Efficient measurement of marine sedimentary porewater pH and oxygen concentrations using optical sensors

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Abstract

Porewater oxygen concentrations and pH exert substantial influence on sediment diagenesis and potentially towards the reliability of palaeoceanographic records. However, these fundamental chemical parameters are not systematically measured during sea-going expeditions. This study presents an easy, inexpensive and effective method to measure marine sediment porewater oxygen and pH levels using opticalsensors. The method was tested with multi-cores during expedition EASI-2 / PS140 onboard RV Polarstern from 22 locations in the Southern Ocean, spanning diverse environments from 0.5 to 4.5 km water depth. The results show that rapid measurements with non-invasive sensors can offer precise and accurate porewater oxygen and pH measurements at a high spatial resolution downcore. This method allows to rapidly identify sedimentary geochemical redox gradients, which would offer valuable information for marine geochemists and paleoceanographers.

1. Introduction

Marine sediments exhibit diverse biogeochemical conditions and redox states, from well oxygenated to anoxic (Canfield and Thamdrup 2009). Reducing conditions in surface sediments can modify the chemistry of the sediment porewaters and in some cases release reduced components back to the overlying seawater (Hinga et al. 1979; Glud 2008). Porewater oxygen is the first among multiple available oxidants in sediments to be consumed during organic matter degradation with associated changes in pH, alkalinity and dissolved inorganic carbon. These chemical changes may entail partial leaching of lithogenic particles and strongly impact the cycling and benthic release of redox sensitive trace metals such as iron and manganese (Raiswell et al. 2018; Lenstra et al. 2021). These processes can also alter the preservation of geochemical paleoceanographic proxies (Rutgers van der Loefff 1990; De Lange et al. 1994), which can restrict down-core reconstructions at some locations. For instance, establishment of truly anoxic conditions in marine sediments can alter the seawater-derived isotopic composition of neodymium, via reduction of authigenic phases or partial

dissolution of detrital particles (Wang et al. 2022). The pH of porewaters can also influence palaeoceanographic records due to precipitation or mobilization of some seawater-tracers (e.g., beryllium; You et al. 1989). Sedimentary oxygen and pH-depth profiles are therefore of key interest for both marine geochemists studying the modern sedimentary environment at the seafloor, as well as paleoceanographers.

Porewater oxygen concentrations and pH are not routinely measured during sea-going expeditions, despite being key fundamental marine chemical parameters (Jørgensen et al. 2022). Essentially, reliable porewater samples for oxygen measurements can be difficult to collect since oxygenation occurs rapidly in atmospheric contact after sediment collection and therefore modifies the initial in situ porewater redox conditions. Thus, reliable porewater oxygen concentration analyses require considerable analytical effort (e.g., using micro-electrodes) and are all too often neglected on expeditions where they are not deemed essential for the immediate scientific question. Similarly, measuring pH in marine sediment porewaters is notoriously difficult. Traditional pH electrodes can suffer from clogging (for example due to iron congregations) and disturb sediments when directly inserted in the core liner. Porewater extraction with rhizons (Seeberg-Elverfeldt et al. 2005) and subsequent pH measurement easily lead to CO_2 outgassing, thereby compromising the in-situ pH values. Calculating sedimentary pH via the carbonate system using dissolved inorganic carbon and alkalinity concentrations (Pierrot, et al. 2011) is in theory a precise but also time-consuming and indirect way to determine pH since it requires the analyses of at least two other independent parameters, which can usually only be performed onshore after the expedition.

In-situ sampling techniques at the seafloor are the best option to avoid porewater extractions and overcome the issue of contamination and eventual chemical alteration due to changing pressure, temperature, as well as microbial and macrofaunal activities occurring when the sediment core travels from the seafloor to the surface (Bischoff et al. 1970; Sayles et al. 1976; Braeckman et al. 2010; Cetiner et al. 2023). The instruments used for in-situ sampling, however, require expert knowledge, and are laborious, expensive and time-consuming to deploy. Microsensors have been widely used for in-situ measurements of sediment oxygen and pH (Revsbech 1983; Cai and Reimers 1993), however these measurements are costly, time consuming, and have a depth limited to few centimeters. While this is enough to characterise the oxygenation gradient in most shelf sediments, deep sea sediments usually exhibit oxygen gradients spanning dozens of centimeters. Alternatively, non-invasive optical techniques have been used in various environmental applications (Werner et al. 2021) including ocean sciences (Gouin et al., 1997; Schröder et al., 2005). Optical contactless sensors have been used, for instance, for monitoring pH in contaminated soil (Blossfeld et al. 2010); measuring oxygen concentrations in lake and coastal sediment (Shimotori et al., 2021,Silberberger et al., 2022), or determining coral oxygen consumption (Castrillón-Cifuentes et al. 2023). However, these optical methods have mostly been used for incubation experiments in laboratory-controlled environments and have never been tested for deep-sea environments.

Here we propose a cheap, simple, fast, and contamination-free method to measure deep ocean sediment porewater and overlying seawater oxygen concentrations and pH using optical

sensors. The procedure was tested in multi-cores collected from 22 locations of the Southern Ocean across diverse environments spanning 0.5 to 4.5 km water depth. Sensor spots were mounted at a 2.5 cm depth resolution on the inner wall of a transparent core liner and allowed accurate and precise porewater oxygen concentration and pH determination directly after sediment retrieval. We illustrate the potential of this method via comparison of the oxygen depth profiles to those of dissolved nitrate, nitrite and ammonium measured on extracted porewaters from these cores, and by calculating diffusive oxygen uptake rates at selected sites. Overall, this method allows a rapid, efficient, and undisturbed assessment of the redox state of marine sediment cores immediately after collection onboard research vessels.

2. Material and methods

2.1. Sediment collection

Sediment coring and porewater analyses were undertaken in the Southern Ocean during expedition EASI-2 / PS140 onboard the R/V Polarstern (Knust 2017) from 28th November 2023 to 1st February 2024 (**Figure 1**; Gutjahr and Esper 2024). Most of the sediments investigated here (**Table S1**) were collected using a 12-tubes multi-corer (MUC67; Henstedt-Ulzburg, Germany), with an inner barrel diameter of 6 cm and a length of 60 cm. One exception was at station PS140_82, where an 8-tubes multi-corer (10 cm diameter) was deployed.

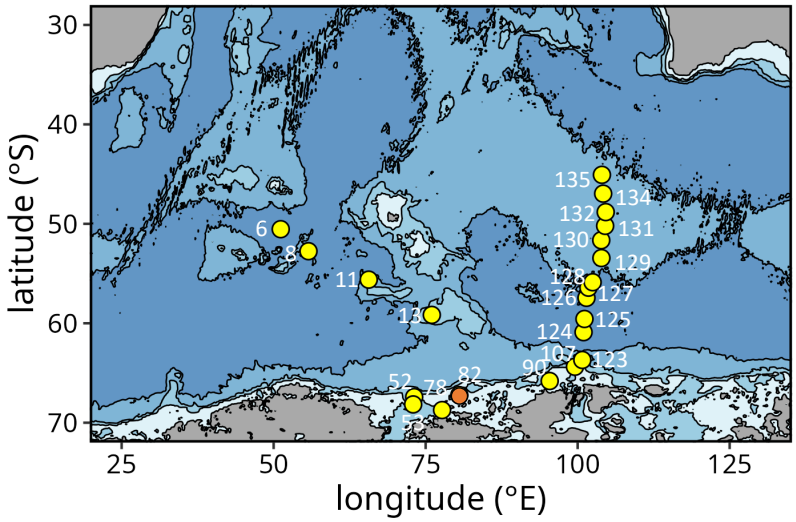

Figure 1: Locations of the multi-core stations discussed in this study: first transect (stations 6 to 13), shelf stations (stations 52 to 107) and second transect (stations 123 to 135). All sediment cores were sampled during the expedition PS140 using a 12-tubes multi-corer (yellow circles), expect at station 82 (orange circle) where an 8-tubes multi-corer was used.

