



Artificially induced migration of redox layers in an Adriatic coastal sediment

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

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Abstract

Long term experimental studies suggest that, under anoxic transient conditions, redox fronts within the sediment shift upwards causing sequential rise and fall of benthic fluxes of reduced species (Mn(II), Fe(II) than S(-II)). Infaunal benthic organisms are associated to different redox fronts as micro-habitats and must be affected by such changes during natural hypoxia events. In order to document geochemical evolution of the sediment during prolonged anoxia in a realistic system, 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 of the experiment (during 9 days). High-resolution porewater profiles were sampled by DET probes and redox sensitive species were analysed (alkalinity, SO_4^{2-} , Mn^{2+} , Fe^{2+}).

After 7 days, anoxia was reached within the chambers. Mn and Fe started diffusing towards the water column giving a rusty color to the seafloor. Infaunal species appeared at the surface. After 20 days, all macro-organisms were dead. Macro-organisms decomposition laying on the seafloor generated important production of sulfides within the chamber generating a downward flux of sulfide towards the sediment where sulfides were quickly oxidized by metallic oxides or precipitated as FeS. Sulfide was no more detectable in the water column and porewaters at the end of the experiment. Therefore, our results suggest that sulfide enrichment in the water column in coastal systems is strongly controlled by the biomass of benthic macrofauna and its decay during hypoxia while its residence time in water column is controlled by iron content (as solid oxides or as dissolved reduced cation) 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 parameters, the most important being nutrient input due to

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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 a mortality of benthic faunas (Diaz and Rosenberg, 2008). In most of cases, anoxia occurs in semi-enclosed environments where water circulation is hampered, leading to increased residence times. Their particular morphology favors stratification and nutrient accumulation. However, this phenomenon is not exclusive to semi-enclosed settings. Many estuaries also show severe hypoxia (Garnier et al., 2001; Hagy et al., 2004; Lanoux et al., 2013; Rabalais et al., 2002), sometimes leading to fish mortality; this includes estuaries only moderately impacted by anthropogenic eutrophication, such as the Loire River mouth (Abril et al., 2003). Also continental seas, such as the Baltic and Black Sea, or the Gulf of Mexico (Rabalais et al., 2002), show a progression of anoxia. Meire and coworkers modeled the evolution of occurrence of hypoxia events in North sea and concluded that riverine runoff could be one of the most important factors that influence occurrence of hypoxia (Meire et al., 2013). In some coastal environments such as Thau lagoon (French Mediterranean), fewer anoxia events have been reported during the 1990s, which has been interpreted as the consequence of efficient environmental policies leading to a reduced phosphorous load to the lagoon (Souchu et al., 1998). More recent studies, however, showed in the same system that this trend did not extend into the 2000s. Despite the decrease of phosphate loads, an important stock of phosphate is still available within the sediment of Thau Lagoon; its recycling under summer conditions triggers high benthic fluxes of phosphorous towards 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 predict therefore a further increase of the areas affected by anoxia and mass mortality events, if great efforts to decrease nutrient supplies to coastal areas are not done (Diaz and Rosenberg, 2008; Meire et al., 2013; Middelburg and Levin, 2009).

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In an international multidisciplinary collaboration, we conducted a series of in situ experiments in the Northern Adriatic (Mediterranean Sea), one of the areas repeatedly affected by seasonal hypoxia. 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., 2012, 2013; meiofauna such as foraminifera, Langlet et al., 2013a, b; nematodes and copepods, Grego et al., 2013a, b; De Troch et al., 2013), which are considered 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, favoring a separation of redox sensitive elements. The separation between iron and manganese oxides in the sedimentary column, for example, is related to different kinetics of reduction/oxidation and therefore of dissolution/precipitation of these metals. This creates a differential recycling speed, finally leading to a different vertical extent of their diffusion (Burdige, 2006). Associated trace metals, including non-redox elements such as cadmium, can be affected by redox oscillations as well (Gobeil et al., 1997; Sundby et al., 2004). Experimental studies have shown that cores incubated under hypoxic conditions released dissolved manganese, iron and sulfide to the overlying water column, confirming that bottom water oxygenation impacts the vertical succession of redox zones, both in the oxic and anoxic part of the sediment (Kristiansen et al., 2002; Sell and Morse, 2006). The role of bioturbation, which limits the upward diffusion of reduced species to the water column, is also very important (Aller, 1984, 1994).

In the Northern Adriatic, hypoxic conditions occur seasonally, impacting the recycling of metal oxides and affecting 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 harmful fishing activities, highlighting the vulnerability of this area to benthic perturbation. The present contribution is part of a multidisciplinary study conducted on a muddy soft-bottom in 24 m depth in the Gulf of Trieste, Northern Adriatic, and 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. The aims were (1) to describe with high vertical resolution the geochemical evolution of the pore and bottom waters slightly above the sediment–water interface during short- and long-term incubation, (2) to better understand the behavior of the main redox fronts during the onset of anoxia, and (3) to provide the geochemical constraints for the studies focusing on the response to anoxia of the various studied faunal compartments.

