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Artificially induced migration of redox layers in a coastal sediment from the Northern Adriatic

E. Metzger[1], D. Langlet[1], E. Viollier[2], N. Koron[3], B. Riedel[4], M. Stachowitsch[4], J. Faganeli[3], M. Tharaud[2], E. Geslin[1], and F. Jorissen[1]

[1]Laboratoire des Bio-Indicateurs Actuels et Fossiles, UMR6112 CNRS LPG-BIAF, Université d'Angers, 2 Boulevard Lavoisier, 49045 Angers Cedex, France
[2]Laboratoire de Géochimie des Eaux, UMR7154 CNRS, Université Paris Diderot, Sorbonne Paris Cité, Institut de Physique du Globe de Paris, 75013 Paris, France
[3]Marine Biology Station, National Institute of Biology, Fornace 41, 6330 Piran, Slovenia
[4]Department of Limnology and Oceanography, University of Vienna, Althanstrasse 14, Vienna 1090, Austria

Correspondence to: E. Metzger (edouard.metzger@univ-angers.fr)

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Abstract. Long-term experimental studies suggest that, under transient anoxic conditions, redox fronts within the sediment shift upwards, causing sequential rise and fall of benthic fluxes of reduced species (Mn(II), Fe(II) and S(-II)). Infaunal benthic organisms are associated with different redox fronts as micro-habitats and must be affected by such changes during natural hypoxia events. In order to document the geochemical evolution of the sediment during prolonged anoxia in the framework of an in situ experiment designed to mimic natural conditions, benthic chambers were deployed on the seafloor of the Northern Adriatic and sampled after 9, 30 and 315 days of incubation. Oxygen and sulfide were measured continuously in the early stages (9 days) of the experiment. High-resolution pore water profiles were sampled by DET probes and redox-sensitive species (S(VI), Mn(II) and Fe(II)) and alkalinity were measured.

Starting oxygen saturation was about 80 % within the chamber. After 7 days, anoxia was established in the bottom waters within the chambers. Mn(II) and Fe(II) started diffusing towards the anoxic water column until they reached the surficial sediment. Being reoxidized there, Mn and Fe reprecipitated, giving a rusty coloration to the seafloor. Infaunal species appeared at the sediment surface. After 20 days, all macro-organisms were dead. Decomposition of macro-organisms at the sediment–water interface generated S(-II) within the entire height of the chamber, leading to a downward flux of sulfides into the sediment, where they were quickly oxidized by metallic oxides or precipitated as FeS. S(-II) was below detection in the water column and pore waters at the end of the experiment. Our results suggest that S(-II) enrichment in the water column of coastal systems, which are episodically anoxic, is strongly controlled by the biomass of benthic macrofauna and its decay during anoxia, whereas its residence time in the water column is controlled by iron availability (as solid oxides or as dissolved reduced cations) within the sediment, even without water circulation.

1 Introduction

The increased occurrence of seasonal anoxia and hypoxia in coastal areas reflects a combination of several factors, the most important being nutrient input due to river runoff and stratification of the water column. Since the 1960s a clear increase in the occurrence of anoxic events has been observed, often associated with mass mortality of benthic faunas (Diaz and Rosenberg, 2008). In most cases, anoxia occurs in environments that are semi-enclosed, shallow and have fine-grained and organic-rich sediment bottoms. This combination restricts water circulation, increases the residence time of water and its solutes, favors stratification and, in areas affected by anthropogenic eutrophication, promotes nutrient accumulation and biomass growth. Oxygen is then depleted by respiration without sufficient resupply. This phenomenon,

however, is not exclusive to semi-enclosed settings. Many estuaries where the residence time of water is supposedly relatively short also show severe hypoxia (Garnier et al., 2001; Rabalais et al., 2002; Hagy et al., 2004; Lanoux et al., 2013), sometimes leading to fish mortality; this includes estuaries only moderately impacted by anthropogenic eutrophication, such as the Loire River mouth (Abril et al., 2003). Furthermore, continental seas such as the Baltic Sea, Black Sea, and the Gulf of Mexico (Rabalais et al., 2002), show an increase in the occurrence and geographic extent of anoxic events. Meire et al. (2013) modeled the evolution of hypoxic events in the Oyster Grounds (central North Sea) and concluded that riverine runoff was a key factor influencing the occurrence of hypoxia. In some coastal environments such as Thau Lagoon (French Mediterranean), a decrease of the occurrence of anoxic events has been reported since the 1990s, which has been interpreted to reflect efficient environmental policies leading to a reduced phosphorus load to the lagoon (Souchu et al., 1998). More recent studies in the same system, however, showed that this trend did not extend into the 2000s. Despite the lower phosphorus loads, a large stock is still available within the sediment of the Thau Lagoon, mainly as shellfish faeces; its recycling under summer conditions (i.e., higher temperature and little wind) triggers high benthic fluxes of phosphorus towards the water column, enhancing primary production and ultimately leading to seasonal hypoxia/anoxia as observed in 2003 and 2006 (Mesnage et al., 2007; Minghelli-Roman et al., 2011). Therefore, coastal systems that experienced decades of eutrophic conditions take time to recover. Furthermore, global warming affects oxygen solubility and water stratification worldwide, promoting hypoxia/anoxia. Several authors therefore predict a further increase of the areas affected by anoxia and mass mortality events if no major efforts to decrease nutrient supplies to coastal areas are undertaken (Diaz and Rosenberg, 2008; Middelburg and Levin, 2009; Meire et al., 2013).

We conducted a series of in situ experiments in the Northern Adriatic (Mediterranean Sea), one of the areas repeatedly affected by seasonal hypoxia (Barmawidjaja et al., 1995; Rabalais, 2010; Giani et al., 2012). They were designed to better understand how anoxia affects benthic macrofauna and meiofauna survival and how fast the impacted zone attains a new ecological equilibrium. The main objective was to simulate short- to longer-term bottom-water anoxia and to study the survival, resilience and recolonization of different groups of benthic organisms (macrofauna Blasnig et al., 2013; Riedel et al., 2013, 2012), meiofauna such as foraminifera (Langlet et al., 2013, 2014), nematodes and copepods (Grego et al., 2013, 2014; De Troch et al., 2013), which are expected to respond differently to anoxia. Seasonal changes in bottom-water oxygenation are known to induce vertical migrations of the major redox fronts in the sediment, modifying vertical separation between redox-sensitive elements. The separation between iron and manganese (oxyhydr)oxides in the sedimentary column, for example, is related to different kinetics of reduction/oxidation and therefore of dissolution/precipitation of these metals (Burdige, 2006). Redox oscillations will enhance the accumulation of manganese on top of the sediment. Associated trace metals, including non-redox elements such as cadmium, can also be affected by redox oscillations (Gobeil et al., 1997; Sundby et al., 2004). Experimental studies have shown that cores incubated under hypoxic conditions successively released dissolved manganese (Mn(II)), iron (Fe(II)) and sulfide S(-II)) to the overlying water column. This demonstrates that bottom-water oxygenation impacts the vertical extent of redox zones (Kristiansen et al., 2002; Sell and Morse, 2006).

