mu mol\,L^{-1}$ for Fe and 35 $\mu mol\,L^{-1}$ for Mn, to 35 $\mu mol\,L^{-1}$ for Fe and 110 $\mu mol\,L^{-1}$ for Mn. Two distinct vertical peaks can be seen, one at depth of 0–0.5 cm and other at 2–4 cm. In the 1 month, 2 months and 1 yr anoxia experiments, the concentrations of Fe were notably lower compared to 7 days anoxia, but still higher than in normoxia. Peaks of increased Fe(II) release into pore waters remain noticeable. Mn profiles in the 7 days and 1 yr anoxia experiments were almost identical to profiles of Fe. Profiles of Mn from 1 month and 2 months anoxia experiments did not show any concentration changes throughout the sediment core. However, the concentrations of dissolved Mn in prolonged anoxia dropped from 150 to 5 $\mu mol\,L^{-1}$.

3.4 Model calculation and fluxes

The comparison between depth profiles of model calculated and measured NH_4^+, PO_4^{3-} and dSi concentrations are presented in Fig. 2. The diagenetic model gave quite a good description of the distribution of nutrients in pore water of 1 month and 1 yr anoxia and 1 month recovery experiments, however, the 1 yr recovery experiment conditions were not reproduced well, since no clear pattern in the measured distribution of nutrient concentrations was observed probably due to enhanced bioturbation. Furthermore, it was also observed that the depth attenuation coefficient increased with the increasing time of the anoxic condition present for both NH_4^+ and PO_4^{3-} from 2.0 to 6.3 and from

11740

1.6 to 3.8, respectively. These data show a more pronounced release of both nutrients due to more intense remineralization processes.

Based on the diagenetic models, the diffusive fluxes were calculated and the data are presented in Table 2. The calculated NH_4^+ benthic fluxes ranged from -34 to $513\,\mu\text{mol m}^{-2}\,\text{day}^{-1}$ and those of PO_4^{3-} from 1.3 to $13.8\,\mu\text{mol m}^{-2}\,\text{day}^{-1}$. The highest NH_4^+ efflux was observed after one month of anoxia. On the other hand, the influx of NH_4^+ into sediments was observed after one year of recovery. The dSi fluxes ranged from -140 to $286\,\mu\text{mol m}^{-2}\,\text{day}^{-1}$. Fe and Mn exhibited the highest effluxes in 7 days and 1 month anoxia reaching values of 16.6 and $20.1\,\mu\text{mol m}^{-2}\,\text{day}^{-1}$, respectively. In these experiments, the influx of Ca into sediment was mainly observed ranging from -10 to $-700\,\mu\text{mol m}^{-2}\,\text{day}^{-1}$ except after 7 days and 1 month recovery. Similar dynamics was found for Mg.

4   Discussion

Our study documents the sequential biogeochemical changes occurring during the OM degradation and nutrient regeneration in relatively OM poor coastal surface sediments of the Gulf of Trieste under various redox conditions: normoxic, anoxic and reoxic. It can be seen that the longer the span of anoxia the less pronounced is the rise of concentrations of NH_4^+ and PO_4^{3-} in pore waters. The majority of NH_4^+ and PO_4^{3-} regeneration in anoxic marine environments likely results from hydrolytic and/or fermentative processes that produce low molecular weight molecules from complex sedimentary OM (Burdige, 2002). The utilization of these compounds by sulphate reducing bacteria then results in the complete mineralization of sedimentary OM (Burdige, 2002). Consequently, the sedimentary C_{org}/N_{org} ratios and C_{org}/P_{org} ratios generally increase with depth in surface coastal marine and estuarine sediments (Hedges and Keil, 1995). This is usually considered as an indication of preferential mineralization of organic nitrogen and phosphorus in sediments and that the more labile fractions have lower C_{org}/N_{org}