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 hydrographic buoy Vida (45°32′55.68″ N, 13°33′1.89″ E). This site was selected in order to avoid damage of the experimental setup by commercial fisheries. The Gulf of Trieste covers an area of 600 km², has a maximal depth of 25 m and is isolated from the rest of the Northern Adriatic by a 100 m deep shoal, leading to a lengthier residence time (about 250 days; Poulain and Hariri, 2013), about 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. The benthic macrofauna is dominated by brittle stars, sponges and tunicates (Fedra et al., 1976; Ogorelec et al., 1991), and is actively bioturbated by polychaetes and bivalves. The sedimentation rate, determined by ²¹⁰Pb, is approximately 1.2 mm yr⁻¹ (Ogorelec et al., 1991). The sediment surface is covered by microalgae, mostly by diatoms (Bertuzzi et al., 1997), which greatly contribute to the sedimentary organic matter (OM) input (Ogrinc et al., 2005). The OM content in superficial sediment is about 0.65 % wet weight (Koron et al., 2013; Ogrinc et al., 2005).

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2.2 Experimental setup

A series of benthic chambers was deployed to mimic anoxic events, and to isolate the sediment and its overlying waters for different periods of time. The cubic benthic chambers were made of Plexiglas, with sides of 50 cm (surface area 0.25 m², volume 0.125 m³). An sealable aperture on one side enabled inserting and take 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 EAGU (Riedel et al., 2008, 2012; Stachowitsch et al., 2007). In order to guarantee a perfect isolation of the benthic chambers (i.e. prevent bioturbation by macroinfauna), their sidewalls were pushed a few cm into the sediment, and additional 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 cause a re-ventilation of chambers. In every chamber, a series of 8 DET gel probes (Davison et al., 1991; Fones et al., 1998; Metzger et al., 2007a) was inserted 24 h to 48 h before termination of the experiment, allowing in situ sampling of porewater at a 2 mm resolution (see below, Fig. 6d). DET gel probes were also deployed in an adjacent control area, hereinafter 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.

2.3 Oxygen and sulfide sensors

Two oxygen and two sulfide Clark-type sensors from Unisense[®] 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 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 channels.

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2.4 DET gel preparation and deployment

For this study, we used a modified version of DGTresearch[®] perspex probes (Metzger et al., 2007a) which enable minimizing probe thickness (3 mm) and vertical channeling. Each probe corresponds to 75 cells of 22 μ L and a vertical resolution of 2 mm. Probes were rinsed in HCl acid and deionized water before assembling. 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 μ m size pore, Millipore, USA). The membrane was fixed onto the probe with commercially available PVC plastic tape (Leroy Merlin[®]), which is sensitive to dissolved H₂S (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 N₂ overnight and kept under nitrous atmosphere until immersion to avoid 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 (\varnothing 20 cm) and then photographed to document their position in the respective chamber as well as to the sediment–water interface. Based on the aperture size and construction, the water exchange during DET insertion was minimal (an estimated 2 L, vs. 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 give time to the sediment to recover from a potential perturbation. The entire retrieval operation (until preservation in nitrous atmosphere) took 3 min at most. DETs were sampled and samples chemically stabilized in the laboratory within 4 h after retrieval.

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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. 6 in total) in order to have two replicates for each chemical profile. The two remaining probes were used as spares.

5 Gel samples serving for metal determinations were eluted in 5 mL of a 10^{-2} molL⁻¹ suprapur[®] nitric acid solution corresponding to a dilution by a factor of about 200 of the pore water (DET gel piece about 25 μ L). Dissolved iron and manganese analyses were performed 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). ⁵⁵Mn and ⁵⁶Fe isotopes were measured at high resolution (HR). At 10 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 6-port valve that rapidly delivers the sample with a high flow vacuum pump and rinses the probe sample lines while the sample is analyzed allowed us to decrease 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- 15 distilled suprapur[®] nitric acid, and the accuracy and precision of measurements were checked using SLRS-4 and 5 certified standards (NRC-CNRC).

20 Gel samples dedicated to sulfate determination were stored in 1 mL of a 10^{-2} molL⁻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 sea- 25 water 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,

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SO_4^{2-} values are normalized to Cl^- and shown as the result of the calculation of: $(\text{SO}_4^{2-}/\text{Cl}^-)_{\text{sample}} \times \text{Cl}^-_{\text{overlying water}}$. Because Cl^- is considered as a conservative chemical species, variations of normalized sulfate with depth cannot be interpreted to reflect mixing processes.

Gel samples used for the determination of 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 hydrogenocarbonate salt. Measurements were done after 1 h of equilibration at a wavelength of 590 nm. Precision was about 0.3 mmolL^{-1} .

3 Results

3.1 Dissolved oxygen in the chamber

In situ dissolved oxygen concentrations obtained from microsensors are shown in Fig. 1. The data logger was started just after chamber closure and stopped about 9 days later just before opening the chamber. The data presented in Fig. 2 are averages values for 1 h periods (i.e. average of 6 values taken every 10 min). Both probes, which were located at two different edges of the chamber and positioned at different distances from the SWI (Ox1 at 5 cm and Ox2 at 4 mm), showed the same trend with initial values of about $190 \mu\text{molL}^{-1}$ and with minimal values close to zero reached about 7 days later. Data show a second order variation with oscillations of variable amplitude, without a clear periodicity. Note that probe 2, situated 5 cm above the SWI (continuous line), shows higher oxygen content in the first five days of experiment, when oxygen is strongly decreasing.