In the Northern Adriatic, hypoxic conditions occur seasonally in late summer, affecting the recycling of metal oxides and bioturbation activity (Faganeli et al., 1985; Hines et al., 1997). Several macrofauna mortality events have been documented (Stachowitsch, 1984, 1991). Moreover, the region is impacted by intense trawl-fishing activities, enhancing the vulnerability to benthic perturbation. The present contribution is part of a multidisciplinary study conducted on a silty-sand bottom at 24 m water depth in the Gulf of Trieste, Northern Adriatic. It presents the evolution of a series of major chemical species in the bottom waters and surficial sediments during a series of in situ anoxia experiments lasting up to 10 months. Benthic meiofauna and foraminifera preferentially inhabit the top layer of the sediment. Nonetheless, some of these organisms live in microhabitats that correspond to the major redox zones. Those species with a deep infaunal microhabitat can cope better under anoxia (Schönfeld, 2001; Jorissen, 2003). Sulfide, however, seems to be a barrier for vertical migration of foraminifera (Moodley et al., 1998) making the sulfate/sulfide redox front dynamics a key parameter of infaunal survival. Our hypothesis was that, during our experiment, both the pore-water chemical composition and the vertical distribution of meiofauna would change. Accordingly, the goals of the present study were (1) to describe with high vertical resolution the geochemical evolution of the pore- and bottom waters slightly above and below the sediment–water interface during short- and long-term incubation, (2) to better understand the behavior of the main redox species (i.e., oxygen, manganese, iron and sulfur) during the onset of anoxia, and (3) to provide the geochemical constraints that would potentially explain the response of the benthic fauna to anoxia.

2 Material and methods

2.1 Study area

The study site is located 2.3 km off Piran (Slovenia) in the southern part of the Gulf of Trieste, Northern Adriatic Sea, at the Marine Biology Station's hydrographic buoy Vida (45°32′55.68″ N, 13°33′1.89″ E). This site was selected because of a minimal risk of damage to equipment by

commercial fisheries. The Gulf of Trieste covers an area of 600 km^2, has a maximal depth of 25 m and is isolated from the rest of the Northern Adriatic by a 100 m-deep shoal. This leads to water residence times of about 250 days (Poulain and Hariri, 2013), which is twice as long as in the Southern Adriatic Sea. The salinity of bottom waters ranges from 36 to 38.5 and bottom-water temperatures range from 8 °C in winter to 20 °C in summer. In late summer, a vertical density gradient can result in bottom-water hypoxia or anoxia (Faganeli et al., 1985). The sediment in the southern part of the Gulf of Trieste is mainly composed of silty sand that is rich in biogenic carbonate (porosity about 0.6, unpublished data). The benthic macrofauna community is dominated by brittle stars, sponges and tunicates (Fedra et al., 1976; Ogorelec et al., 1991) and the sediment is actively bioturbated by polychaetes, bivalves and irregular sea urchins. The sedimentation rate, determined by ^{210}Pb, is approximately 1.2 mm yr^{-1} (Ogorelec et al., 1991). The sediment surface is covered by microalgae, mostly diatoms (Bertuzzi et al., 1997), which greatly contribute to the sedimentary organic carbon (OC) input (Ogrinc et al., 2005). The OC content in superficial sediment is about 0.65 wt % (Koron et al., 2013; Ogrinc et al., 2005).

2.2 Experimental setup

A series of benthic chambers was deployed in situ to mimic anoxic events and to isolate the sediment and its overlying waters for different periods of time. We assumed that no ventilation occurs during anoxia events and therefore decided against stirring. An abundant literature shows the influence of hydrodynamics on benthic fluxes and suggests that stirring is suitable to homogenize the chemical composition of the overlying water and to keep a realistic benthic boundary layer in order to determine benthic fluxes (Sundby et al., 1986; Hall et al., 1989; Boudreau, 2001; Viollier et al., 2003). However, since the project was intended to investigate whether benthic organisms respond to biogeochemical changes in the surface sediment, the aim of the present study was not to measure benthic fluxes but to describe changes in pore-water chemistry during the development of anoxia. The cubic benthic chambers were made of Plexiglas®, with sides of 50 cm (surface area 0.25 m^2, volume 0.125 m^3). A sealable aperture on one side enabled inserting and removing probes during/after deployment. The three chambers used for our analyses were deployed for 9 days, 1 month and 10 months (Table 1). The "9 days" chamber was equipped with a camera and a set of chemical sensors and has previously been described as an EAGU (Experimental Anoxia Generating Unit, Riedel et al., 2008, 2012; Stachowitsch et al., 2007). In order to optimize the isolation of the benthic chambers (i.e., prevent bioturbation by macroinfauna), the sidewalls were pushed a few centimeters into the sediment; additionally, 20 cm-high inox steel plates were pushed into the sediment parallel to the walls. Finally, the area around the chambers was covered with ceramic tiles to minimize the risk that burrowing could re-ventilate the chambers. In every chamber, a series of 8 DET (Diffusive Equilibrium in Thin films) gel probes (Davison et al., 1991; Fones et al., 1998; Metzger et al., 2007) was inserted 24 to 48 h before termination of the experiment, allowing in situ sampling of pore water at a 2 mm resolution (see below, Fig. 6d). DET gel probes were also deployed in an adjacent control area, hereafter referred to as "Normoxic" (Fig. 6a). The distance between the chambers did not exceed 10 m and all deployment areas were chosen for their visually homogeneous sediment without macrofauna multi-species clumps.

Table 1. Time schedule of deployment for each chamber.

Chamber name	Deployment dates initial	final
9 days	02/08/10	11/08/10
1 month	27/07/10	25/08/10
10 months	24/09/10	05/08/11

2.3 Oxygen and sulfide sensors

Two oxygen and two sulfide Clark-type sensors from Unisense® (Revsbech, 1989) were placed within the first chamber, which was opened after 9 days. The four probes were placed at each corner of the chamber. One of each pair was positioned 5 cm above the sediment–water interface, the second one at about 4 mm. Sensors were connected to a specially designed data logger from Unisense®, yielding a measurement every 10 min for each of the four sensors.

2.4 DET gel preparation and deployment

For this study, we used a modified version of DGTresearch© perspex probes (Metzger et al., 2007), which minimize probe thickness (3 mm) and vertical channeling. Each probe corresponds to 75 cells of 22 µL and a vertical resolution of 2 mm. Probes were rinsed in HCl acid and deionized water before assemblage. A mixture of 1.5 % w/w of ultra-pure agarose (USB Corporation, USA) in deionized water (milli-Q®) was placed in a microwave oven until complete dissolution of the agarose powder. The hot gel was poured into the probe and a glass plate was pressed over it to remove excess hydrogel. After cooling, the remaining excess gel was removed with a Teflon-coated razor blade. Next, the gel was covered with a PVDF hydrophilic membrane (0.2 µm size pore, Millipore, USA). The membrane was fixed onto the probe with commercially available PVC plastic tape (Leroy Merlin®), which is sensitive to dissolved H_2S (Jézéquel et al., 2007). Gels were stored for at least 24 h in deionized water, which was replaced twice.

Before deployment, DET probes were degassed with N_2 overnight and kept under nitrous atmosphere until immersion

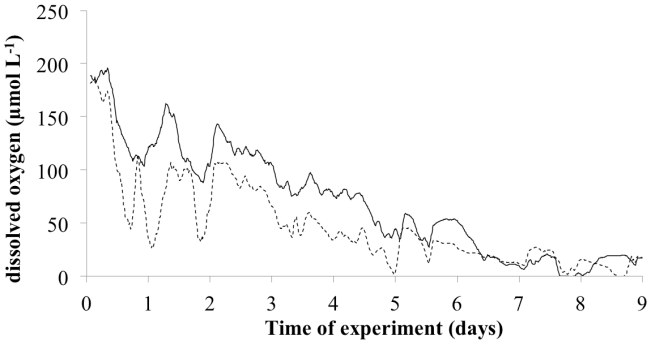

Fig. 1. In situ dissolved oxygen concentration inside EAGU chamber (9-day incubation time). Dashed line: oxygen probe 5 cm above SWI. Full line: oxygen probe 4 mm above SWI. Sulfide was always below detection limit for both probes.

to minimize oxygen contamination from the gel to the anoxic sediment during insertion. The DETs were inserted into the sediment of the chamber by Scuba divers through the sealable aperture in the chamber wall (Ø 20 cm) and then photographed to document their relative position in the chambers as well as the precise location of the sediment–water interface. Based on the aperture size and construction, the water exchange during DET insertion was minimal (an estimated 2 L, versus the 125 L content of each chamber). Although the time needed for equilibration of the DET probes is generally only about 4 h (Harper et al., 1997), the gels in the present study were deployed from 24 to 48 h because of operational limitations and to enable the sediment to recover from potential perturbation. The entire retrieval operation (until preservation in nitrous atmosphere) took 3 min at most. DETs were sampled and the samples chemically stabilized in the laboratory within 4 h after retrieval.