11741

and C_{org}/P_{org} ratios than the bulk sedimentary OM (Hedges and Keil, 1995; Ingall and Jahnke, 1997). In anoxic conditions, higher pore water NH_4^+ and PO_4^{3-} levels can be also related with the higher density of decaying infaunal organisms providing additional easily degradable "fresh" OM to microbes (Riedel et al., 2013). It was demonstrated, using ^{15}N incubations, that in the deep Skagerrak sediments the pore water NH_4^+ is the main end product of anoxic N mineralization (Thamdrup and Dalsgaard, 2000). A build-up of NH_4^+ in pore waters can also be a consequence of other processes in the N cycle, which can be important in anoxic environments and can simultaneously proceed in microniches. One of them is dissimilatory nitrate reduction to ammonium (DNRA) (Gardner et al., 2006) which can supersede respiratory denitrification as a process of NO_3^- removal from the system, when labile organic matter is more available, redox potential and ambient NO_3^- concentrations are low, and when H_2S production is high (Canfield et al., 2005). The NO_3^- behaviour in sediments of the Gulf of Trieste was somewhat unusual since it was expected to decrease in anoxic pore waters due to denitrification, which rapidly removes NO_3^-. Results of the 2 months anoxia experiment indicated a possible breach in anoxia, since increased concentrations of NO_3^- were seen at two separate depths suggesting that there was an active sediment reworking (outside chamber) and laterally pumping of overlying oxygenated water into deeper layers of chamber sediment (Čermelj et al., 1997). Anamox (anaerobic ammonium oxidation), another important nitrogen process, might be running simultaneously (Dalsgaard et al., 2005) and might explain the increased values of NO_3^- in anoxic conditions, which is probably formed as a byproduct in CO_2 reduction, especially in the 2 months and 1 yr anoxia experiments (van de Graaf et al., 1997). Within the current knowledge of N cycling in marine sediments, it is suggested that in environments with relatively high C_{org} concentrations and high free H_2S concentrations, respiratory denitrification is suppressed (because of enzyme inhibition), therefore making DNRA and anammox more important processes for N recycling (Burgin and Hamilton, 2007). Bottom water hypoxia and anoxia typically lead to increased regeneration of P from sediments and thus increased recycling of P in the system (Conley et al., 2009). Significant

11742

amount of P is released from Fe-(oxy)hydroxides upon transition from oxic to anoxic conditions (Ogrinc and Faganeli, 2006; Faganeli and Ogrinc, 2009). Enhanced microbial and chemical dissolution of Si_{biog} (opal) proceeded in anoxic conditions (Canfield et al., 2005; Belias et al., 2007) and remained high in recovery phases.

Distribution of Mn, Fe, Ca and Mg in pore waters (Fig. 3) further support the thesis of an active microbial metabolism in sediments. Results of Fe and Mn in the 7 days anoxia experiment show an enhanced release of these species to the water column indicating an active Fe and Mn reduction/respiration in these layers. The results clearly show Fe and Mn reduction processes since the concentrations of dissolved species notably rise. When the system is subjected to prolonged anoxic conditions, the importance of Fe and Mn reduction from our set of results (Fig. 3) becomes less evident. These processes are energetically more favourable than sulphate reduction (Froelich et al., 1979) and even though the DET results (Metzger et al., 2013) indicate that sulphate reduction is the preferential anaerobic microbial process in early diagenesis in these coastal sediments, Fe and Mn reduction can proceed in some microniches. DET results of SO_4^{2-} concentrations during anoxia experiments (Metzger et al., 2013) also clearly showed the migration of redox layers towards SWI and the increasing importance of sulphate reduction over prolonged anoxia spans. The prevalence of sulphate reduction, as a major anaerobic path of early OM diagenesis in coastal marine sediments, over other electron acceptors, was demonstrated for surface sediments in the Gulf of Trieste (Hines et al., 1997). In anoxic conditions, Ca and Mg pore water concentrations indicate lower carbonate dissolution or even carbonate precipitation as previously postulated for surface anoxic sediments of the Gulf of Trieste (Čermelj et al., 2001; Ogrinc et al., 2003).