2.2. Sensors specifications

In this study, we used oxygen and pH sensitive optical sensors spots (5 mm diameter) and a multi-meter from PyroScience GmbH (Germany, https://www.pyroscience.com/). The excitation and emission light was transmitted through an optical fiber (SPFIB- LNS) between the sensor and the meter. We used the oxygen sensors OXSP5-SUB, designed specifically for aquatic applications; and the pH sensors PHSP5-PK8, sensitive to a pH range between 7.0 to 9.0. These pH sensors were calibrated on the NIST pH scale. The measured pH was then

converted to total hydrogen scale (Badocco et al., 2021) which lowered the pH by 0.04. The technology of these optical sensors is based on the REDFLASH indicator luminescence. This indicator is excited with red light (wavelength of 610-630 nm) transmitted by the meter, which produces luminescence in the near infrared (760-790 nm).

2.3. Preparation and calibration of the sensors

A drop of silicon glue was applied to the back of the sensors to glue these on the inner side of a transparent liner at a 2.5-cm vertical resolution (**Figure S1**) with the oxygen sensors on one side and the pH sensors on the other. The liner was then kept in a dark (due to the light-sensitivity of the sensors) and dry place for at least 12 h to make sure the glue was completely dry. The sensors were subsequently calibrated by filling the liner with freshly made calibration solutions, following the instructions from the manufacturer. The oxygen calibration was undertaken using well oxygenated (by mixing and shaking) high-purity water (Milli-Q), and sodium sulfite solution (30 g/L) for the 100% and 0% oxygen saturation calibration points, respectively. The pH calibration was achieved with aqueous solutions of citric acid (10 g/L; pH = 2.4) and sodium carbonate (10 g/L; pH = 11.7).

2.4. Oxygen and pH measurements using optical sensors

The measurements were performed as soon as possible after retrieval of the sediment core in the ship's sediment laboratory, starting with the oxygen and then pH analyses. The laboratory had no windows so we assume that our measurements were carried out under a steady lightening and that the sensors were not impacted from the sunlight UV. The optical multi-analyte meter was plugged to a laptop, and the optical fiber connected to the appropriate channel before initiating the measurement using the manufacturer's software ("Pyro-Workbench"). The temperature probe (TSUB21), also connected to the meter, was introduced into the core liner past the upper plug into the water overlying the sediment, allowing continuous measurement and online temperature correction throughout the analysis (assuming the same temperature for the overlying water and sediment porewaters).

The measurements were performed from the bottom of the core upwards, moving from one sensor to the next until reaching the overlying water (**Figure S2**). This was undertaken by placing the tip of the optical fiber against the wall of the transparent plastic liner, at the level of the sensor, staying as still as possible for 30 seconds in order to get about 30 data points per measurement. The entire core length was measured as well as the overlying seawater. After measurement, the sediment was gently removed from the liner to not damage the sensors. The core liner and sensors were cleaned with Milli-Q water and stored in a dark and dry place until the next multicore deployment.

2.5. Other measurements

2.5.1. Winkler titration

At the first four stations (PS140_6, 8, 11 & 13), dissolved oxygen concentrations from the seawater overlying the sediment in the multi-corer were measured onboard via colorimetric titration (Winkler 1888). Briefly, alkaline sodium iodide and manganese II chloride solutions were added to the seawater samples immediately after seawater collection. Sample bottles were

closed, making sure no air bubble was introduced inside, and shaken for at least 30 seconds, allowing the formation of a $Mn(OH)_2$ precipitate. The samples were then stored in the fridge and titrated within a day. Sulfuric acid was added to the samples to convert iodide to iodine, which was then titrated with a sodium thiosulfate solution. The oxygen concentrations were then calculated from the volume of sodium thiosulfate used for the titration.

2.5.2. pH-electrode

At the shelf stations (PS140_52, 53, 78, 90 and 107), porewater was extracted by rhizon-samplers (0.22 µm mash-size; Rhizosphere®) from another core of the same multi-core deployments. The pH was then measured in the extracted pore water immediately with a WTW 3310 pH-electrode with an InLab Micro electrode (Mettler Toledo) using a three-point calibration (pH = 4; 7; 10).

2.5.3. Porewater nutrient concentrations

For porewater sampling, and following porosity and nutrient analyses, the transect stations were processed at GEOMAR Kiel (Germany) and the shelf stations at Radboud University (Netherlands). The corresponding protocols varied slightly between these two institutions (**Text S1**) and are briefly summarised here.

At most multi-core stations, a sediment core was sliced within a glove bag under an oxygen-free argon atmosphere. Sediment samples were then transferred into 50 mL centrifuge tubes and centrifuged onboard the Polarstern. The separated porewater was then filtered and stored in a -20°C freezer until analyses at the home institutions. At Radboud University, the nitrite and nitrate concentrations were determined using the Griess assay method (Griess 1879). Ammonium was determined using a colorimetric method with phenol-hypochlorite for sea-water, with a detection limit of 0.01 µM (Helder and De Vries 1979). At GEOMAR Kiel, nitrate, nitrite and ammonia concentrations were measured photometrically including replicate analyses of selected depths covering the entire range of concentrations observed in these samples.

2.5.4. Sediment porosity

Sediment porosity, defined as the volume fraction of water in the sediment, was determined by drying and weighing of sediment samples. At Radboud University, samples were dried at 60°C for 1 week until the samples were dry and porosity was determined from weight-loss upon drying. At GEOMAR Kiel, the wet sediment was weighed, lyophilized and weighed again. The mass fraction was determined from the difference of the two weights.

2.5.5. Diffusive oxygen flux calculations

Benthic diffusive oxygen fluxes were calculated using Fick's law of diffusion (Equation. 1):

$$J = -\emptyset * D_s * \frac{dC}{dz} \qquad \textit{Equation 1}$$

Where, J is the diffusive flux in mmol m^{-2} d^{-1}, $\emptyset$ in the porosity in cm^3 cm^{-3}, D_s is the molecular diffusion coefficient for oxygen in cm^2 d^{-1}, corrected for temperature, pressure, salinity and

tortuosity. $\frac{dC}{dz}$ represents the vertical oxygen concentration gradient at the sediment-water interface in mmol L^{-1} cm^{-1}.

3. Results and discussion

3.1. Porewater measurements with optical sensors

Overall, the use of the optical sensors for the measurement of oxygen concentrations and pH worked efficiently, and provided immediate data (less than 10 min acquisition per parameter and core) at a high resolution (2.5 cm). Here we present data from all 22 stations which were analysed from the Southern Ocean abyssal plains to the Antarctic shelves (**Figure 1**).

3.1.1. Oxygen concentrations

The measured oxygen concentrations spanned the complete marine O_2 range from 0 to 375 µmol/L (**Figure 2**). Overall, the obtained profiles are relatively smooth, with a measurement precision (0.33 µmol/L) being much smaller than the variations in concentrations. The cores collected from the deep ocean (i.e., during the transects) feature a decrease in oxygen concentrations with depth, yet without reaching anoxic conditions within the recovered sediment columns of up to 32 cm. Most of the cores collected from the shallower Antarctic shelf display more oxygenated overlying waters, while depth profiles clearly capture the oxic/anoxic sediment boundary, which is likely due to the higher overlying primary biological productivity and associated higher organic matter degradation rates at the seafloor and in the sediment (Jørgensen et al. 2022).