2.5 DET preservation and analyses

In total, 8 DET probes were inserted within each incubation chamber. Two probes were dedicated for each type of analysis (e.g., six in total) in order to have two replicates for each chemical profile. The two remaining probes were used as spares.

Gel samples serving for metal determinations were eluted in 5 mL of a 0.01 mol L^{-1} suprapur® nitric acid solution corresponding to a dilution factor of about 200 of the pore water (DET gel piece about 25 µL). Dissolved iron and manganese were analyzed with a High-Resolution ICP-MS Element II from ThermoScientific. This ICP-MS enables working in different resolution modes (LR = 400, MR = 4000 and HR=10 000) to better discriminate between elements of interest and possible interferences (Krachler, 2007). Mn and Fe were measured at high resolution (HR). At the beginning of each measurement session, the instrument was first tuned to produce maximum sensitivity and stability while also maintaining low oxide formation (UO/U $\leq$ 5 %). In order to minimize analytical time and sample volume, we worked with the SC-FAST automation system coupled to a cyclonic spray chamber (Mahar et al., 2008). A six-port valve rapidly delivers the sample with a high-flow vacuum pump and rinses the probe sample lines while the sample is analyzed. This allowed us to decrease the analytical time and volume for each sample to 2.5 min and 2 mL. Multiple standard solutions were prepared using 1000 ppm SPEX standard solutions and laboratory-distilled suprapur® nitric acid, and the accuracy and precision of measurements were checked using SLRS-4 and 5 certified standards (NRC-CNRC). The overall uncertainty was estimated to be below 6 %.

Gel samples dedicated to sulfate determination were stored in 1 mL of a 0.01 mol L^{-1} zinc acetate solution in order to fix all sulfide present in the solution as ZnS, avoiding oxidation into sulfate. Before ionic chromatography analysis, samples were diluted to a final dilution of 800. Standard solutions were prepared with filtered subsurface seawater from the Bay of Biscay with a salinity of 34. Sulfate and chloride were measured using a Metrohm 792 Basic IC with a 100 mm Metrosep A supp 5 column. Precision was about 2 %. In order to point out ongoing biogeochemical processes, SO_4^{2-} values are normalized to Cl^- and shown as the result of the calculation: $(SO_4^{2-}/Cl^-)_{sample} \times Cl^-_{overlying\ water}$. Because Cl^- is considered to be a conservative chemical species, variations of normalized sulfate with depth cannot be due to mixing processes.

Gel samples used to determine alkalinity were stabilized directly in 1 mL of the colorimetric reagent that was used for spectrophotometric measurement. A bromophenol blue formic acid reagent was prepared according to Metzger et al. (2013) following the technique proposed by Sarazin et al. (1999). Standard solutions were made with sodium hydrogen carbonate salt. Measurements were done after 1 h of equilibration at a wavelength of 590 nm. Precision was about 0.3 mmol kg^{-1}.

3 Results

3.1 Dissolved oxygen and sulfide in the chamber

In situ dissolved oxygen and sulfide concentrations obtained from microsensors are shown in Fig. 1. The data logger was started directly after chamber closure and stopped about 9 days later prior to opening the chamber. The data presented in Fig. 1 are averaged values for 1 h periods (i.e., average of 6 values taken every 10 min). Oxygen probes, which were located at two different edges of the chamber and positioned at different distances from the SWI, both showed the same trend, with initial values of about 190 µmol L^{-1} (about 80 % oxygen saturation) and with minimal values close to zero reached about 7 days later. Data showed a second-class variation with oscillations of variable amplitude, without a clear periodicity. Note that during the first

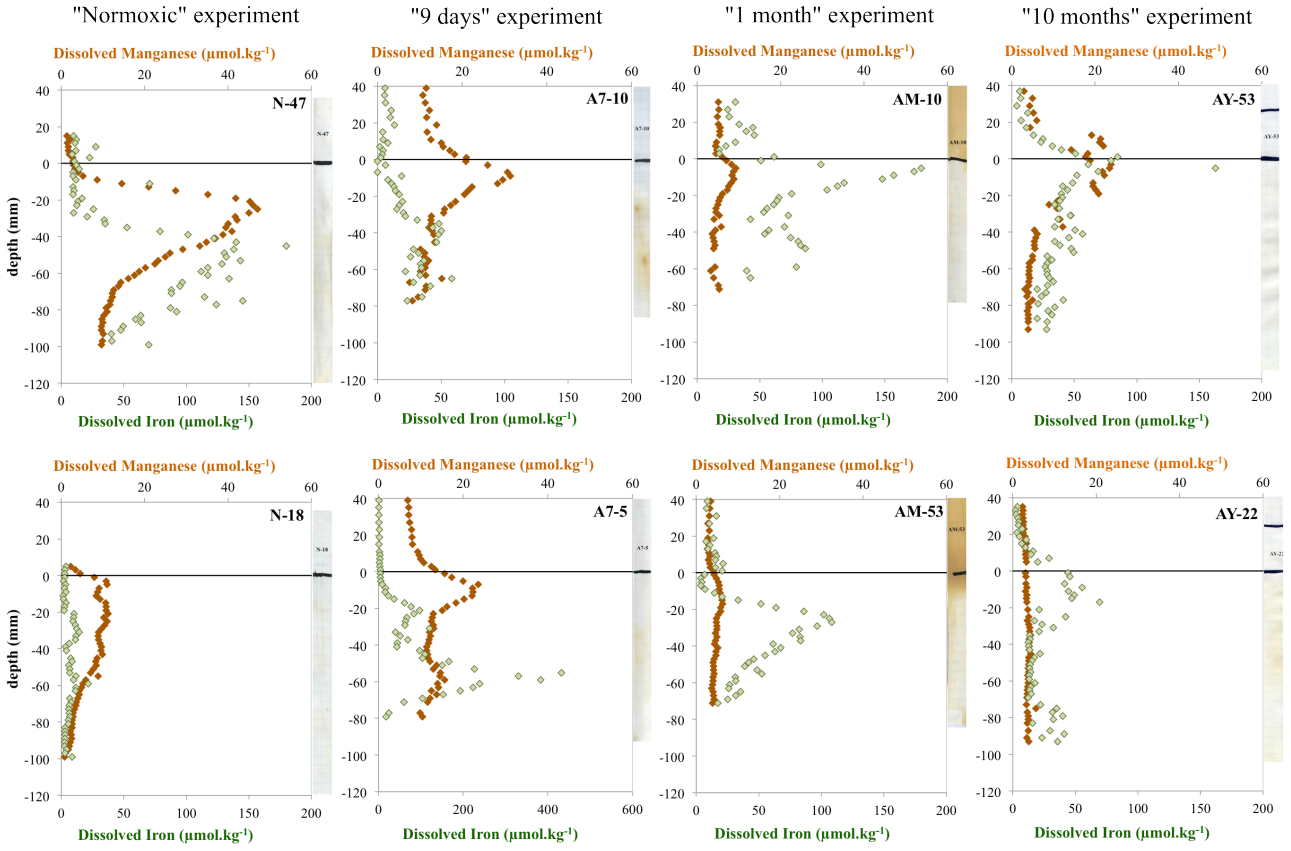

Fig. 2. Pore-water dissolved manganese (orange diamonds) and iron (green triangles) distribution from DET probes. From left to right: "Normoxic" situation, "9 days" incubation, "1 month" incubation", "10 months" incubation. White tape sulfide sensor corresponding to the DET probe is shown for each profile.