In the recovery experiments, the normoxic biogeochemical conditions of metals were almost completely restored in 7 days even though this was not completely true for higher organisms (infauna). Reoxygenation of previously anoxic sediments promotes OM remineralization (Hulthe et al., 1998; Bastviken et al., 2004). Unfortunately, data on pore water nutrient concentrations in 7 days recovery period following an O_2 water

11743

penetration are missing. We observed, however, a peak of NO_3^- at a depth of 4–5 cm in the 7 days reoxygenation phase, which may be a consequence of enhanced bioturbation also clearly evident in NH_4^+, dSi and Fe pore water profiles especially in the 1 yr recovery experiment. Nitrification was a likely cause of relative NH_4^+ depletion. When oxic conditions reappears P precipitates quickly as authigenic carbonate fluorapatite, $FePO_4$ or it is adsorbed onto Fe-hydroxides (Ogrinc and Faganeli, 2006), most probably onto goethite having a large sorption capacity for phosphate (Arčon et al., 1999). This is confirmed by the rapid decrease of pore water Fe concentrations after 7 days of recovery precipitating as Fe-oxyhydroxides. Increased pore water Ca concentrations in longer recovery experiments reflect enhanced carbonate dissolution in oxic conditions (Ogrinc et al., 2003).

The differences between N, P and Si cycling in oxic, anoxic and reoxic phases can be estimated by comparing their benthic diffusive fluxes and burial. The amount of N_{tot}, $P_{tot.}$ and Si_{biog} buried in sediment was calculated from the sedimentation rate (ω) and the concentration (C) of sedimentary N_{tot}, P_{tot} and Si_{biog} in the deepest measured sediment layer (approximately 7 cm), since they are nearly constant and less affected by bioturbation, using the following equation:

$$\text{Burial} = \omega C \rho (1 - \Phi) \tag{6}$$

ρ is the dry density (2.5 g cm^{-3}; Ogorelec et al., 1991), Φ porosity (0.55) and ω sedimentation rate (1.2 mm yr^{-1}) estimated from ^{210}Pb measurements (Faganeli et al., 1991). Burial fluxes of N_{tot}, $P_{tot.}$ and Si_{biog} amounted to 170, 30 and 6800 µmol m^{-2} day^{-1}, respectively. Comparison between benthic fluxes (Table 2) and burial revealed that the intensive recycling of dissolved inorganic N at the SWI is enhanced in anoxic conditions while P benthic fluxes appear extremely low even in anoxic phases despite the evident increase of Fe (and Mn) fluxes particularly in early anoxic stages (Table 2). This suggests an important role of P precipitation as authigenic carbonate fluoroapatite (Ingall and Jahnke, 1997). Si recycling appears much less intensive compared to burial flux in all redox phases indicating rather low Si_{biog} solubility.

11744

Conversely, carbonates seem more reactive showing precipitation (Ca and Mg influx) in anoxic conditions. The comparison between diffusive and laboratory incubated benthic fluxes in oxic and anoxic conditions, reported previously for the same sampling point (Faganeli and Ogrinc, 2009), reveals lower values of NH_4^+ and PO_4^{3-} diffusive fluxes for both conditions which can be attributed to the presence of bioturbation, not included in modelling approach, and differences in experimental approach. Benthic fluxes integrate the processes in the whole sedimentary column while diffusive fluxes consider changes at SWI.

5   Conclusions

1. The study of sequential nutrient regeneration and OM degradation in surface sediments of the Gulf of Trieste under normoxic, anoxic and reoxic conditions were primarily focused into variations of pore water composition. NH_4^+ and PO_4^{3-} regeneration was more intensive in anoxic phases but prolonged span of anoxia reduced their increase. Consequently, the solid phase N_{tot} and P_{org} contents decreased increasing C_{org}/N_{tot} and C_{org}/P_{org} ratios. Higher pore water NH_4^+ levels were presumably also a consequence of dissimilatory nitrate reduction to NH_4^+ that is a concurrent process of denitrification in removing NO_3^-. The presence of NO_3^- in anoxic phases can be explained by the presence of anammox and laterally pumping of oxygenated water by benthic infauna. Enhanced dissolution of Si_{biog} was also observed in anoxic phases. Anoxic phases were characterized by higher pore water Fe and Mn concentrations as a result of reduction/respiration which is prevailed by sulphate reduction. The decreased pore water Ca and Mg concentrations compared to normoxia indicated carbonate precipitation.

2. Reoxygenation was characterized by enhanced bioturbation. Nitrification caused NH_4^+ decrease and P precipitated quickly as carbonate fluorapatite, $FePO_4$ and it

11745

is adsorbed onto Fe-hydroxides since Fe (and Mn) reoxidized quickly. Increased Ca levels suggested enhanced carbonate dissolution.