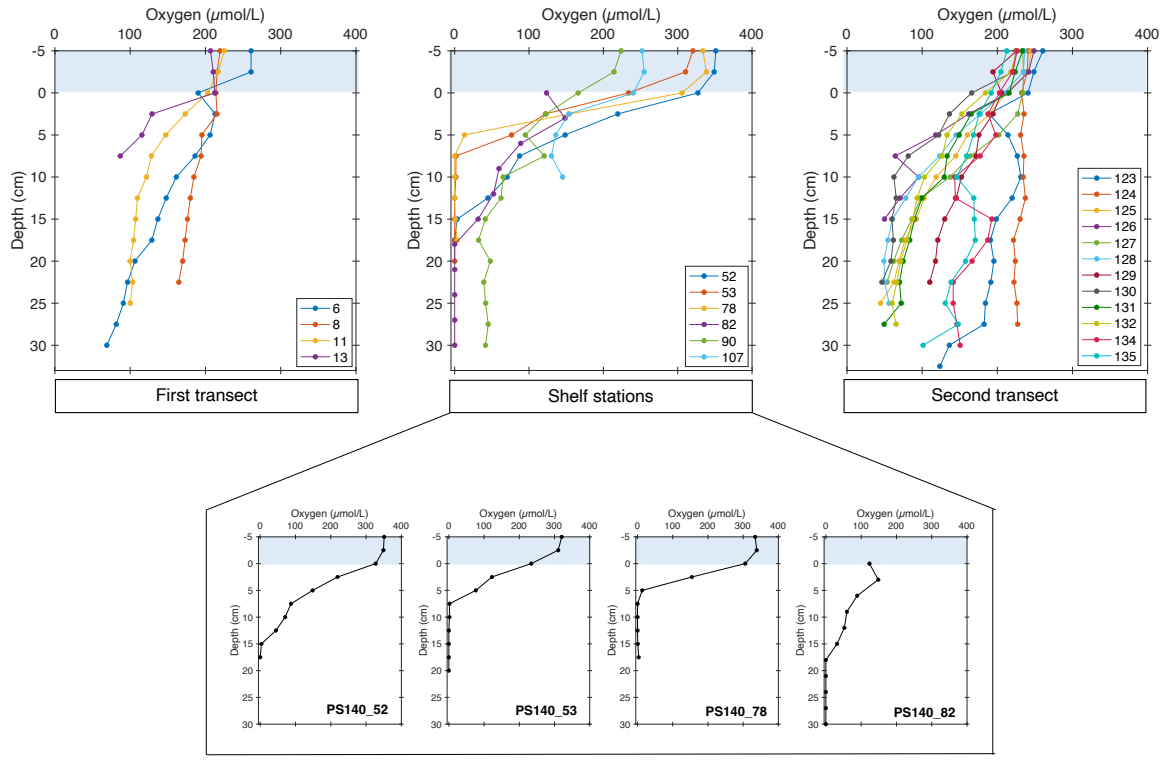

Figure 2: Sediment porewater and overlying seawater oxygen concentrations (blue shading) measured with optical oxygen sensors during expedition PS140. Station numbers are given as colors.

3.1.2. pH

The measured porewater pH exhibited moderate variations, ranging from 7.3 to 8.5 (**Figure 3**). Analogously to the oxygen concentrations, the measured pH levels display coherent profiles downcore, with the measurement's precision (0.002 pH units) much smaller than the recorded pH variations. The pH from the deepest stations (first transect) displays higher values (~8.4) which remained relatively constant downcore, while the shallower shelf stations exhibit pH values slightly lower (< 8.2), decreasing with sediment depth - again likely due to higher organic carbon influx and resulting biologically mediated organic matter degradation within the sediment (**Figure 4**). Unfortunately, the pH could not be measured during the second transect, due to the sensors damage at the end of the shelf stations (see section 3.3).

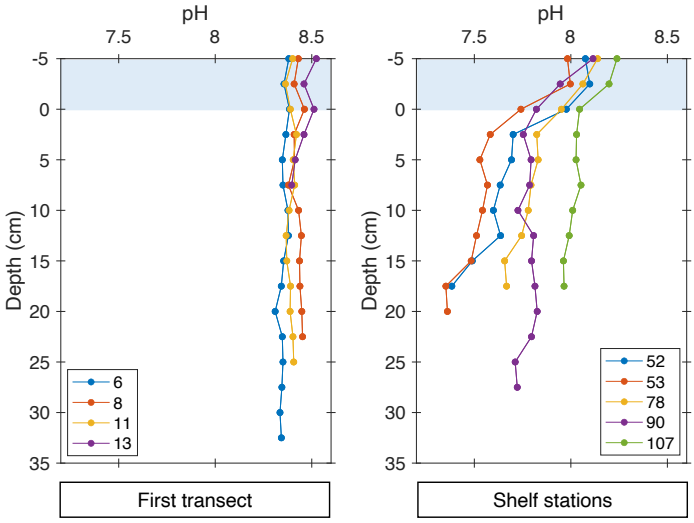

Figure 3. Sediment porewater and overlying seawater (blue shading) pH values measured with optical pH sensors. Station numbers are given as colors.

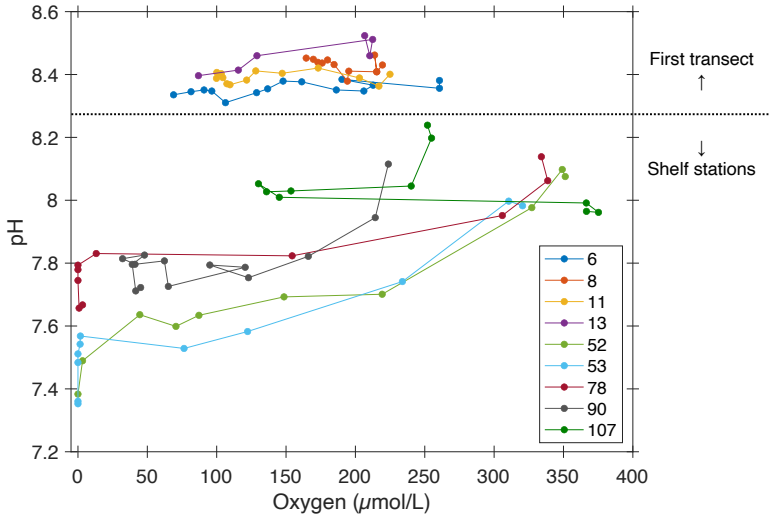

Figure 4: Sediment porewater and overlying seawater oxygen concentrations vs. pH measured with optical pH sensors. Station numbers are given as colors.

3.2. Comparison with other measurements

To assess the quality of the porewater data measured with the optical sensors, we compared these with data obtained employing other methods.

3.2.1. Data quality

This method allowed us to obtain oxygen concentrations and pH values with averaged standard errors of 0.33 µmol/L and 0.002 pH units respectively. Stations PS140_124, 126 and 129 presented an unrealistic increase in oxygen concentration at the bottom of the cores, which likely resulted from contamination with ambient air during the core liner transport. These unreliable data points are shown in **Figure S3** but will not be presented in the main results of this paper. It should be noted that the other 19 cores did not show any sign of contamination or other issues. Ideally, the quality of the measurements can be checked by measuring external parameters such as oxygen concentration via Winkler titration, pH from a pH-electrode and porewater nutrients concentrations (e.g., nitrate, nitrite and ammonia).

3.2.2. Winkler titration

In the first section of the cruise (stations PS140_6, 8, 11 & 13), the seawater overlying the multi-cores was analysed for dissolved oxygen concentrations via conventional Winkler titration. For these locations, we observe that oxygen concentrations obtained with the sensors are in good agreement with the ones measured by titration (**Figure 5 & 6; Table 1**), suggesting good accuracy of the contactless measurements.

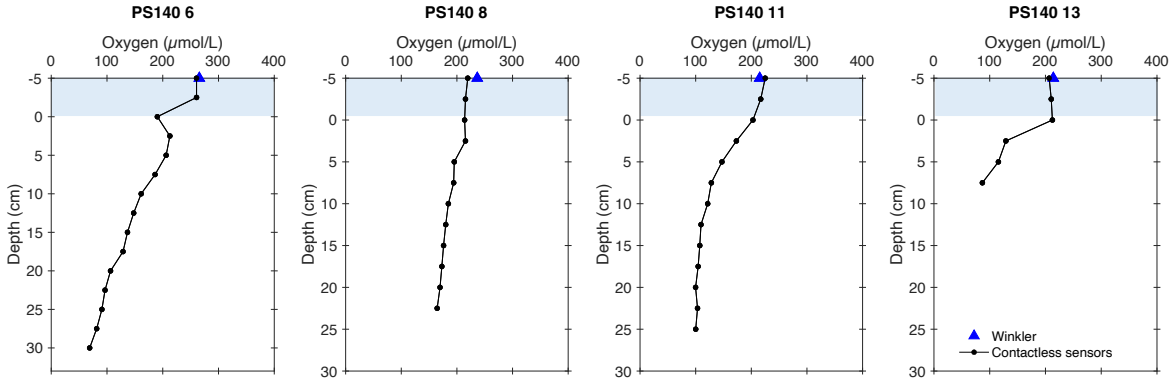

Figure 5. Sediment porewater and overlying seawater (blue shading) oxygen concentrations measured with optical oxygen sensors (black circles) and overlying water oxygen obtained with the Winkler titration (blue tringle).