5 days of the experiment, probe 2, situated 4 mm above the SWI (full line on Fig. 1), showed a higher oxygen content than the probe located 5 cm above SWI (dashed line). A linear regression yields an estimated oxygen consumption rate about 10 mmol m^{-2} d^{-1}. Sulfide concentration for both probes was below detection limit during the whole experiment (< 0.3 µmol L^{-1}).

3.2 Dissolved manganese and iron

Figure 2 shows the vertical distribution of Mn(II) and Fe(II) between 4 cm above the SWI and 10 cm depth in the sediment, for four different treatments. From left to right: the profiles from a reference sediment ("Normoxic") and for the "9 days", "1 month" and "10 months" experiments. Results from different probes are shown separately, yielding eight profiles (two replicates for each treatment, upper and lower panel). In the "Normoxic" profiles, Mn(II) and Fe(II) show contrasted results between the two replicates. Profiles from DET N47 (upper panel) show large peaks of Mn(II) and Fe(II), while profiles from DET N-18 (lower panel) show smaller variations. Manganese peaks develop from 0 to 6 cm depth with maxima of 47 and 11 µmol kg^{-1}, respectively, at about 2 cm depth. Iron peaks develop from 2 to 10 cm depth with maxima of 180 and 22 µmol kg^{-1} at about 4.5 and 6 cm depth, respectively. After 9 days of incubation, the vertical distribution of Mn and Fe is different. Mn profiles show similar trends for both replicates (A7-10 and A7-5), with elevated values from 2 cm above the SWI to 3 cm below. Maxima occur about 1 cm below the SWI, with values of 31 and 24 µmol kg^{-1}, respectively. Iron profiles show peaks developing between 1 and 8 cm below the SWI, with maxima of 58 and 423 µmol kg^{-1} at 5.5 and 6.5 cm depth, respectively. At the end of the "9 days" experiment, relatively elevated Mn concentrations are present in the overlying water compared to the "Normoxic" profile (7 to 12 µmol kg^{-1} instead of 1 µmol kg^{-1}). In the "1 month" experiment, Mn in the overlying waters decreases to about 4 µmol kg^{-1}. The pore-water distribution shows relatively weak maxima compared to the "9 days" experiment (9 and 6 µmol kg^{-1} around 1 cm below the SWI for DET AM-10 and AM-53, respectively). Iron peaks have their maxima at 0.5 and 2.5 cm below the SWI, with concentrations of about 179 and 108 µmol kg^{-1}, respectively. A secondary Fe peak is visible directly above the SWI in both profiles. DET AY-53 from the "10 months"

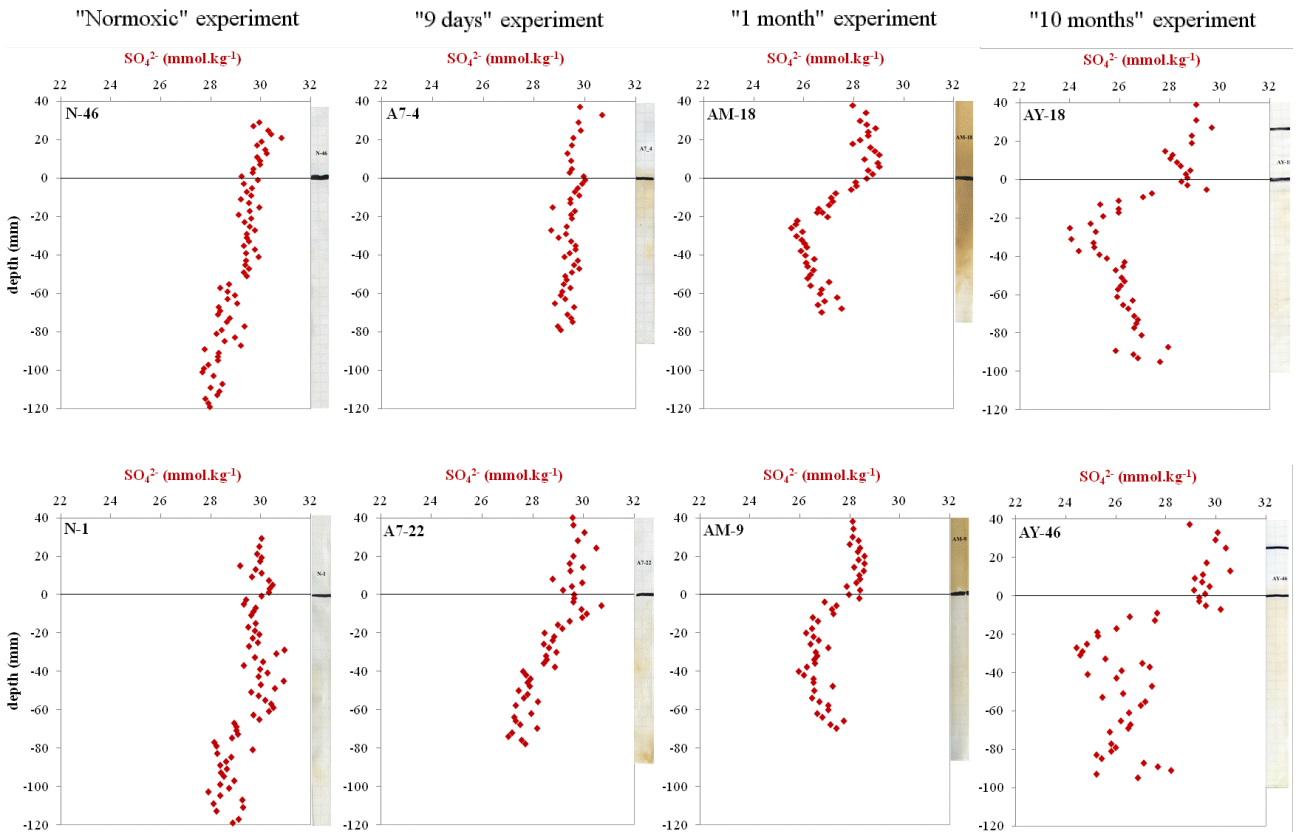

Fig. 3. Normalized dissolved sulfate distribution in pore water from DET probes.

experiment (upper panel) shows concomitant peaks of Mn and Fe, with maximum values at the SWI (23 µmol kg^{-1} for Mn and 80 µmol kg^{-1} for Fe). The second profile, AY-22 (lower panel), shows a fairly constant Mn concentration with low values (around 3 µM), whereas Fe peaks around 1 cm depth with a maximum concentration of 70 µmol kg^{-1}.

3.3 Sulfate

The vertical distribution of sulfate concentrations in the pore waters is presented in Fig. 3. "Normoxic" profiles show rather constant values of about 30 mmol kg^{-1} down to 5 cm below the SWI. Deeper down, sulfate slightly decreases by about 2 mmol kg^{-1} until the bottom of the profiles (12 cm depth). Spatial variability is apparently higher for the "9 days" DETs. DET A7-22 (lower panel) shows a decrease of sulfate from 1 cm below the interface (slope = 0.04 mmol/mm; $r^2 = 0.83$), whereas no decreasing trend is present in DET A7-4 (upper panel, slope = 0.0052 mmol mm^{-1}; $r^2 = 0.15$). Minimal SO_4(II) concentrations are about 29 and 27 mmol kg^{-1} for DET AW-4 and AW-22. The "1 month" DETs show lower sulfate concentrations (28–29 mmol kg^{-1}) in the overlying water than those described above. Below the SWI, the sulfate concentration decrease is more important than before (about 3 mmol kg^{-1}), reaching 26 mmol kg^{-1} at 2 cm depth, and apparently increases slightly deeper down, to reach 27 mmol kg^{-1} at the bottom of the profile (i.e., 6.5 cm depth). The sulfate profiles of the "10 months" experiment are very similar to those of the "1 month" DETs. However, the decrease below the SWI is sharper and stronger (about 4 mmol kg^{-1}). The sulfate gradients below the SWI seem to be sharper and shallower depending on incubation duration.