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3.2 Dissolved manganese and iron

Figure 2 shows the vertical distribution of total dissolved manganese and iron between 4 cm above the SWI and 10 cm depth in the sediment, for four different treatments. From the left to the 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 8 profiles (2 replicates for each treatment, upper and lower panel). In the “Normoxic” profiles, manganese and iron show contrasted results between the two replicates. Profiles from DET N-47 (upper panel) show large peaks of manganese and iron, while profiles from DET N-18 (lower panel) show smaller variations. Mn peaks develop from 0 to 6 cm depth with maxima of 47 and 11 μmolL^{-1} , respectively, at about 2 cm depth. Fe peaks develop from 2 to 10 cm depth with maxima of 180 and 22 μmolL^{-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 occurred about 1 cm below the SWI, with values of 31 and 24 μmolL^{-1} , respectively. Iron profiles show peaks developing between 1 and 8 cm below the SWI, with maxima of 58 and 423 μmolL^{-1} at 5.5 and 6.5 cm depth, respectively. At the end of the “9 days” experiment, relatively elevated concentrations of Mn are present in the overlying water, compared to the “normoxic” profile (7 to 12 μmolL^{-1} instead of 1 μmolL^{-1}). In the “1 month experiment”, Mn in the overlying waters decreases to about 4 μmolL^{-1} . The pore water distribution shows relatively weak maxima compared to the “9 days” experiment (9 and 6 μmolL^{-1} around 1 cm below the SWI for DET AM-10 and AM-53, respectively). Fe peaks have their maxima at 0.5 and 2.5 cm below the SWI, with concentrations about 179 and 108 μmolL^{-1} , respectively. A secondary Fe peak is visible directly above the SWI in both profiles. DET AY-53 from the “10 months experiment” (upper panel) shows concomitant peaks of Mn and Fe, with maximum values at the SWI (23 μmolL^{-1} for Mn and 80 μmolL^{-1} for Fe). The second profile, AY-22 (lower panel), shows a fairly constant Mn concentration with low values

(around 3 μM), whereas Fe shows a peak centered around 1 cm depth with a maximum concentration of 70 μmolL^{-1} .

3.3 Sulfate

The vertical distribution of the sulfate concentrations in the pore waters is presented in Fig. 3. “Normoxic” profiles show rather constant values about 30 mmolL^{-1} down to 5 cm below the SWI. Deeper down, sulfate slightly decreases by about 2 mmolL^{-1} until the bottom of the profiles (12 cm depth). The “9 days” DETs show basically the same pattern. However, in DET A7-22 (lower panel) the decrease of sulfate starts 1 cm below the interface, whereas no decreasing trend is present in DET A7-4 (upper panel). Spatial variability seems to be higher, with minimal values of 29 and 27 for DET A7-4 and A7-22, respectively. The “1 month” DETs show lower sulfate concentrations (28–29 mmolL^{-1}) in the overlying water than those described above. Below the SWI, concentrations decrease to 26–27 mmolL^{-1} at 2 cm depth and seem to increase slightly deeper down, to reach 27 mmolL^{-1} at the bottom of the profile (i.e. 6.5 cm depth). The “10 months” experiment shows sulfate profiles very similar to those of the “1 month” DETs. The minimal values, however, reach lower values of about 24–25 mmolL^{-1} .

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 mmolL^{-1}). Nonetheless, a downward alkalinity increase is evident in both replicates, starting at 7 and 11 cm depth, respectively. 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 mmolL^{-1} for DETs A7-06 and A7-07 respectively), 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 mmolL^{-1} in the two replicates. The “1 month” DETs show a relatively large variability between the two

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replicates. The overlying waters have a higher alkalinity than before (about 5 mmol L^{-1} instead of $3.5\text{--}4 \text{ mmol L}^{-1}$ in “normoxic” and “9 days” chambers). Below the SWI, alkalinity increases slightly to 7 and 6 mmol L^{-1} for DET AM-44 and AM-51, respectively. Values remain more or less constant downward until a rapid increase starting at 3.5 and 5.5 cm depth, respectively. Alkalinity reaches respectively 14 and 8 mmol L^{-1} at 7 cm depth. The “10 months” profiles show contrasted patterns between the two replicates. DET AY-40 (upper panel) shows an alkalinity increase with depth starting 2 cm below the SWI, reaching a maximum of 13 mmol L^{-1} . Conversely, DET AY-05 shows little variation with depth and values fluctuate only within a range of 1 mmol L^{-1} . The overlying waters of both replicates show alkalinity concentrations of about 3.5 mmol L^{-1} , comparable to the “Normoxic” values.

3.5 H_2S -sensitive white tape coloration

The white tapes were used to seal agarose pieces behind a membrane in order to protect them from particles, bacteria, etc. and to prevent them from falling out of the probe. Additionally, PVC tapes react with free H_2S , producing a brown-grey coloration, when sulfide reacts with the trace metals present in the tape, especially with the rutile (TiO_2), which is used to give the PVC tape a white color (Jézéquel et al., 2007). Figure 5 shows the collection of the originally white tapes used for each different DET probe at each different experiment during this study (6 DET \times 4 experiments). The tapes are shown together with the different pore water profiles to facilitate further discussion. After retrieval, the tapes were glued in a notebook with squares of half-centimeter height (visible in the figure). The “Normoxic” tapes show a predominantly white coloration 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 show also a very

dark coloration above the SWI. Finally, the “10 months” tapes show a predominantly whitish coloration, comparable to the “normoxic” tapes.