Table 1: Oxygen concentrations measured in the MUC overlying waters with the optical sensors and with the Winkler titration methods.

	Sensors		**Winkler**	
Station	**O_2 (µmol/L)**	**2SD**	**O_2 (µmol/L)**	**2SD**
PS140_6	261	3.2	266	117.0
PS140_8	219	2.0	237	23.7
PS140_11	225	10.8	215	0.4
PS140_13	207	0.6	214	3.9

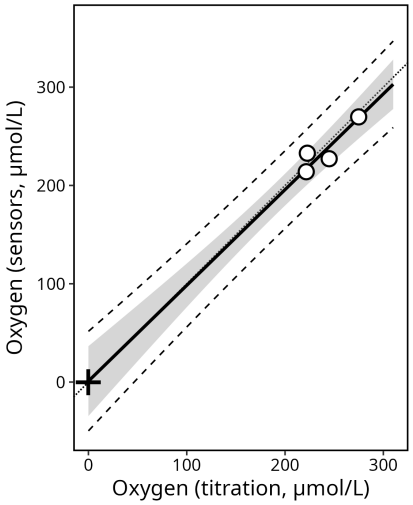

Figure 6. Sediment overlying seawater oxygen concentrations measured with optical sensors vs the Winkler titration method. The black line shows a linear regression between sensor and titration data and assuming convergence of both at zero oxygen concentration (black cross) (R^2 = 0.99, p = 0.0003, residual standard error = 16 µmol/kg). Shaded area and dashed lines indicate the 95 % confidence and prediction intervals, respectively. Thin dotted line in background is 1:1 correlation (mostly overlapping with regression line).

3.2.3. pH

At the shelf stations the porewater was extracted from one core and directly analysed using a conventional pH-electrode. The resulting pH values partially deviate from the ones measured with the sensors by up to 0.3 pH units (**Figure 7 & 8**). This offset could be due to the fact that these two pH measurements were performed on different sediment cores from the same multi-corer deployment. Another explanation is that the electrode measurements may not be reliable since the porewater extraction by rhizons induce exposition to ambient air. The pH measured in the overlying water is very similar for both methods, supporting the fact that the rhizon sampling may be unreliable here. We thus consider that the use of optical sensors is a more reliable for porewater pH measurements than using a conventional pH-electrode, yet this suggestion will need confirmation in future studies.

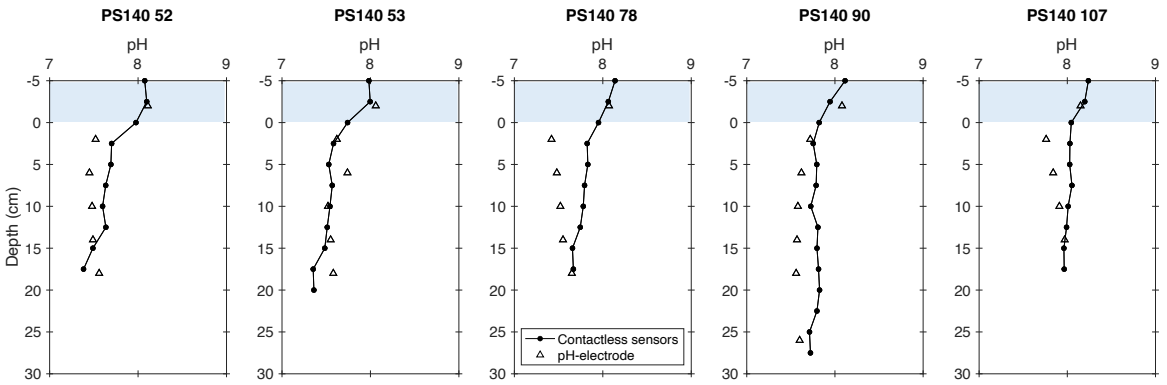

Figure 7. Sediment porewater and overlying seawater (blue shading) pH values obtained using optical pH sensors (circles) and pH electrode (triangles).

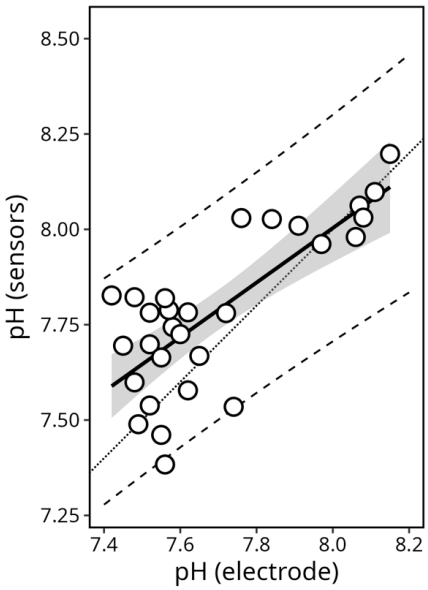

Figure 8. Sediment porewater pH measured using optical sensors vs pH electrode ($R^2 = 0.57$, $p = 10^{-6}$, residual standard error = 0.14 pH units). Shaded area and dashed lines indicate the 95 % confidence and prediction intervals, respectively. Thin dotted line in background is 1:1 correlation.

3.2.4. Nutrients concentrations

Nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) concentrations were measured from the sediment porewater at 14 stations (**Figure S4**) to further evaluate the reliability of our oxygen profiles from various depositional environments. Profiles from three representative stations are shown here (**Figure 9**): station 53 represents a typical shallow shelf station (731 m), station 124 the deepest open-ocean station (4515 m) and station 128 a typical open ocean station (3797 m).

Station 53 presents high NO_3^- concentrations (22 µmol/L) near the sediment surface with a peak of NO_2^- (3.6 µmol/L) at around 5 cm sediment depth, followed by a rapid depletion in both concentrations at ~7 cm. This depletion is associated with an increase in NH_4^+ downcore, which is in line with aerobic and anaerobic ammonium oxidation in the sediment (**Figure 9**). Deep stations 124 and 128 feature minor variations in concentrations with depth, with generally high NO_3^- (> 25 µmol/L) and low NO_2^- (< 0.5 µmol/L) and NH_4^+ (< 10 µmol/L). The low NH_4^+

concentration downcore is in line with the oxygenated porewater (> 200 µmol/L between 0 to 28 cm for PS140_124), which suggests limited organic matter influx and respiration without oxygen limitation in the sampled depths. Overall, the porewater nutrients concentrations measured at these stations are consistent with the variations in oxygen concentrations measured with the sensor spots, suggesting a good accuracy of the contactless oxygen measurements.