3.4 Alkalinity

The alkalinity measurements of pore waters from the four experiments are shown in Fig. 4. The "Normoxic" profiles suggest little variation of alkalinity in the overlying waters and downwards through the SWI (3.5 mmol kg^{-1}). Nonetheless, a downward alkalinity increase is evident in both replicates, starting at 7 cm depth for DET N-40 and 11 cm depth for DET N-8. The two "9 days" DETs show similar profiles with constant values in overlying waters and in the upper part of the sediment (3.5 and 4 mmol kg^{-1} for DETs A7-06 and A7-07), and increasing concentrations in the deeper part of the sediment (starting at 4 and 6 cm below SWI, respectively). Values reach 8.5 and 11 mmol kg^{-1} in the two replicates. The "1 month" DETs show a relatively large variability between the two replicates. The overlying waters have a higher

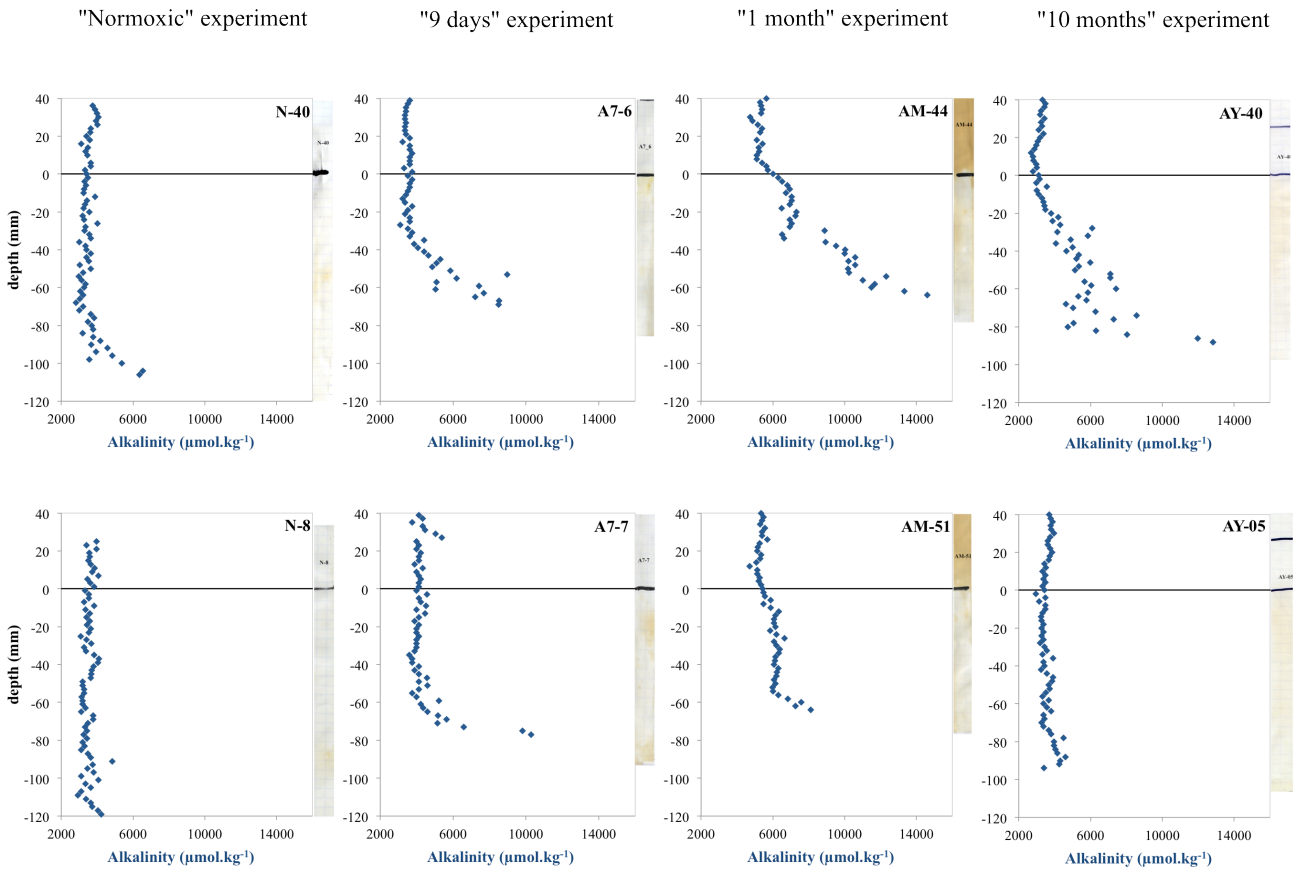

Fig. 4. Pore-water alkalinity distribution from DET probes.

alkalinity than before (about 5 mmol kg^{-1} instead of 3.5–4 mmol kg^{-1} in "Normoxic" and "9 days" chambers). From 1 cm above the SWI to the first cm below, alkalinity increases slightly to 7 and 6 mmol kg^{-1} for DETs AM-44 and AM-51. Values remain more or less consistant downward until a rapid increase starting at 3.5 and 5.5 cm depth, respectively. Alkalinity, respectively between DET AM-44 and AM-51 mentionned just above reaches 14 and 8 mmol kg^{-1} at 7 cm depth. The "10 months" profiles show contrasting patterns between the two replicates. DET AY-40 (upper panel) shows an alkalinity increase, with depth starting 2 cm below the SWI and peaking at 13 mmol kg^{-1}. Conversely, DET AY-05 shows little variation with depth and values fluctuate only within a range of 1 mmol kg^{-1}. The overlying waters of both replicates show alkalinity concentrations of about 3.5 mmol kg^{-1}, comparable to the "Normoxic" values.

3.5 H_2 S-sensitive white tape coloration

Figure 5 shows the collection of the originally white PVC tapes used for each different DET probe at each experiment (6 DET × 4 experiments). The tapes are shown together with the respective pore-water profiles to facilitate discussion. After retrieval, the tapes were glued in a notebook at half-centimeter height (visible in the figure). The "Normoxic" tapes are predominantly white below the SWI. The "9 days" tapes show dispersed brownish areas within the sediment, indicating the release of H_2S into the pore waters. The "1 month" tapes show much more continuous dark-brown zones below the SWI, but the pore-water variability seems to be very high. Contrary to the previous experiments, the "1 month" tapes also show a very dark coloration above the SWI. Finally, the "10 months" tapes are mostly whitish, comparable to the "Normoxic" tapes.