3. Diffusive benthic fluxes at the SWI, calculated from pore water modelling using diffusion-reaction model, showed high anoxic NH_4^+ effluxes and Ca (and Mg) influxes according to described processes. PO_4^{3-} fluxes were very low despite pronounced anoxic Fe and Mn effluxes. High NH_4^+/PO_4^{3-} flux ratios in anoxic and reoxic phases suggest an excess of N in the benthos. Nutrient budgets at the SWI, i.e. comparison between diffusive benthic and burial fluxes, showed intensive anoxic recycling of inorganic N but low P and Si recycling in all redox phases.

References

Aller, R. C.: Topics in geobiology: the effects of macrobenthos on chemical properties of marine sediment and overlying water, in: Animal–Sediment Relations: The Biogenic Alteration of Sediments, edited by: McCall, P. L. and Tevesz, M. J. S., Plenum Press, New York, 53–102, 1982.

Aller, R. C. and Yingst, J. Y.: Relationship between microbial distribution and the anaerobic composition of organic matter in surface sediments of Long Island Sound, Mar. Biol., 56, 29–42, 1988.

Arčon, I., Ogrinc, N., Kodre, A., and Faganeli, J.: EXAFS and XANES characterization of sedimentary iron in the Gulf of Trieste (N Adriatic), J. Synchrotron. Radiat., 6, 659–660, 1999.

Aspila, K. I., Agemian, H., and Chau, H. S. Y.: A semi-automated method for the determination of inorganic, organic and total phosphate in sediments, Analyst, 101, 187–197, 1976.

11746

Bastviken, D., Persson, L., Odham, G., and Tranvik, L.: Degradation of dissolved organic matter in oxic and anoxic lake water, Limnol. Oceanogr., 49, 109–116, 2004.

Bellias, C., Dassenakis, M., and Scoullos, M.: Study of N, P and Si fluxes between fish farm and sediment and seawater, results of simulation experiments employing a benthic chamber under various redox conditions, Mar. Chem., 103, 266–275, 2007.

Berner, R. A.: Early Digenesis, Princeton University Press, Princeton, 241 pp., 1980.

Brunet, R. C. and Garcia-Gil, L. J.: Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments, FEMS Microbiol. Ecol., 21, 131–138, 1996.

Burdige, D. J.: Sediment pore waters, in: Biogeochemistry of Marine Dissolved Organic Matter, edited by: Hansell, C., and Carlson, C., Academic, New York, 611–664, 2002.

Burgin, A. J. and Hamilton, S. K.: Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways, Front. Ecol. Environ., 5, 89–96, 2007.

Canfield, D. E., Thamdrup, B., and Krstensen, E.: Aquatic Geomicrobiology, Advances in Marine Biology, vol. 48, Elsevier, Amsterdam, 640 pp., 2005.

Conley, D. J., Bjorck, S., Destouni, G., Gustafsson, B. G., Hietanen, S., Kortekaas, M., Kuosa, H., Markus Meier, H. E., Muller-Karulis, B., Nordberg, K., Norkko, A., Nurmberd, G., Pitkanen, H., Rabalais, N. N., Rosemberg, R., Savchuk, O. P., Slomp, C. P., Voss, M., Wulff, F., and Zillen, L.: Hypoxia-related processes in the Baltic Sea, Environ. Sci. Technol., 43, 3412–3420, 2009.

Čermelj, B., Bertuzzi, A., and Faganeli, J.: Modelling of pore water nutrient distribution and benthic fluxes in shallow coastal waters (Gulf of Trieste, northern Adriatic), Water Air Soil Poll., 99, 435–444, 1997.

Čermelj, B., Ogrinc, N., and Faganeli, J.: Anoxic mineralization of biogenic debris in nearshore marine sediments (Gulf of Trieste, northern Adriatic), Sci. Total Environ., 266, 143–152, 2001.

Dalsgaard, T., Thamdrup, B., and Canfield, D. E.: Anaerobic ammonium oxidation (Anammox) in the marine environment, Res. Microbiol., 156, 457–464, 205.