4 Discussion

4.1 Experimental strategy

5 One of the main aims of our study was to provide the geochemical constraints for the studies on macrofaunal and meiofaunal behavior (Langlet et al., 2013a, b; Grego et al., 2013b, Riedel et al., 2013). It was also designed to obtain new insights about biogeochemical processes operating during our experimental anoxia, in analogy with natural environments. Our experimental and measurement plan was defined by the following constraints:

1. Very little space within the benthic chambers to multiply core sampling and instrumentation.
2. High-resolution profiles (millimeter scale) necessary to well describe the meiofaunal microhabitats at a centimeter scale in a coastal environment.
- 15 3. Limited diving times at this depth to conduct manually in situ profiling and automated in situ profilers not miniaturized to fit inside the chambers.

Despite these constraints, we successfully obtained a dataset enabling the description of the evolution of the environmental conditions relevant for the macrofauna and meiofauna. The use of static in situ electrodes (Unisense[®]) combined to a data logger on one hand and the DET gels (Davison et al., 1991; Fones et al., 1998) on the other hand optimally circumvented the depth and space constraints (see below). The first method allowed to record hypoxia development in the early stage of our experiments. The second allowed to obtaine vertical profiles with a sample every 2 mm, although the sampling volume is only about 25 μ L, limiting certain analyses. Two DET replicates,

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obtained in different areas of the chambers, were realized for each type of analysis, limiting the sampling time and analytical cost but giving clues about lateral heterogeneity within the sediment. Assuming that within one week the oxygen was depleted and sulfide produced (Riedel et al., 2008; Stachowitsch et al., 2007), we focused on dissolved metal species and on sulfate. The analytical techniques chosen to determine the concentrations of these chemicals (inductively coupled plasma-mass spectrometry and ionic chromatography, respectively) are not instantaneous. We therefore decided to study alkalinity as an integrative parameter that could be analyzed quickly (by colorimetry) in the field laboratory (Metzger et al., 2013). Alkalinity is known to rise in anoxic conditions (Berner et al., 1970; Metzger et al., 2007b; Mucci et al., 2000).

In summary, for each benthic chamber we deployed 8 DET probes: 2 for alkalinity determination by colorimetry; 2 for metal determination (Mn, Fe) by ICP-MS; 2 for anion determination (Cl^- , SO_4^{2-}) by chromatography and 2 spare DETs.

4.2 Sedimentary geochemistry under: summer “normoxic” conditions

A previous study showed that describing pore water chemistry on a centimeter scale is inadequate at this site (Hines et al., 1997). In September 1993, when bottom waters were hypoxic and the water column was stratified, Hines et al. (1997) could not present conclusive evidence for the diffusion of reduced species from the sediment into the overlying water, because their vertical resolution was too low. They were, however, able to demonstrate that anaerobic mineralization processes were as important as aerobic processes. They suggested that an important part of benthic oxygen consumption was due to the upward diffusion of reduced components such as Mn^{2+} and Fe^{2+} towards the water column. Our results from the “normoxic” DETs show that manganese diffuses upward towards the SWI and the overlying waters and is oxidized there. Reduced iron, however, remains confined within the sediment. Iron maxima from both replicates are clearly located below the manganese maxima (Fig. 2), suggesting that free oxygen does not oxidize dissolved iron. Indeed, oxygen consumption calculated based on the oxygen electrode profiles measured in the “9 days” chamber (Fig. 1, Table 2) is about

10 mmol m⁻² d⁻¹. Such a rate corresponds in the Adriatic to an oxygen penetration depth of about 5 mm (Epping and Helder, 1997). 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). In the next section we discuss the further evolution of manganese and iron mobility during anoxia, in order to verify the hypothesis of Hines and co-workers (1997) that manganese and iron are important consumers of oxygen during strong hypoxia and/or anoxia. Sulfate concentrations (Fig. 3) suggest that sulfate-reduction was not a dominant metabolic pathway in “Normoxic” conditions. We only observed sulfate concentration decrease below 5 cm depth (at most ≤ 10 % of sulfate consumed 12 cm below the SWI). The white tapes showed a very slight discoloration only in scattered zones within the sediment. In other shallow-water environments these qualitative probes showed a dark grey/brown coloration 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, unpublished data).

The “Normoxic” samples were taken in early August 2010, when temperature was not very high compared to the monthly average. In this area, marine snow events occur very often and almost every summer (Malej, 1995). In 2010, marine snow first developed late in August, suggesting that the sediment at the sampling station was not yet under “summer conditions”, characterized by considerable input of fresh organic material. The temporal oxygen decrease from the “9 days” experiment indicates a benthic 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. A previous study in the Gulf of Trieste suggested that, during summer, oxygen uptake approached 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 a 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 could be at least one order of magnitude higher, although no measurements are available for our study area. The time needed to completely con-

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sume 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 (Riedel et al., 2008; Stachowitsch et al., 2007). In fact, during previous EAGU deployments, all free oxygen within the chamber was consumed after 2 to 3 days, depending on the experiment. Those studies also showed that sulfide was produced within the chamber less than one day after oxygen had been totally consumed. The oxygen uptake rates calculated for the previous experiments varied from 40 to 80 mmol m⁻² d⁻¹ (Table 2). This indicates a release of sulfide from the sediment after the rapid total consumption of all oxidants other than sulfate (e.g., nitrate, Mn and Fe oxides) in the surface sediment and the water column.

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 in the time needed to reach total anoxia mainly reflect the highly contrasting amounts of decaying macrofauna.

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 in a previous study showed lower values in our study station than in a station from the Bay of Piran (Hines et al., 1997), potentially reflecting a larger sediment grain size and a lower organic carbon content at our station. Note, however, that these 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 were more important, especially in the top layer of the sediment. In our “9 days” experiment, oxygen concentration at the sea floor was about 200 μmol L⁻¹, corresponding to a saturation rate of about 80 %.