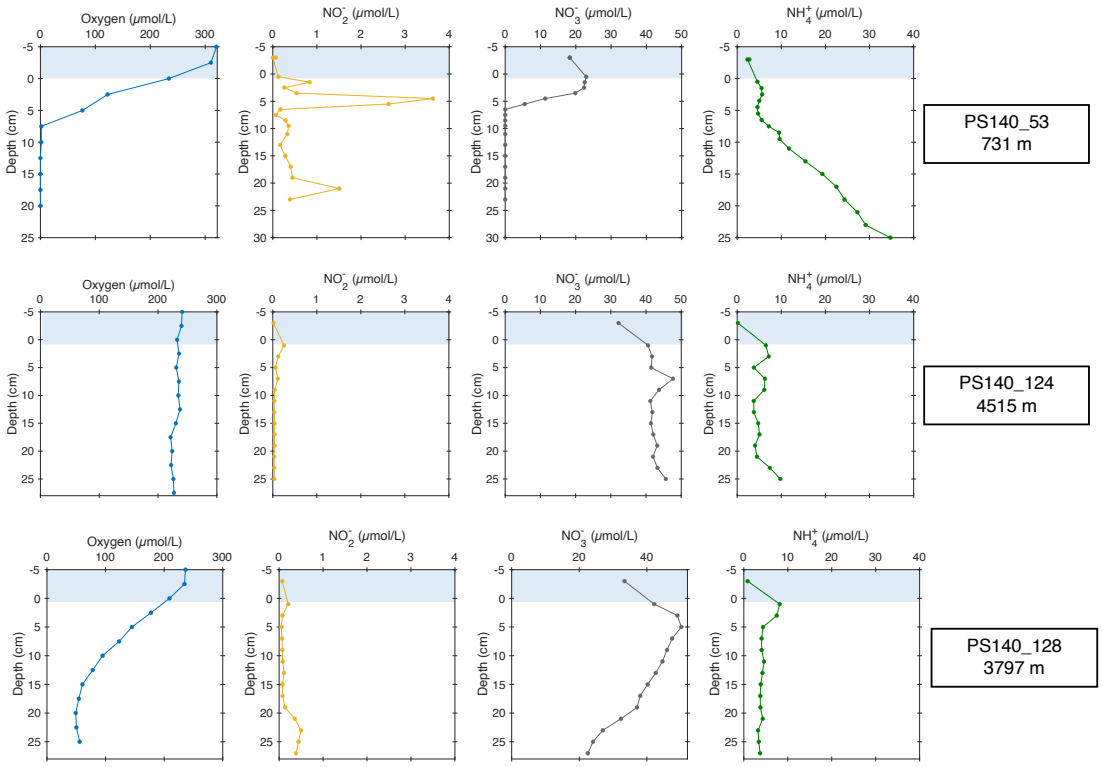

Figure 9: Oxygen, nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+) concentrations in sediment porewaters and overlying seawater (blue shading) at stations PS140_53, 124 and 128.

3.2.5. Sediment oxygen uptake

Benthic oxygen uptake was calculated using Fick's law of diffusion (**Equation 1**). As expected, the sediment oxygen uptake is generally higher at the shelf stations (on average 35 µmol m^{-2} d^{-1}) compared to the open-ocean ones (on average 17 and 12 µmol m^{-2} d^{-1}, for the transects 1 and 2 respectively; **Figure 10**). The highest calculated oxygen uptake is observed at station 78 (104 µmol m^{-2} d^{-1}). Benthic oxygen uptake increases at shallow water depth, which is in line with global estimates of oxygen uptake rates (Jørgensen et al. 2022).

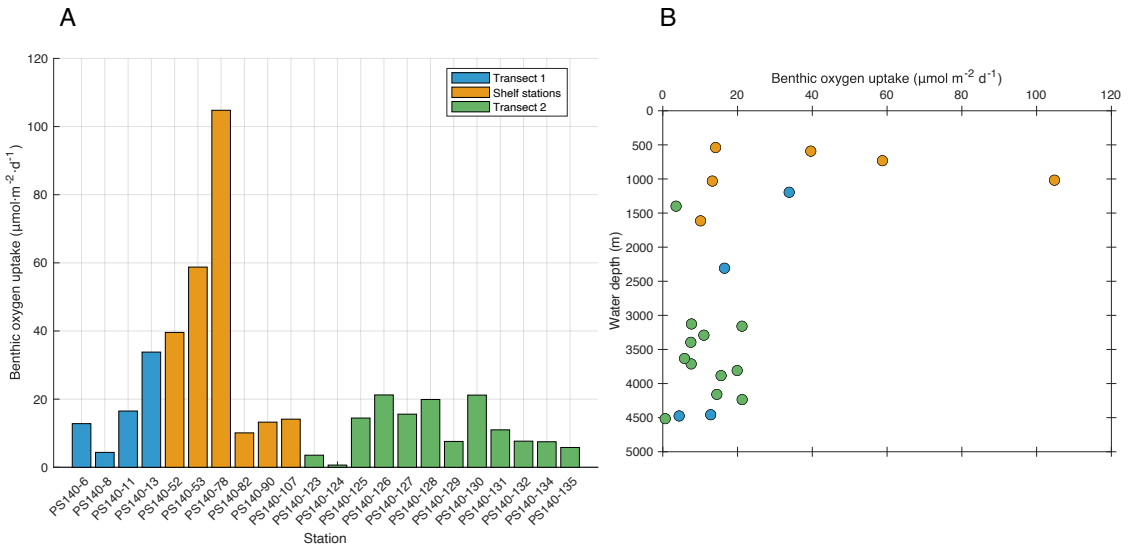

Figure 10. Benthic oxygen uptake for all 22 stations (A) and versus depth (B).

3.3. Limitations of the method and recommendations

The non-invasive optical sensors allow for efficient and convenient high-quality porewater O_2 and pH measurements in deep-sea sediment cores right after retrieval on the research vessel. However, a few issues related to the application at sea should be considered.

3.3.1. Limited lifetime of the sensors

One of the clear advantages of the optical sensors is that they are fast-reacting and that they do not consume the analytes (O_2 or H^+; Werner et al., 2021). However, the sensors can be damaged – due for example to coarse sediment material – but can be easily replaced. In this study, by the end of our 10-weeks expedition during which the core liner had been deployed more than 25 times in sediments bearing considerable amounts of coarse ice rafted debris, the sensors showed signs of usage. It should be noted that the sensors may last even longer when used at other locations (e.g., where softer sediments dominate). The oxygen sensors were more robust than the pH ones and could be used until the end of the cruise. Yet, apart from some clearly destroyed sensors which had to be replaced, we have no indication that the measurements were compromised by sensor and liner wear.

3.3.2. Sensor calibrations

The pH sensors used in this study (PHSP5-PK8) are calibrated on the NIST pH scale. For future marine applications, we recommend using the sensors PHSP5-PK8T, which are designed for marine measurements and calibrated on the pH total scale.

It should also be noted that the calibration of the sensors could potentially drift over time because multiple sensors are glued in the liner, which has or develops scratches randomly spread on its transparent walls from repeated deployment. Ideally, repeated calibrations should be undertaken to monitor and correct an eventual shift of the calibration and/or of the sensors' effectiveness. At station PS140_90, the oxygen concentration decreases down core, but without reaching anoxic conditions, despite being associated with an increase in NH_4^+ (**Figure**

11). We suspect that this could indicate an inaccuracy of the sensors caused by such a drift. We thus consider that the O_2 profile at stations PS140_90 and 104 are questionable. After these stations, a new calibration was performed, and the following measurements appeared to be reliable again. This issue stresses the fact that regular sensor calibrations are essential for reliable oxygen measurements, and that the measurements should ideally be cross-checked with Winkler titrations and/or complementary nutrients analyses.

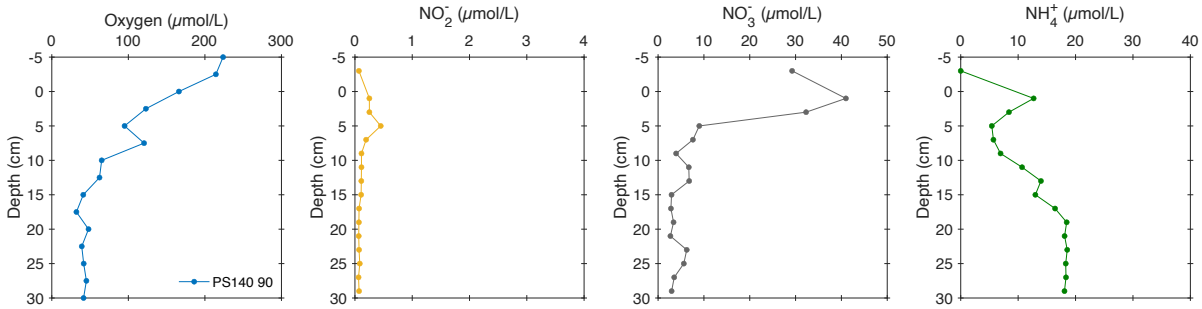

Figure 11: Oxygen, nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+) concentrations in sediment porewaters and overlying seawater (blue shading) at the station PS140_90.