DeMaster, D. J.: The supply and accumulation of silica in the marine environment, Geochim. Cosmochim. Ac., 45, 1715–1732, 1981.

De Troch, M., Roelofs, M., Riedel, B., and Grego, M.: Structural and functional responses of harpacticoid copepods to anoxia in the Northern Adriatic: an experimental approach, Biogeosciences, 10, 4259–4272, doi:10.5194/bg-10-4259-2013, 2013.

11747

Diaz, R. J. and Rosenberg, R.: Spreading dead zones and consequences for marine ecosystems, Science, 321, 926–929, 2008.

Engstrom, P., Dalsgaard, T., Hulth, S., and Aller, R. C.: Anaerobic ammonium oxidation by nitrite (anammox): implications for N_2 production in coastal marine sediments, Geochim. Cosmochim. Ac., 69, 2057–2065, 2005.

Faganeli, J., Avčin, A., Fanuko, N., Malej, A., Turk, V., Tusnik, P., Vriser, B., and Vukovič, A.: Bottom layer anoxia in the central part of the Gulf of Trieste in the late summer of 1983, Mar. Pollut. Bull., 16, 75–78, 1985.

Faganeli, J., Planinc, R., Pezdič, J., Smodiš, B., Stegnar, P, and Ogorelec, B.: Marine geology of the Gulf of Trieste (northern Adriatic): geochemical aspects, Mar. Geol., 99, 93–108, 1991.

Faganeli, J. and Ogrinc, N.: Oxic-anoxic transition of benthic fluxes from the coastal marine environment (Gulf of Trieste, northern Adriatic Sea), Mar. Freshwater Res., 60, 700–711, 2009.

Froelich, P. N., Klinkhammer, M. L., Bender, N. A., Luedtke, G. R., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V.: Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis, Geochim. Cosmochim. Ac., 43, 1075–1090, 1997.

Gardner, W. S., McCarthy, M. J., An, S., Sobolev, D., Sell, K. S., and Brock, D.: Nitrogen fixation and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in Texas estuaries, Limnol. Oceanogr., 51, 558–568, 2006.

Grasshoff, K., Kremling, K., and Ehrhardt, M.: Methods of Seawater Analysis, 3rd edn., Wiley-VCH, Weinheim, 632 pp., 1999.

Grego, M., Stachowitsch, M., De Troch, M., and Riedel, B.: Cell Tracker Green labelling vs. Rose Bengal staining: CTG wins by points in distinguishing living from dead anoxia-impacted copepods and nematodes, Biogeosciences, in preparation, 2013

Grego, M., Stachowitsch, M., and De Troch, M.: Meiofauna winners and losers of coastal hypoxia: case study harpacticoid copepods, Biogeosciences, submitted, 2013.

Hedges, J. I. and Keil, R. G.: Sedimentary organic matter preservation: an assessment and speculative synthesis, Mar. Chem., 49, 81–115, 1995.

Hedges, J. I. and Stern, J. H.: Carbon and nitrogen determinations of carbonate-containing solids, Limnol. Oceanogr., 29, 195–212, 1984.

11748

Hines, M. E., Faganeli, J., and Planinc, R.: Sedimentary anaerobic microbial biogeochemistry in the Gulf of Trieste, northern Adriatic Sea: influences of bottom water oxygen depletion, Biogeochemistry, 39, 65–86, 1997.

Hulthe, G., Hulth, S., and Hall, P. O. J.: Effect of oxygen on degradation rates of refractory and labile organic matter in continental margin sediments, Geochim. Cosmoschim. Ac., 62, 1319–1328, 1998.

Hunter, W. R., Levin, L. A., Kitazato, H., and Witte, U.: Macrobenthic assemblage structure and organismal stoichiometry control faunal processing of particulate organic carbon and nitrogen in oxygen minimum zone sediments, Biogeosciences, 9, 993–1006, doi:10.5194/bg-9-993-2012, 2012.

Ingall, E. and Jahnke, R.: Influence of water-column anoxia the elemental fractionation of carbon and phosphorus during sediment diagenesis, Mar. Geol., 139, 219–229, 1997.