4.3 Vertical redox fluctuations vs. lateral heterogeneity

Previous EAGU deployments in the nearshore area off Piran by Stachowitsch and co-workers showed a typical pattern of oxygen and sulfide concentrations within the cham-

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ber. After closure, oxygen was quickly depleted, reaching undetectable amounts in few days. Sulfide tended to appear and show an increased concentration about one day after zero oxygen concentration was attained (Riedel et al., 2008, 2012; Stachowitsch et al., 2007). 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 manganese, iron and sulfur (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 use of metallic oxidants (i.e. manganese and iron oxides) in hypoxia conditions ultimately leads to their exhaustion, allowing the upward diffusion of sulfides and their flux into the overlying waters. Therefore, a temporal succession of reduced compound release of manganese, iron and sulfur is generally interpreted as an upward migration of redox layers after exhaustion of all free oxygen and other possible oxidants. Conform to this conceptual model, we expected that after total oxygen consumption in the EAGU chambers, a flux of manganese and iron into the chamber would occur due to the upward migration of redox fronts. After approximately three days, metallic oxides should have been consumed and sulfides should start diffusing into the chamber. Considering the manganese, iron, sulfate and alkalinity profiles (Figs. 3–5), 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. After “1 month”, the position of the Mn maxima does not change, but their intensity decreases from about $30 \mu\text{mol L}^{-1}$ to less than $10 \mu\text{mol L}^{-1}$, strongly suggesting that sediment Mn-oxides become exhausted due top bacterial reduction. After “10 months”, the two profiles are contrasted; one is nearly straight, suggesting that all manganese has been consumed, whereas the second profile still shows a maximum of about $60 \mu\text{mol L}^{-1}$ 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 Mn during the experiment is evident.

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Reduced iron profiles show a more complex picture, with some of the profiles showing a double peak indicative of a more complex sedimentological history. For instance, double Fe peaks may occur after rapid sediment deposits burying a surficial sediment enriched in metal oxides (Deflandre et al., 2002). In our data, Fe 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, pictures A to F), which indicates reoxidation of upward diffusing reduced iron by oxidants such as oxygen or nitrate.

The sulfate profiles point to sulfate reduction below 6 cm depth in the “Normoxic” profiles. After “9 days”, sulfate reduction is visible only a few millimeters below the SWI. In the following weeks, the sulfate gradient becomes steeper, with a decrease of about 5 mmolL⁻¹ in the first 2 cm observed in the “10 months” profile.

Summarizing, our data set strongly suggests that the successive redox layers, which can be interpreted as microhabitats for infaunal meiofaunal communities, shifted upwards during the experiment. However, this upward shift was slower than expected, because no sulfide release was observed during the 9 first days of the experiment, unlike previous studies in the area using the same analytical approach (Riedel et al., 2008, 2012; Stachowitsch et al., 2007).

Alkalinity (Fig. 4) increases concomitantly with the sulfate decrease. This indicates that sulfate reduction dominates the anaerobic mineralization processes, as in many other coastal environments (Dedieu et al., 2007; Metzger et al., 2007a; Middelburg and Levin, 2009).

The temporal variability of the vertical distribution of Mn, Fe, sulfate and alkalinity, discussed above, very clearly constrains the temporal evolution of the macro- and meiofauna. The sulfide probes (white tapes) allow us to discuss sulfide release into the water column in somewhat more detail. Figure 5 shows a very large spatial variability of the sulfide distribution in the benthic chambers, confirming the considerable heterogeneity of the sediment. In fact, the DET probes strongly suggest that free sulfides are minimal within the sediment: only a few DETs show clear brown-grey patches. Surprisingly, the

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overlying waters show a different pattern. Although most chambers show no sulfide in the overlying waters, all DET deployed in the “1 month” chamber show an intense discoloration of the tapes above the SWI; this strongly contrasts with the absence of sulfides in the sediment of four of the DET probes. Only two of the DET’s show sulfide penetration into the sediment, about 2 cm in DET AM-53, and about 5 cm in DET AM18. This contrast between sulfide-rich overlying waters and sulfide-poor sediment strongly suggests that FeS precipitation may limit free sulfide accumulation and therefore that deep sediment is not a source of sulfide, as suggested by the Kristiansen model and other studies on anoxic basins (Brüchert et al., 2003; Metzger et al., 2013). Rather, sulfide is produced at the SWI or slightly above. Figure 6f shows the black coloration produced by the decomposition of several brittle stars (introduced in the chambers at the beginning of the experiment as “visible anoxia probes”) after 3 weeks of incubation. Figure 6g shows that all cores sampled in the “1 month” chamber had a very dark layer at the SWI, vs. the homogenous grey coloration in cores taken outside the chamber. These macroscopic observations strongly suggest that the decomposition of epibenthic macroorganisms has generated a thin layer of dark, FeS-rich sediment at the SWI. 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-completed overlying waters, as shown in previous studies (Riedel et al., 2008). After a few days of incubation (while oxygen was decreasing), dead infaunal organisms appeared on the seabed. They clearly migrated to the sediment surface and died due to the disappearance of the oxic layer on top of the sediment. The organic carbon (OC) content in the sampled cores showed no clear vertical trend, indicating 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 no Corg input. Our interpretation is that the presence of sulfide in the overlying waters, accompanied by the presence of a very dark layer at the SWI around the remains of dead organisms, is due to the decomposition

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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 free sulfides 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 sulfides formed at the SWI, as indicated by the brownish upper sediment of two of the DET's. 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 maximum concentration occurred at the SWI for the other replicate (AM-10).