4 Discussion

4.1 Sedimentary geochemistry under summer "Normoxic" conditions

According to oxygen electrode profiles measured in the "9 days" chamber (Fig. 1, Table 2), the oxygen consumption rate in our study site is about 10 mmol m^{-2} d^{-1}. This rate corresponds in the Adriatic to an oxygen penetration depth of about 5 mm (Epping and Helder, 1997). Manganese profiles from the "Normoxic" DETs show a gradient across the SWI, indicating that Mn(II) diffuses upward towards the SWI

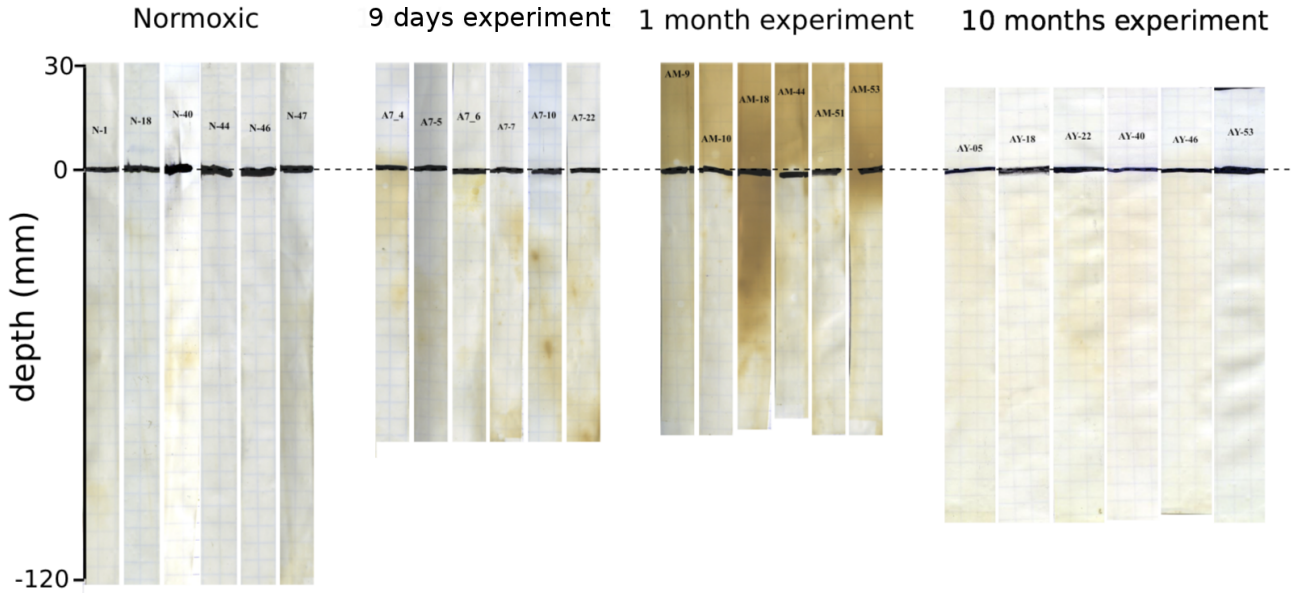

Fig. 5. Dissolved H_2S occurrence during DET deployment as indicated by PVC white tapes (brown coloration).

and the overlying waters and is oxidized there. Reduced iron, however, remains confined within the sediment as suggested by the deep location of iron peaks in Fig. 2 (from 2 to 10 cm depth). These results suggest that there is little chance for Fe(II) to react directly with free oxygen because its penetration would not exceed a few millimeters. Therefore, iron oxidation, which under "Normoxic" conditions takes place in deeper sediment layers, is probably due to other oxidants such as manganese oxides or nitrate (measured in the pore waters by Koron et al., 2013). An earlier study investigated the seasonal evolution of metabolic pathways of mineralization processes in the same area (Hines et al., 1997). In September 1993, when bottom waters were hypoxic and the water column was stratified, Hines and coworkers demonstrated that anaerobic mineralization processes were as important as aerobic processes. They suggested that considerable benthic oxygen consumption was due to the upward diffusion of reduced components such as Mn(II) and Fe(II) towards the water column. They were, however, unable to observe the efflux of reduced metals at the centimeter resolution they used. The present study improved the vertical resolution of profiles. Despite considerable lateral heterogeneity, it provides evidence of Mn(II) diffusion towards the bottom water even while the water column was well oxygenated. In the next section we discuss the further evolution of manganese and iron mobility during anoxia in order to verify the hypothesis of Hines et al. (1997) that manganese and iron are important consumers of oxygen during strong hypoxia and/or anoxia. Sulfate concentrations (Fig. 3) decrease below 5 cm depth, showing very slight gradients (at most $\leq 10\,\%$ of sulfate was consumed 12 cm below the SWI). The white tapes were very slightly discolored only in scattered zones within the sediment. In other shallow-water environments these qualitative probes turned dark grey/brown when sulfide concentrations reached millimolar amounts, a few centimeters below SWI (e.g., Thau Lagoon, Jézéquel et al., 2007; Metzger et al., 2013; Arcachon Basin, Metzger, unpublished data).

Table 2. Oxygen uptake estimated from previous studies in the Northern Adriatic and corresponding organic carbon percentage when available.

Reference	mmol m^{-2} d^{-1}	OC (%)
This study	−9.93	0.7
Riedel et al. (2008)	−77.17	–
Stachowitch et al. (2007)	−40 to −80	–
Epping et al. (1997)	−3 to −30	0.3 to 1.7
Bertuzzi et al. (1996)	−5 to −30	0.5 to 1.8

The "Normoxic" samples were taken in early August 2010, when temperature was lower than the monthly average. In this area, marine snow events are common, occurring almost every summer (Malej, 1995). In 2010, marine snow first developed in late August, suggesting that the sediment at the sampling station was not yet under "late summer conditions", characterized by considerable input of fresh organic material. During our experiment we estimated an oxygen uptake of about 10 mmol m^{-2} d^{-1}. This value is very low compared to those obtained at other sites for the same season and region. A previous study in the Gulf of Trieste showed a summer oxygen uptake approaching 30 mmol m^{-2} d^{-1} (Bertuzzi et al., 1997). This large difference can be explained by the fact that the sediment at their station had much

higher organic carbon content (1.7 % at the surface) than our sites (0.65 %, Koron et al., 2013; Hines et al., 1997). After a marine snow deposit, oxygen consumption rates should be higher, although no measurements are available for our study area. The time needed to completely consume all oxygen in the benthic chamber (7 days, Fig. 1) in our "9 days" experiment is very long compared to previous observations with the same device in the same period of the year (Stachowitsch et al., 2007; Riedel et al., 2008). In those experiments, respiration of the enclosed macrofauna led to a rapid oxygen decrease in the chamber (i.e., anoxia after maximum 4 days), with calculated oxygen uptake varying from 40 to 80 mmol m^{-2} d^{-1} (Table 2). Those studies also showed sulfide production less than 1 day after oxygen depletion. This indicates a rapid total consumption of all oxidants other than sulfate (e.g., nitrate, Mn and Fe oxides) in the surface sediment and the water column, which did not occur in our experiment.

The main difference between the present experiment and all previous ones is that the latter were conducted over macro-/megafaunal multi-species slumps, whereas for the present experiment, areas without visible macrofauna were selected. In our opinion, the large differences in oxygen consumption and the time needed to reach total anoxia mainly reflect the highly contrasting respiration by and decay of macrofauna, or enhanced deposition of labile carbon by fauna.

In summary, in our "Normoxia" sediments, diagenetic processes are not very intense for summer conditions in a coastal area of the supposedly eutrophic Northern Adriatic. Sulfate reduction rates reported by Hines et al. (1997) were lower at our study station than at their station in the Bay of Piran, located a few kilometers southeast of the buoy (our station) and closer to shore (Hines et al., 1997). This may reflect a larger sediment grain size and a lower organic carbon content at our station. Note, however, that those authors showed that, in late summer (September 1993), when the water column was stratified and oxygen saturation at the bottom was 45 %, sulfate reduction rates near the buoy increased from about 0 to 300 nmol cm^{-3} d^{-1} in the top sediment layer. In our "9 days" experiment, the oxygen concentration at the sea floor was about 200 µmol kg^{-1}, corresponding to a saturation degree of about 80 %; this suggests very low sulfate reduction rates, especially near the SWI.