Kemp, M., Faganeli, J., Puškaric, S., Smith, E. M., and Boynton, W. R.: Pelagic-benthic coupling and nutrient cycling, in: Ecosystems at the Land-Sea Margin: Drainage Basin to Coastal Sea, edited by: Malone, T. C., Malej, A., Harding Jr., L. W., Smodlaka, N., and Turner, R. E., American Geophysical Union, Washington DC, USA, 295–339, 1999.

Langlet, D., Baal, C., Geslin, E., Metzger, E., Zuschin, M., Riedel, B., Stachowitsch, M., and Jorissen, F.: Foraminiferal species responses to in situ experimentally induced anoxia in the Adriatic Sea, Biogeosciences, in press, 2013.

Langlet, D., Geslin, E., Baal, C., Metzger, E., Zuschin, M., Riedel, B., Stachowitsch, M., and Jorissen, F.: Foraminiferal survival after one year of experimentally induced anoxia, Biogeosciences, published, 2013.

Lerman, A.: Geochemical Processes: Water and Sediment Environments, Wiley, New York, 481 pp., 1979.

Metzger, E., Langlet, D., Viollier, E., Koron, N., Riedel, B., Faganeli, J., Tharaud, M., Geslin, E., Jorissen, F., and Stachowitsch, M.: Artificially induced migration of redox layers in a coastal sediment from the northern Adriatic, Biogeosciences, accepted, 2013.

Mozetič, P., France, J., Kogovšek, T., Talaber, I., and Malej, A.: Plankton trends nd community changes in a coastal sea (northern Adriatic): bottom-up vs. top-down control in relation to environmental drivers, Estuar. Coast. Shelf Science, 115, 138–148, 2012.

Ogorelec, B., Mišič, M., and Faganeli, J.: Marine geology of the Gulf of Trieste (northern Adriatic): sedimentological aspects, Mar. Geol., 99, 79–92, 1991.

11749

Ogrinc, N. and Faganeli, J.: Phosphorus regeneration and burial in near-shore marine sediments (the Gulf of Trieste, northern Adriatic Sea), Estuar. Coast. Shelf S., 67, 579–588, 2006.

Ogrinc, N., Faganeli, J., and Pezdič, J.: Determination of organic carbon remineralization in near-shore marine sediments (Gulf of Trieste, northern Adriatic) using stable carbon isotopes, Org. Geochem., 34, 681–692, 2003.

Ogrinc, N., Fontolan, G., Faganeli, J., and Covelli, S.: Carbon and nitrogen isotope compositions of organic matter in coastal marine sediments (the Gulf of Trieste, N Adriatic Sea): indicators of sources and preservation, Mar. Chem., 95, 163–181, 2005.

Riedel, B., Zuschin, M., Haselmair, A., and Stachowitsch, M.: Oxygen depletion under glass: behavioural responses of benthic macrofauna to induced anoxia in the northern Adriatic, J. Exp. Mar. Biol. Ecol., 367, 17–27, 2008.

Riedel, B., Pados, T., Pretterebner, K., Schiemer, L., Steckbauer, A., Haselmair, A., Zuschin, M., and Stachowitsch, M.: Effect of hypoxia and anoxia on invertebrate behaviour: ecological perspectives from species to community level, Biogeosciences, in review, 2013.

Stachowitsch, M.: Anoxia in the northern Adriatic Sea: rapid death, slow recovery, Geol. Soc. Spec. Publ., 58, 119–129, 1991.

Stachowitsch, M., Riedel, B., Zuschin, M., and Machan, R.: Oxygen depletion and benthic mortalities: the first in situ experimental approach to documenting an elusive phenomenon, Limnol. Oceanogr. Meth., 5, 344–352, 2007.

Thamdrup, B. and Dalsgaard, T.: The fate of ammonium in anoxic manganese oxide-rich marine sediment, Geochim. Cosmochim. Ac., 64, 4157–4164, 2000.

Van de Graaf, A. A., de Brujin, P., Robertson, L. A., Jetten, M. S. M., and Kuenen, J. G.: Methabolic pathway of anaerobic ammonium oxidation on the basis of N-15 studies in a fluidized bed reactor, Microbiology-UK, 143, 2415–2421, 1997.

Welker, C., Sdrigotti, E., Covelli, S., and Faganeli, J.: Microphytobenthos in the Gulf of Trieste (northern Adriatic Sea): relationship with labile sedimentary organic matter and nutrients, Estuar. Coast. Shelf S., 55, 259–273, 2002.