Importantly, after prolonged anoxia this source of sulfides at the SWI disappears, since no more free sulfide 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 sulfide apparently diffuses into the sediment and disappears by precipitation together with reduced metals, or is oxidized by the sedimentary lattice. Within the sediment, sulfate reduction continues, but the produced sulfide no longer diffuses upward, as suggested by the absence of brown coloration of the white PVC tapes. It seems that sandy sediment behaves as auto depurative systems limiting residence time of free dissolved sulfide within the sediment and in overlying waters.

4.4 Representativity of the in situ experiments

Do our long-term (up to 10 months) in situ closed benthic chambers realistically show how anoxia impacts the physic-chemical conditions of the bottom waters and the superficial sediment layers, as well as the response of the living organisms? One bias of our experimental design is that it blocks bottom water ventilation and organic and mineral

input. Another bias is the entrapment of organisms, since some have the ability to migrate to less hostile environments. The latter concern is probably minor here because we deployed our chambers on sediment without visible macroepifaunal. Moreover, successful longer-distance migration or escape of such epifauna and infauna is unlikely considering the hundreds to thousands of square kilometers affected by anoxia. The lack of bottom water renewal is considered a key factor leading to hypoxia in the bottom waters (Middelburg and Levin, 2009). In “natural” anoxia, considerable organic matter input to the sediment – due to strong primary production and high phytoplankton mortality – increase 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 system seems to admirably mimic this suite of events on a small scale. It successively: (1) stopped water exchange (2) led to a total benthic oxygen consumption and a concomitant upward migration of redox zones (3) induced mass mortality of all macrofauna, and (4) produced significant amounts of sulfide at the sediment–water interface due to the anaerobic decomposition of dead macrofauna. Summarizing, our experimental setup, despite certain constraints, satisfactorily mimicked the course of events in the natural ecosystem.

5 Conclusions

The long-term incubation experiment conducted on the muddy sandy bottom in the Northern Adriatic near Piran enabled us to document, under realistic in situ conditions, how prolonged anoxia may change the geochemistry of the pore waters of the superficial sediment and the overlying bottom waters. Despite the apparent upward migration of several redox species (iron, manganese, sulfate), 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

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of important sulfide production, its residence time within the chamber is limited due to iron present as oxide minerals or as dissolved reduced components.

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Table 1. Time schedule of deployment for each chamber.

chamber name	deployment dates	
	initial	final
9 days	02 Aug 2010	11 Aug 2010
1 month	27 Jul 2010	25 Aug 2010
10 months	24 Sep 2010	25 Aug 2011

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

reference	$\text{mmol m}^{-2} \text{d}^{-1}$	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

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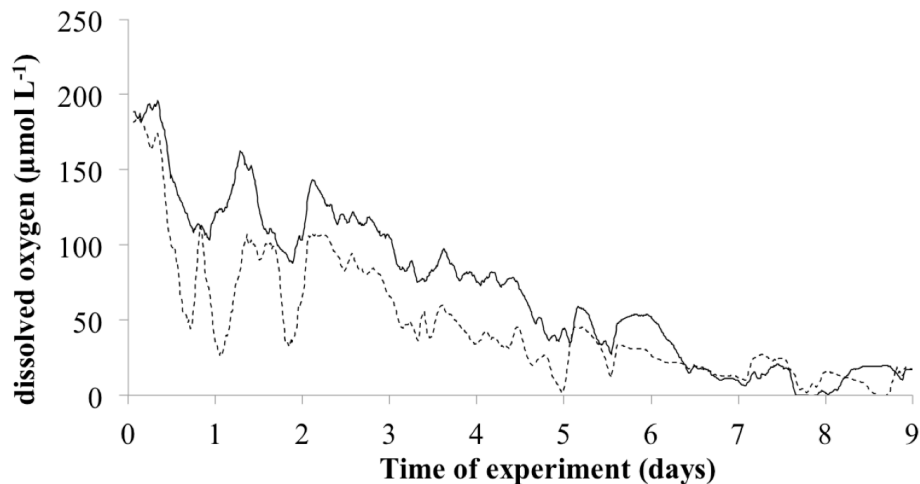


Fig. 1. In situ dissolved oxygen concentration inside de chamber of EAGU (9 days incubation time). Dotted line: oxygen probe 5 cm above SWI. Continuous line: oxygen probe 4 mm above SWI.