3.3.3. Oxygen contamination

The method can in principle and ideally be performed on deck immediately after the gear has been secured and while the sediment cores are still closed in the corer (Blaser and Raddatz 2018). Thereby, the risk of contamination by atmospheric oxygen is minimised and pore water data are immediately available and can be used for sampling planning. On our expedition in the Southern Ocean, however, the rough weather and extreme cold did not allow to perform the measurements on deck, but the sediment cores had to be removed from the multi-corer and relocated inside the ship laboratories before performing the measurements. Unfortunately, this could induce an oxygen contamination during the short time when the sediment is in contact with the ambient air, such as observed at stations PS140_124, 128 and 129 (**Figure S3**). However, this contamination seemed to have occurred only in the last centimeter of the bottom of the core, and – according to our dataset – can be mostly avoided by careful handling.

3.3.4. Loss of sediment material

Another important aspect to consider with this application is that the sediment collected inside the sensor-bearing core liner cannot be sampled with standard procedures, i.e., by pushing the sediment out of the liner with a tight-fitting piston in order to slice the sediment into centimeter-scale samples. This piston procedure would scrap off or damage the sensors (**Figure S5**). Instead, the sediment should be gently 'washed out' from the core liner using water. To avoid the complete loss of sediment material, we suggest to use the sediment from the sensor-bearing liner for applications that do not require sediment slicing, e.g., bulk sieving for macrofauna. Alternatively, the piston sampling method may be modified to allow some safety space for the sensors where the piston does not scratch. Conversely, the core liner could be modified with depressions on the inside wall to host the sensors. This might also reduce the wear of the sensors, but would need to be tested on its practicality.

4. Conclusions

The method presented in this study, applied during expedition EASI-2 /PS140 in the Southern Ocean, showed that non-invasive optical sensors can provide accurate, precise and high-resolution measurements of deep ocean sediment porewater oxygen concentrations and pH. The deep marine environment did not pose any obvious problems for this method, and while the coarse sediments led to wear of the sensors and required replacement and recalibration, this did not significantly compromise our measurements. This simple and reliable method could easily be implemented to any expedition using transparent core liners or be adapted to limnology applications. The use of opticalsensors in further studies will enable to quickly increase the amount of available marine porewater data, which is currently needed for many palaeoceanographic and marine geochemistry applications.

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Supplementary material

Text S1

Methods GEOMAR Kiel

For the transect stations, a sediment core was sliced every 2-cm, within a glove-bag under an oxygen-free argon atmosphere, at room-temperature. A small sediment fraction was sampled for subsequent porosity measurement, and the remaining sediment was then transferred into centrifuge tubes and centrifuged for at least one hour onboard the Polarstern. The resulting overlying porewater was then filtered through 0.2 µm (under oxygen-free conditions as well) stored in the -20°C freezer until measurements at GEOMAR, Kiel.

Methods Radboud University

At station 53 two cores were collected and brought into a temperature-controlled lab-container set at 4°C. The first core was brought into an argon filled glove-bag, after which two bottom water samples were collected with a syringe and subsequently the core was sliced every 1 cm until 10 cm depth and subsequently every 2 cm until the bottom of the core into 50 ml centrifuge tubes. The samples were centrifuged for 45 min at 4000 rpm in a temperature-controlled centrifuge set at 2°C. After centrifugation, the samples were brought into a second argon filled glove-bag. Here the bottom water and porewater samples were filtered over 0.45 µm and subsequently frozen at -20°C until analyses. The second core was sliced in pre-weighted 50 mL centrifuge tubes in the same resolution as core 1 and subsequently stored at -20°C until analyses.

Table S1. Multi-core stations presented in this study.

Station	Latitude (°S)	Longitude (°E)	Water depth (m)	Sediment recovery (cm)
PS140_6	-50.5	51.2	4459	33
PS140_8	-52.8	55.7	4472	23
PS140_11	-55.6	65.6	2296	25
PS140_13	-59.2	76.0	1184	8
PS140_52	-67.4	73.1	592	18
PS140_53	-68.2	72.9	731	20
PS140_78	-68.7	77.7	1020	18
PS140_82	-67.2	80.5	1612	30
PS140_90	-65.8	95.4	1026	30
PS140_107	-64.4	99.6	546	20
PS140_123	-63.7	100.8	1399	33
PS140_124	-60.9	101.0	4515	30
PS140_125	-59.6	101.1	4166	25
PS140_126	-57.4	101.5	4228	18
PS140_127	-55.6	101.8	3880	23
PS140_128	-55.9	102.5	3797	25
PS140_129	-53.4	103.9	3905	25
PS140_130	-51.7	103.9	3168	23
PS140_131	-50.2	104.5	3111	28
PS140_132	-48.8	104.6	3129	28
PS140_134	-47.0	104.2	3328	30
PS140_135	-45.1	104.0	3643	30

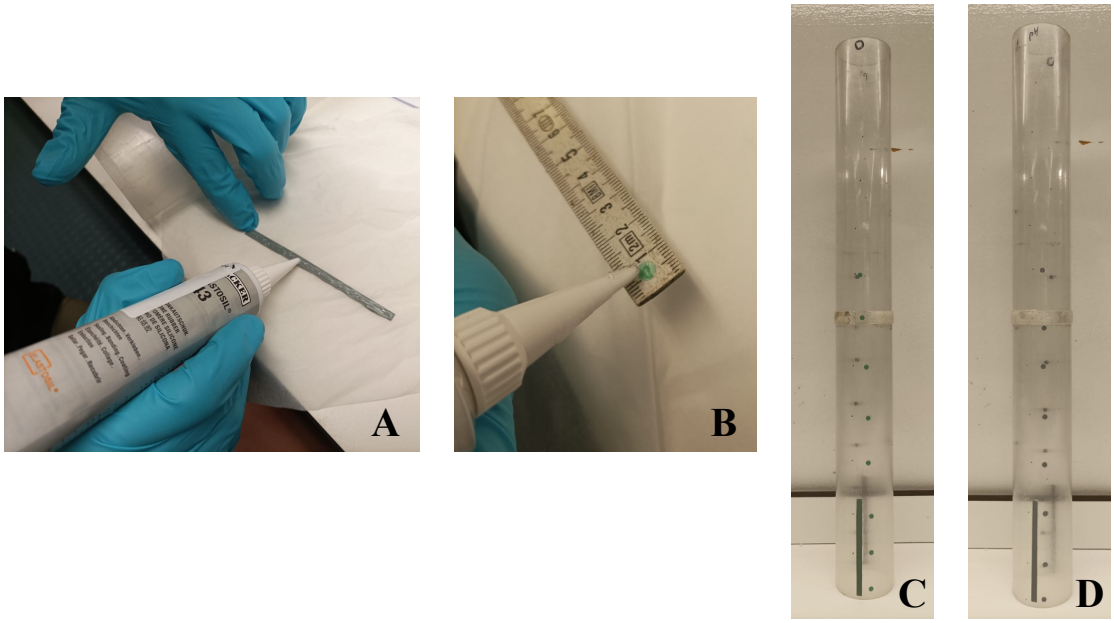

Figure S1. Core-liner preparation: silicon glue application on the sensors strip (A) and on the sensor spots (B); 60 cm long transparent core-liner with oxygen sensors on one side (C) and pH sensors on the other (D).