11750

Table 1. Parametres used in the diffusion-advection-reaction model. Values marked with [a] were measured values, the others were output model data.

Parameters	Units	Value	Description
D_s (NH_4^+)	$10^{-6}\,cm^2\,s^{-1}$	9.06–10.9	Sediment diffusion coefficient[a]
D_s (PO_4^{3-})	$10^{-6}\,cm^2\,s^{-1}$	2.78–3.40	Sediment diffusion coefficient[a]
D_s (dSi)	$10^{-6}\,cm^2\,s^{-1}$	4.54–5.56	Sediment diffusion coefficient[a]
D_s (Ca)	$10^{-6}\,cm^2\,s^{-1}$	3.72–4.56	Sediment diffusion coefficient[a]
D_s (Mg)	$10^{-6}\,cm^2\,s^{-1}$	3.17–3.81	Sediment diffusion coefficient[a]
D_s (Mn)	$10^{-6}\,cm^2\,s^{-1}$	3.05–3.73	Sediment diffusion coefficient[a]
D_s (Fe)	$10^{-6}\,cm^2\,s^{-1}$	2.76–3.37	Sediment diffusion coefficient[a]
Ω	$Cm\,yr^{-1}$	0.15	Sedimentation rate[a]
Φ		0.49–0.62	Porosity in sediments[a]
k_m	$10^{-7}\,s^{-1}$	17–1083	Rate constant for silicate dissolution
K_N		1.3	Equilibrium constant for NH_4^+
K_P		2	Equilibrium constant for PO_4^{3-}
β_N	cm^{-1}	1.81–6.32	Attenuation depth constant for NH_4^+
β_P	cm^{-1}	0.73–3.88	Attenuation depth constant for PO_4^{3-}
$C_{z=0}$	$\mu mol\,L^{-1}$	0.31–1.56	Concentration of $NH_4^{+\,a}$
$C_{z=0}$	$\mu mol\,L^{-1}$	0.98–55.5	Concentration of $PO_4^{3-\,a}$

Table 2. Diffusive benthic fluxes of nutrients and metals from different experiments calculated from diffusion–advection–reaction model and pore water concentration gradients.