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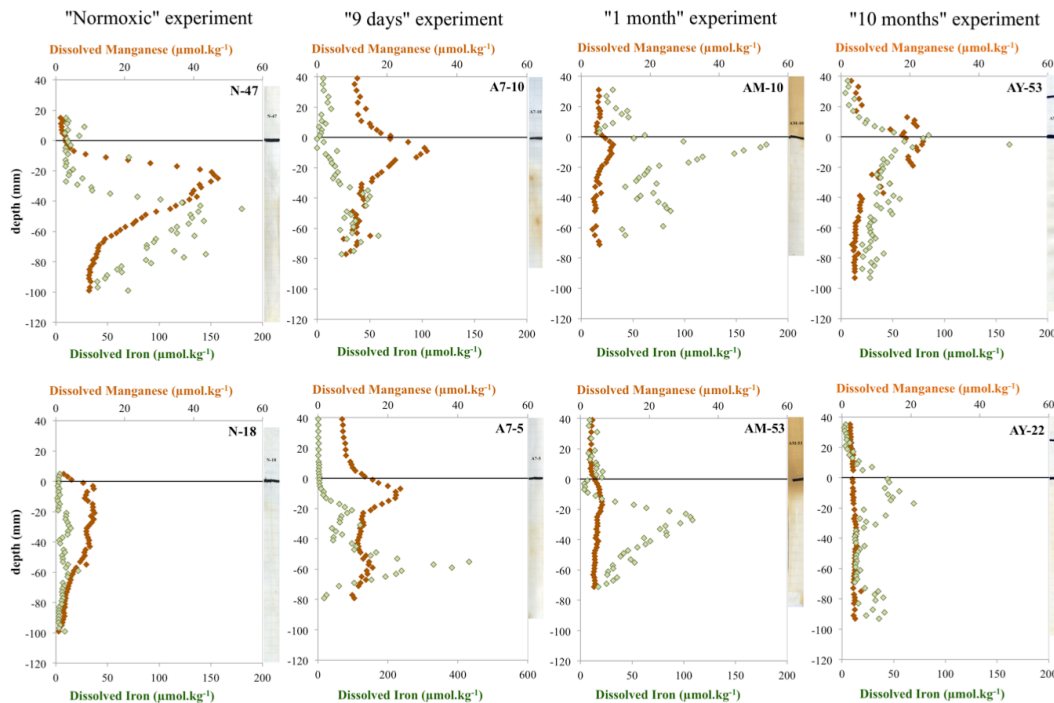


Fig. 2. Pore water dissolved Manganese (orange diamonds) and Iron (green diamonds) distribution from DET probes. From the left to the right: “normoxic” situation, “9 days” incubation, “1 month” incubation, “10 months” incubation. White tape sulfide sensor corresponding to the DET probe is shown for each profile.

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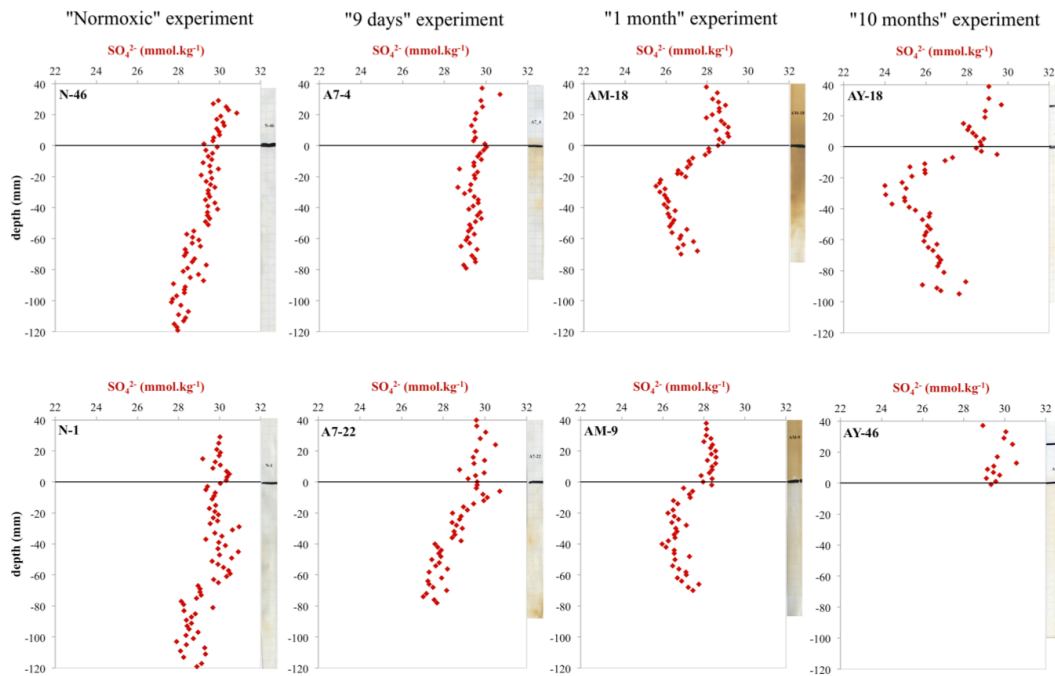


Fig. 3. Normalized dissolved sulfate distribution in pore water from DET probes.