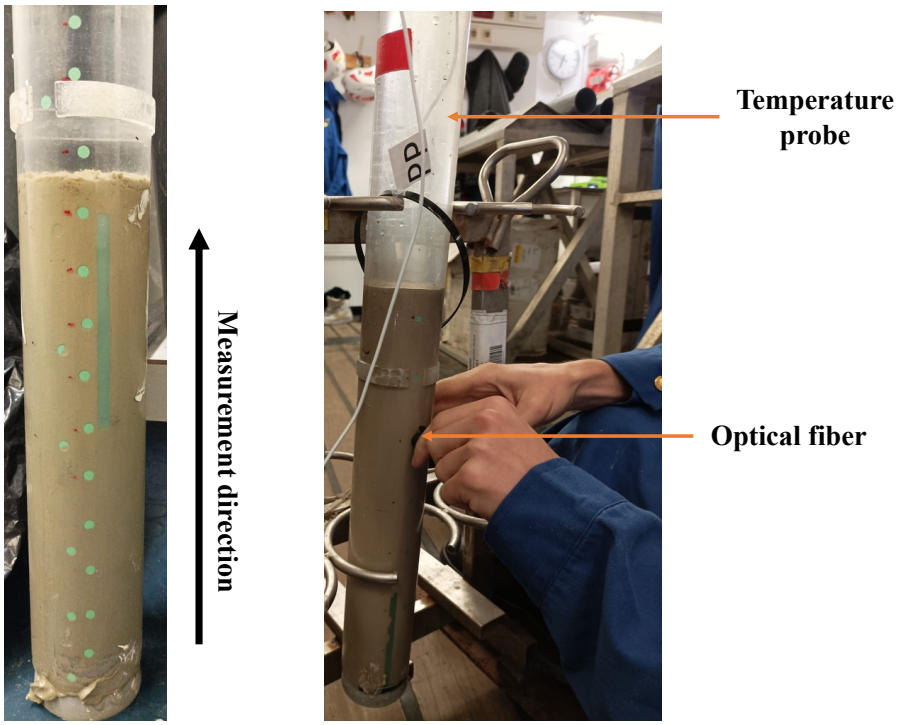

Figure S2. Overview of the measurement using the optical fiber and contactless sensors.

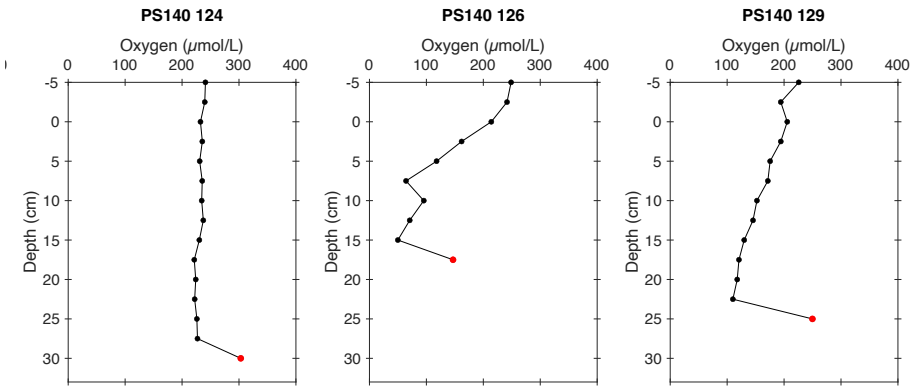

Figure S3: Sediment porewater oxygen concentrations at stations PS140_124, 126 and 129. The red datapoints represent unrealistic measurements, which were not shown in the main results.

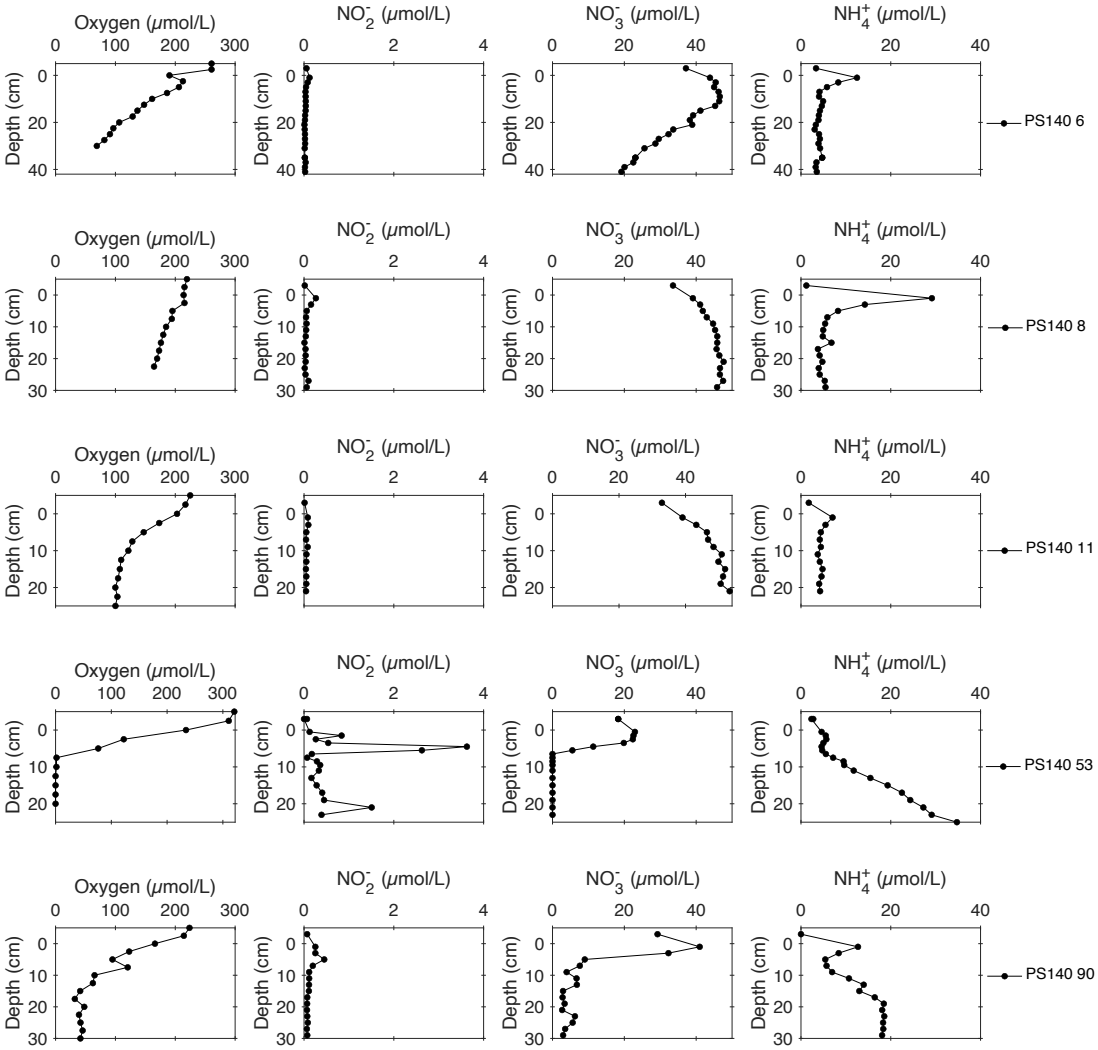

Figure S4: Oxygen, nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+) concentrations in sediment porewaters at stations PS140_6, 8, 11, 53 and 90.