| Date	Eksperiment	T °C	NH_4^+	PO_4^{3-}	dSi	Mn	Fe	Ca	Mg
				$\mu mol\,m^{-2}\,day^{-1}$				$mmol\,m^{-2}\,day^{-1}$	
3 Aug 2010	normoxia	23.0	108	13.4	36.5	3.69	−0.21	−0.07	−0.40
11 Aug 2010	7d anoxia	25.2	194	13.8	−140	8.17	16.6	−0.19	−1.09
18 Aug 2010	7d recovery	24.5			61.5	0.45	3.14	0.07	0.07
25 Aug 2010	1mo anoxia	25.5	513	4.72	97.8	20.1	7.66	−0.70	−2.63
22 Sep 2010	1mo recovery	20.5	47.9	7.51	181	−2.87	7.75	0.37	0.12
23 Sep 2010	2mo anoxia	21.5	343	7.39	78.7	5.64	−0.05	−0.45	0.31
5 Aug 2011	1y anoxia	24.7	196	1.32	286	1.87	3.17	−0.35	−1.05
22 Oct 2011	1y recovery	17.0	−34.0	2.24	75.7	7.11	2.32	−0.01	−0.98
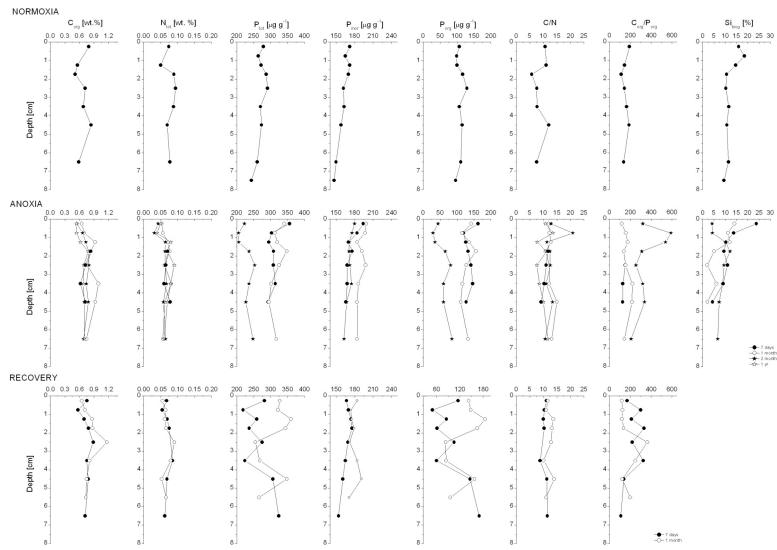
Fig. 1. Distribution of C_{org}, N_{tot}, P_{tot}, P_{inorg}, P_{org}, C/N and C_{org}/P_{org} ratios together with Si_{biog} in sediment solid phase during normoxic-anoxic-reoxic experiments performed in the Gulf of Trieste.
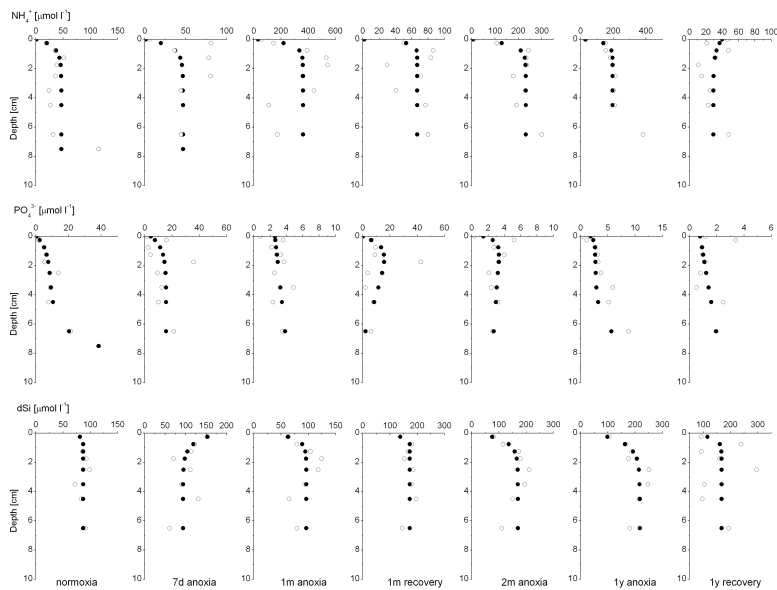
11753

Fig. 2. Depth profiles of pore water NH_4^+, PO_4^{3-} and dSi together with model calculation data during various experiments in the Gulf of Trieste. Measured data – white dots; model calculation data – black dots.
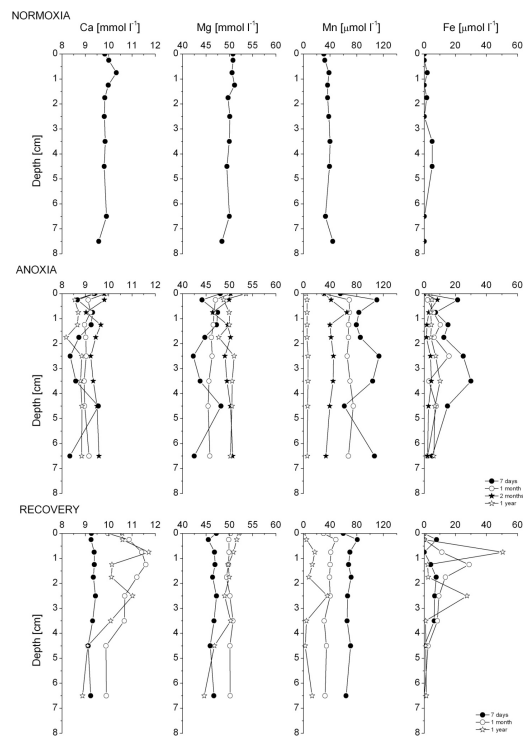
Fig. 3. Depth profiles of Ca, Mg, Mn and Fe in pore waters during normoxic–anoxic–reoxic experiments performed in the Gulf of Trieste.