4.2 Vertical redox fluctuations versus lateral heterogeneity

Previous EAGU deployments in the nearshore area off Piran by Stachowitsch and co-workers Riedel et al. (2008, 2012) and Stachowitsch et al. (2007) showed a typical pattern of oxygen and sulfide concentrations within the chamber. After closure, oxygen was quickly depleted and sulfide began to accumulate (see above). Also, laboratory experiments using cores sampled in other environments showed a clear relationship between oxygen concentration in the bottom waters and sediment-to-water-column fluxes of Mn(II), Fe(II) and S(-II) (Kristiansen et al., 2002; Sell and Morse, 2006). The kinetics experiment performed by Kristiansen and co-workers clearly showed that reduced compounds accumulated more in the overlying water during more severe hypoxia. They showed that long-term reductive dissolution of manganese and iron (oxyhydr)oxides under hypoxic conditions ultimately leads to their exhaustion, allowing the upward diffusion of sulfides and their flux into the overlying waters. Therefore, a temporal succession in the release of Mn(II), Fe(II) and S(-II) is generally interpreted as an upward migration of redox layers after exhaustion of all free oxygen and other possible oxidants (e.g., Balzer, 1982; Sundby et al., 1986; Aller, 1994; Skoog and Arias-Esquivel, 2009). Following this conceptual model, we expected that, after total oxygen consumption in the EAGU chambers, a flux of Mn(II) and Fe(II) into the chamber would occur due to the upward migration of redox fronts. After approximately 3 days, metallic oxides should have been consumed and S(-II) should have started diffusing into the chamber as it has occurred in previous EAGU experiments. Considering the Mn(II), Fe(II), SO_4(-II) and alkalinity profiles (Figs. 3 to 5), our data set supports this model. Manganese maxima occur 2 cm below SWI in the "Normoxic" profiles and shift upwards to 1 cm below SWI after 9 days ("1 week" profiles). After "1 month", the position of the Mn(II) maxima does not change, but their intensity decreases from about 30 µmol kg^{-1} to less than 10 µmol kg^{-1}, strongly suggesting that sediment Mn-oxides become exhausted due to reduction. After "10 months", the two profiles contrasted: one is nearly straight, suggesting that all solid manganese oxides have been consumed, whereas the second profile still shows a maximum of about 60 µmol L^{-1} near the SWI. This important difference points to considerable lateral heterogeneity within the sediment of our chambers, complicating the interpretation of the temporal trends. Nonetheless, despite this spatial heterogeneity, the overall upward shift of manganese redox front during the experiment is evident.

Reduced iron profiles show a more complex picture, with some profiles showing a double peak, indicating a more complex sedimentological history. For instance, double Fe(II) peaks may occur after rapid sediment deposits, burying a surficial sediment enriched in metal oxides (Deflandre et al., 2002). In our data, Fe(II) maxima are located 6 cm below SWI after 9 days and have migrated to the SWI in one of the "1 month" profiles. Evidence of iron diffusion into the chamber is given by the progressive orange coloration of the seabed (Fig. 6, photos A to F), which indicates reoxidation of upwardly diffusing Fe(II) by oxidants such as oxygen or nitrate.

Sulfate profiles point to sulfate reduction below 6 cm depth in the "Normoxic" profiles. After "9 days", SO_4(-II) reduction appears to occur only a few millimeters below the SWI. In the following weeks, the sulfate gradient becomes steeper, with a decrease of about 3 and 5 mmol kg^{-1} in the first 2 cm

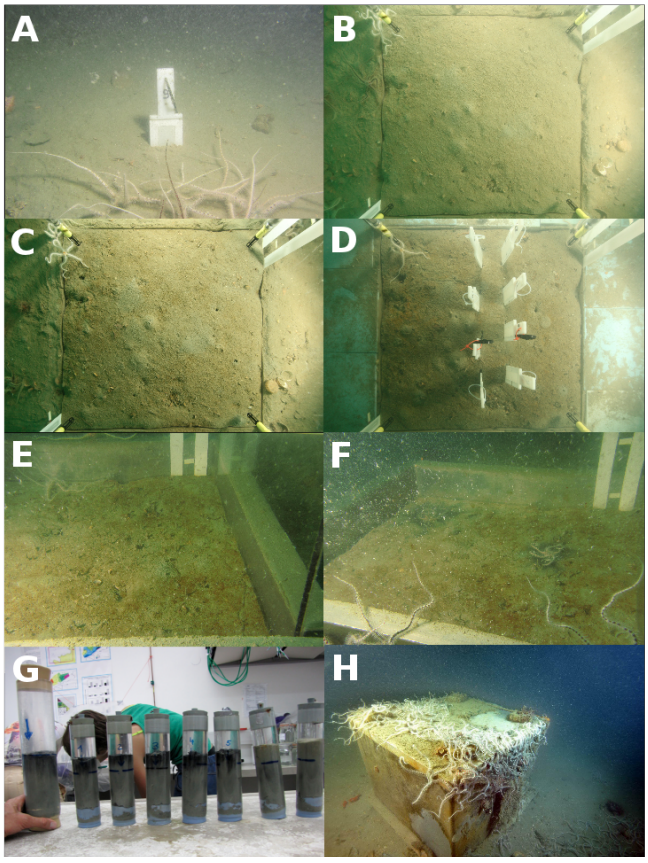

Fig. 6. (A): "Normoxic" DET probe on seabed. **(B)**: "9 days" chamber (EAGU) directly after chamber closure. **(C)**: "9 days" chamber after 8 days. **(D)**: "9 days" chamber directly before opening of the chamber. **(E)**: "1 month" chamber on 10 August. **(F)**: "1 month" chamber on 17 August. **(G)**: six cores on the left sampled inside the "1 month" chamber. Two cores on the right sampled outside the "1 month" chamber. **(H)**: photo of "10 months" chamber 1 month before opening (photo: T. Makovec).

in the "1 month" and "10 months" profiles, respectively. The sulfide probes (white tapes; Fig. 5) show a very large spatial variability of the free sulfide distribution in the benthic chambers, confirming the considerable heterogeneity of the sediment. In fact, the DET probes point to minimal concentrations of free sulfide within the sediment: only a few DETs show brown-grey patches.

Summarizing, our data set strongly suggests that the successive redox layers, which can be interpreted as microhabitats for infaunal meiofauna communities (Jorissen, 2003), shifted upwards during the experiment. Nonetheless, this upward shift was slower than expected because no S(-II) release was observed during the first 9 days of the experiment, unlike previous studies in the area using the same analytical approach (Riedel et al., 2008, 2012; Stachowitsch et al., 2007). These results support the model of successive release of reduced compounds towards the water column under anoxic conditions (e.g., Balzer, 1982; Sundby et al., 1986; Aller, 1994; Skoog and Arias-Esquivel, 2009), and underline the importance of manganese and iron recycling under anoxic conditions in different coastal settings.

The upward shift of redox layer documented here seems to have constrained the temporal evolution of the macro- and meiofauna. Copepods drastically decreased with anoxia duration: no living individuals were found after 1 month (Grego et al., 2014). The foraminifera, however, retained high densities throughout the experiment (Langlet et al., 2013), underlining that copepods were more sensitive to redox conditions than foraminifera. The foraminiferal abundance of the first half-centimeter was affected by anoxia, while the deeper microhabitats did not change over time, suggesting that shifts of redox zonation did not affect infaunal organisms. The next section gives an explanation of what controlled foraminifera dynamics as discussed in detail in Langlet et al.(2013, 2014).