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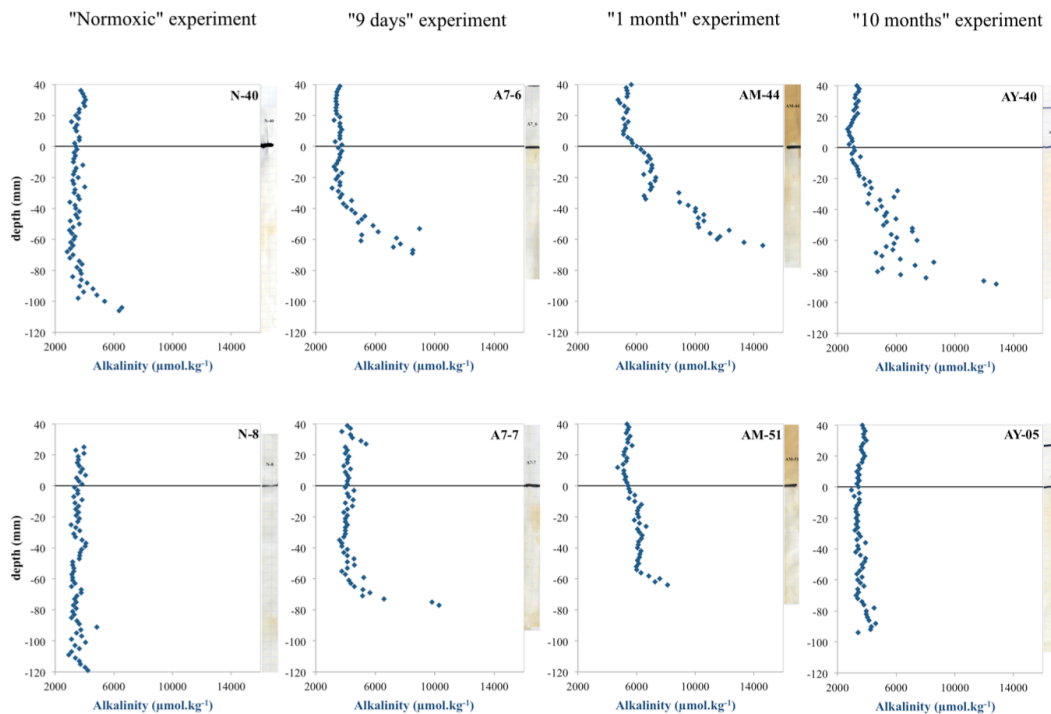


Fig. 4. Pore water alkalinity distribution from DET probes.

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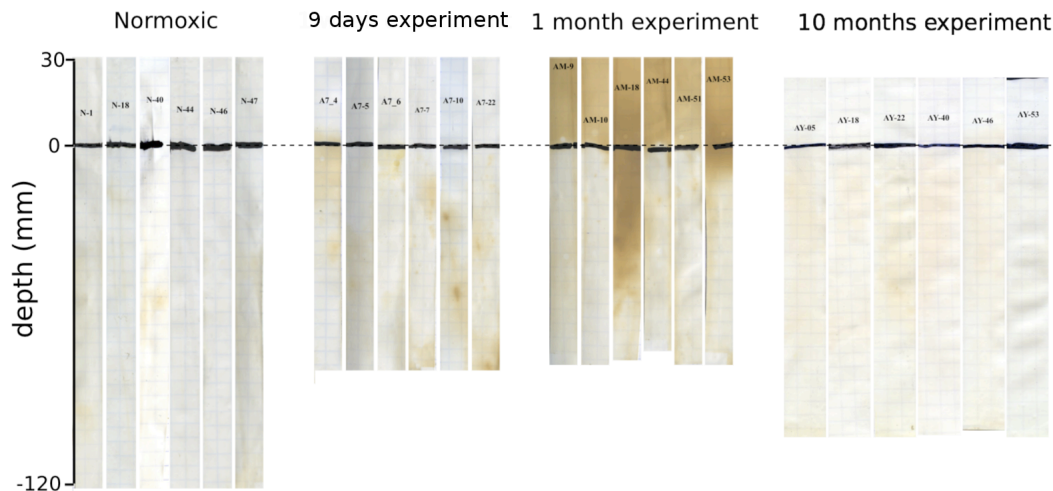


Fig. 5. Dissolved H_2S occurrence during DET deployment through PVC white tapes (brown coloration).

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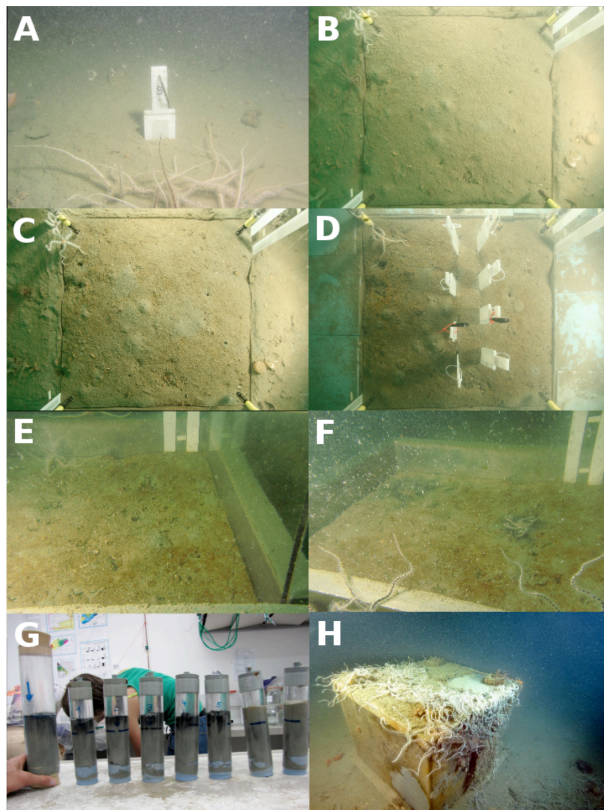


Fig. 6. (A) “Normoxic” DET probe on the seabed. (B) “9 days” chamber or EAGU right after closure of the chamber. (C) “9 days” chamber or EAGU after 8 days. (D) “9 days” chamber or EAGU right before opening of the chamber. (E) “1 month” chamber the 10 August. (F) 1 month chamber the 17 August. (G) 6 cores on the left sampled inside the “1 month” chamber. 2 cores on the right sampled outside the “1 month” chamber. (H) “10 months” chamber shot 1 month before opening.

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