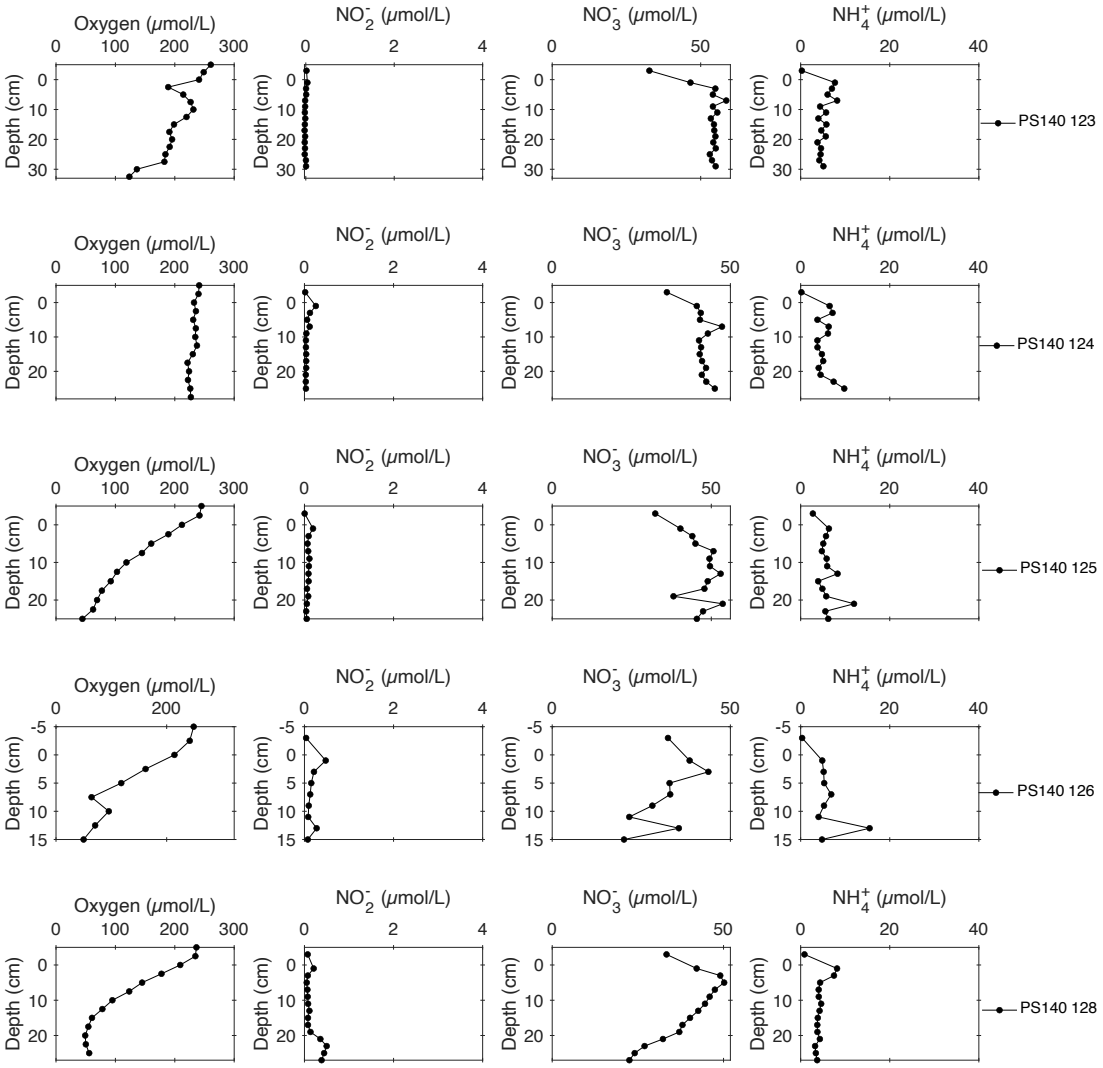

Figure S4 (suite): Oxygen, nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+) concentrations in sediment porewaters at stations PS140_123, 124, 125, 126 and 128.

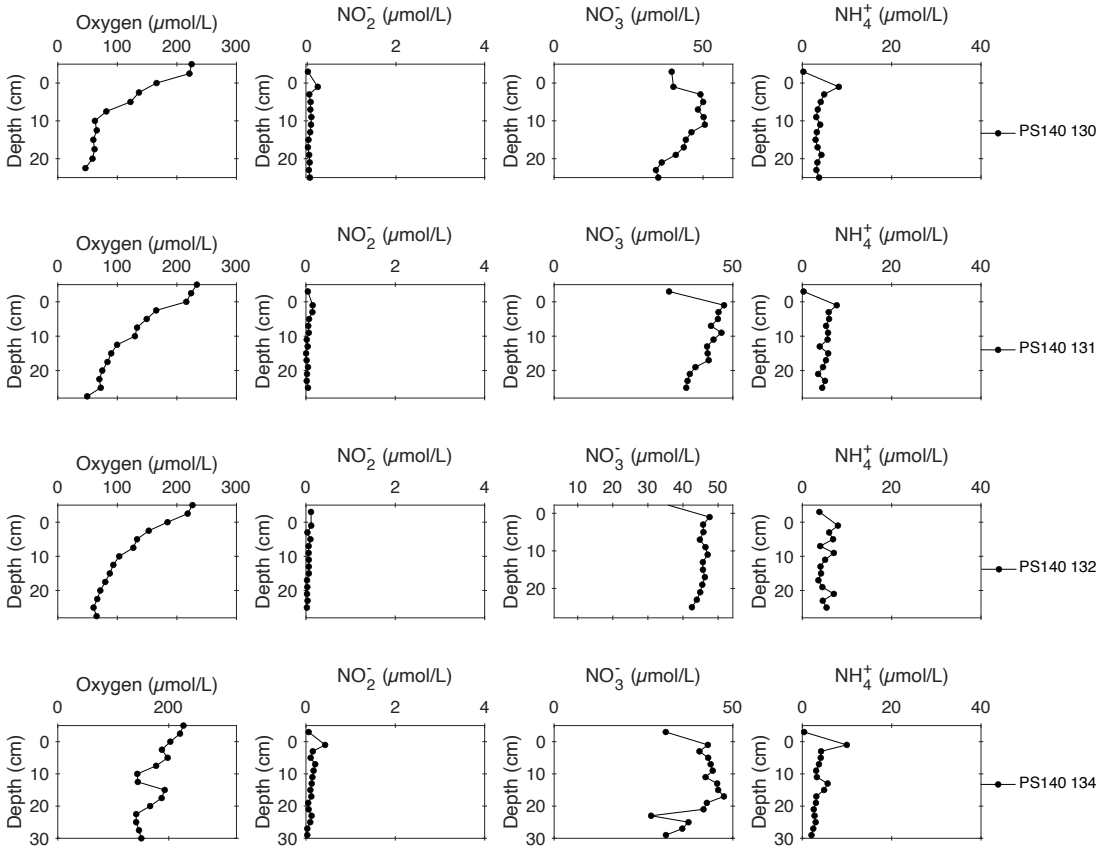

Figure S4 (suite): Oxygen, nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+) concentrations in sediment porewaters at stations PS140_130, 131, 132 and 134.

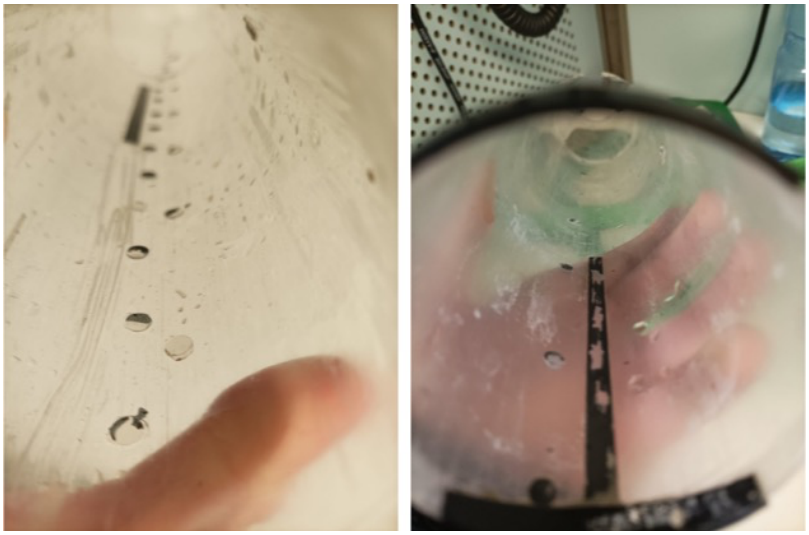

Figure S5. Damaged sensors.