4.3 Unexpected sulfide feature

Surprisingly, the overlying waters show a different pattern for free sulfide (S(-II)) from what we expected (i.e., an increasing efflux of sulfide from the sediment during anoxia). Although most chambers show no S(-II) in the overlying waters, the tapes on all the DETs deployed in the "1 month" chamber were intensely discolored above the SWI; this strongly contrasts with the absence of S(-II) in the sediment of four of the DET probes. Only two of the DETs demonstrate sulfide penetration into the sediment, about 2 cm in DET AM-53, and about 5 cm in DET AM-18. This contrast between sulfide-rich overlying waters and sulfide-poor sediment strongly suggests that FeS precipitation limits S(-II) accumulation and therefore that deep sediment is not a source of sulfides(-II), as indicated by the Kristiansen model and other studies on seasonally anoxic basins (Brüchert et al., 2003; Metzger et al., 2013). Rather, S(-II) is produced at the SWI or slightly above. Figure 6f shows the black coloration produced by the decomposition of several brittle stars after 3 weeks of incubation. These were introduced in the chambers at the beginning of the experiment as "visible anoxia probes" because most chambers were not equipped with sensors. We consider the presence of this introduced epifauna to have had a negligible influence on the sedimentary processes because its biomass is small (particularly compared with the infauna). These individuals represent a minimum contribution of the otherwise dominant macroepifauna (which we rigorously avoided when positioning our chambers in order to focus on developments within the sediment). Importantly, the presence (and decomposition) of a full macroepifauna in "natural" anoxia events supports and strengthens our interpretations about the influence of decaying organic material on the sediment surface. Figure 6g shows that all cores sampled in the "1 month" chamber had a very dark layer at the SWI, versus the homogeneous grey coloration in cores taken outside the chamber. These macroscopic observations strongly suggest that the decomposition

of infaunal macroorganisms has generated a thin layer of dark sediment at the SWI, probably rich with iron sulfide precipitates. The visual analysis of time-lapse photographs taken with the EAGU indicates that, during the first week of the experiment, brittle stars were still alive; they tiptoed ("arm-tipping") in order to raise their respiratory organs higher in the progressively oxygen-depleted overlying waters, as shown in previous studies (Riedel et al., 2013). After a few days of incubation (while oxygen decreased), infaunal organisms migrated to the sediment surface and died at the SWI when oxygen disappeared. The organic carbon (OC) content in the "1 month" cores showed no clear vertical trend and no significantly higher contents that would suggest any organic matter supply due to macrofaunal mortality (Koron et al., 2013). Since the OC content of the sediment is controlled by the balance between input and mineralization processes, the absence of a clear Corg signal does not mean there is no Corg input; it can suggest a rapid remineralization of dead organisms. The presence of S(-II) in the overlying waters, accompanied by the presence of a very dark layer at the SWI around the remains of dead organisms, is probably due to the decomposition of these organisms, mainly by sulfate-reducing bacteria. In fact, during hypoxic events, Hines et al. (1997) observed maximum sulfate reduction rates in the top of their sediment cores, corroborating our hypothesis. Because macrofaunal remains are mainly decomposed on top of the sediment, produced S(-II) can diffuse into the overlying waters without being oxidized by sedimentary metal oxides. This would explain the intense brown coloration of the white tapes above the SWI (Fig. 5). Accordingly, the sediment column acts as a sink rather than a source for S(-II) formed at the SWI, as indicated by the brownish color on the upper part of the PVC tapes of two of the DETs. The deep penetration of sulfide in two of the profiles could be explained by the presence of relict burrows. For DET AM-53, such a burrow could explain why no dissolved iron was measured in pore waters shallower than that depth, whereas the maximum concentration occurred at the SWI for the other replicate (AM-10).

Importantly, after prolonged anoxia this source of S(-II) at the SWI disappears: no S(-II) was observed in the "10 months" probes. Note here that DET probes were inserted immediately before opening the chambers and are representative of chemical conditions within the chamber at the end of the incubation. Between 1 month and 10 months of incubation, all produced S(-II) apparently diffuses into the sediment and disappears by precipitation together with reduced iron and manganese, or is oxidized by the iron and manganese (oxyhydr)oxides from the sedimentary lattice. Within the sediment, sulfate reduction continues, but the produced S(-II) is never detected (i.e., no discolored PVC tapes). Accordingly, sandy sediment apparently behaves as an auto-depurative system, where metallic (oxyhydr)oxides limit the residence time of S(-II) within the sediment and in overlying waters. Indeed, the iron concentration within the sediment is about $350\,\mu mol\,g^{-1}$ at the surface and a few decimeters below (Hines et al., 1997). This stock of iron is mainly coated onto the surface of silicates as Fe_2O_3 (Arčon et al., 1999) and constitutes a large reservoir of reducible iron. Langlet et al. (2013) reported that foraminifera survived 10 months of anoxia. Abundant literature has reported foraminiferal survival under anoxic conditions, but this is the first time that in situ long-term experiments were conducted. Langlet et al. (2013) suggest that the additional input of Corg at 1 month led to an increase of top-layer foraminiferal density. S(-II) is a toxin that, even at micromolar concentrations, impairs biological processes necessary for organisms' metabolism, meaning that the sulfate/sulfide redox layer act as a bottom barrier for infaunal foraminifera microhabitats (Bagarinao, 1992; Giere, 2008; Moodley et al., 1998). Nonetheless, it seems that the control of pore-water S(-II) content by the (oxyhydr)oxides of the sedimentary lattice prevented foraminifera to be poisoned and was, in consequence, a key parameter enabling long-term survival of benthic foraminifera under anoxia.

4.4 Representativeness of the in situ experiments

Do our long-term (up to 10 months), in situ, closed benthic chambers realistically show how anoxia impacts the chemical conditions of the bottom waters and the superficial sediment layers, as well as the response of the living organisms? The lack of bottom-water renewal (ventilation) is a key factor leading to hypoxia in bottom waters (Middelburg and Levin, 2009). In "natural" anoxia, considerable organic matter input to the sediment – due to high primary production and subsequent phytodetritus deposition – increases the sedimentary oxygen demand. This, in turn, triggers anoxic events, leading to mass-mortality events, causing an even higher oxygen demand (Deslous-Paoli et al., 1998; Souchu et al., 1998; Stachowitsch, 1984, 1991). Our experimental design does mimic the stratification-related blockage of bottom-water ventilation and organic and mineral input into the sediment. It does not, however, mimic mixing in the sub-pycnocline layer, although bi-directional (tidal) and circular bottom-water currents during "natural" anoxia would be expected to have a homogenizing effect rather than in themselves governing benthic processes. Another potential bias is the entrapment of organisms, since some might be able to migrate to less hostile environments. We can exclude this as a substantial issue because we deployed our chambers on sediment without visible macroepifauna. Moreover, successful longer-distance migration or escape of such epifauna and infauna is unlikely in anoxia events extending across hundreds to thousands of square kilometers. Despite the inherent problems in extrapolating from the small to the large scale, our system successively (1) stopped water exchange, (2) led to a total benthic oxygen consumption and a concomitant upward migration of redox zones, (3) induced mortality of the macroinfauna, and (4) produced significant amounts of S(-II) at the sediment–water interface due to the

anaerobic decomposition of the freshly emerged organisms. Summarizing, our experimental setup, despite certain constraints, satisfactorily mimicked the course of events in the natural ecosystem. The setup also provided new results that indicate the prominent role of benthic biomass and the sedimentary content of metallic (oxyhydr)oxides in controlling S(-II) residence time in (1) the pore waters which probably allowed meiofauna long-term survival and, more important regarding epifauna survival, in (2) the anoxic water column of sandy coastal settings.

5 Conclusions

The long-term incubation experiment conducted on the silty sand sediment in the Northern Adriatic Sea near Piran enabled us to document, under realistic in situ conditions, how prolonged anoxia changes the geochemistry of the pore waters of the superficial sediment and the overlying bottom waters. Despite the apparent upward migration of several redox species (Fe(II), Mn(II), SO_4(-II)), there is no obvious release of sulfide from the sediment into the overlying waters. On the contrary, sulfides are apparently produced at the sediment–water interface, after the death and subsequent anaerobic degradation of macrofaunal organisms. Our experiment shows that, despite an important sulfide release to the water column (i.e., saturation of H_2S sensors above the SWI), its residence time within the chamber is limited due to iron present either as oxide minerals that oxidize sulfide or as dissolved reduced components that precipitates as iron sulfide minerals. This suggests that sandy sediments can act as efficient sinks for sulfide during anoxia events.

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