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Abstract

It is frequently assumed that taking samples of soft marine sediments using surface-based gravity coring equipment causes minimal disruption to their sedimentological, biogeochemical, and biological condition. This assumption was evaluated by examining the potential disturbances caused when obtaining soft-sediment samples either by SCUBA or Craib-coring, comparing sediment oxygen microprofiles, benthic oxygen flux rates and sediment solid phase analyses (chlorophyll a (Chl a), organic carbon, and porosity) between both methods and against reference values measured in situ by benthic lander. The two sampling methodologies were tested in shallow coastal environments on the west coast of Scotland and generally the results obtained from cores collected using SCUBA exhibited values closest to those observed in situ. Oxygen penetration depth was significantly shallower in cores obtained by Craib-corer compared with the SCUBA cores. Craib cores also produced higher oxygen uptake rates which could be caused by greater levels of sediment disturbance during sampling. In addition, more homogenous levels of Chl a in the top 1 cm of the Craib cores, compared with the SCUBA samples, may indicate either resuspension or compression during gravity coring. Using SCUBA for shallow-water soft-sediment sampling permits steady and controlled core-tube insertion and extraction, and more measured retrieval of the cores to the surface; this probably accounts for the observed differences. Whereas benthic lander-based in situ measurement would be the preferred method for analyzing sediment parameters in detail in this type of environment, SCUBA-based sampling offers a more accurate alternative to surface-based gravity coring.

The ability to extract sediment samples that retain their in situ sedimentological, biogeochemical, and biological conditions is central to many marine and limnic investigations. The widespread demand for such observations has resulted in the application of a large array of different sediment sampling techniques (Blomqvist 1991). However, comparative assessments of these techniques and how well they represent in situ conditions are limited and focus mainly on the biological parameters measured in the samples (Blomqvist 1991). Glud et al. (1994, 1999) found shallower oxygen penetration depths (OPD), steeper oxygen concentration gradients and higher sediment oxygen uptake rates near the sediment surface in deep sea sediment cores incubated on board ship (ex situ) compared to the OPD and oxygen uptake rates recorded by an in situ benthic lander (Tengberg et al. 1995). Enhanced sediment nutrient concentrations have also been found in porewaters extracted ex situ (by core slicing and centrifugation) compared with data retrieved in situ using passive-equilibration "peepers" (Jahnke et al. 1989; Hammond et al. 1996; Aller et al. 1998). Hall et al. (2007) found sharp sub-surface maxima of the ratio of dissolved organic carbon (DOC) to dissolved organic nitrogen (DON) and carbohydrates in deep-sea retrieved sediment cores, which indicated a significant release of these substances from the sediment to the overlying water column which, in turn, did not

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match in situ measured fluxes and sediment trap data. In all of these cases, the observed artefacts were attributed to core-warming and decompression, causing lysis of cells during the transit of cores from the deep-sea to the surface. Raised temperature plus increases in the availability of labile organic matter will stimulate microbial activity and metabolic rates (Hall et al. 2007). As a result of these findings, it was recommended that reliable data on benthic respiration rates in deep-sea sediments could only be obtained based on in situ measurements made directly at the sea bed.

In situ measurement is often not possible as not all parameters can be measured in this way and measurement depth within the sediment tends to be restricted to only the top 20–30 cm. Access to expensive and highly specialized in situ sampling equipment, such as benthic landers, may also be limited, either because of financial reasons or a lack of expertise. For these reasons it is likely that ex situ measurement applied to samples obtained using sediment corers, dredges and grabs will remain essential techniques for some time to come (Schultz 2006).

In shallow coastal environments, investigations of potential artifacts introduced as a result of the techniques used for sampling soft sediments are even less common (e.g., Blomqvist 1985, 1991; Somerfield and Clarke 1996; Rabouille et al. 2003). This lack of critical evaluation has resulted in a limited literature on which to justify the basis for selecting a particular sampling method. Moreover, it is often assumed that the extracted sediment samples are virtually undisturbed (e.g., Craib 1965; Loh et al. 2002; Mulsow et al. 2006) because they do not experience the same magnitude of changes in temperature and pressure as those extracted from deep-sea environments.

Vessel-based equipment commonly employed in the extraction of sediment samples for ex situ analyses includes the box-corer (e.g., Carlton and Wetzl 1985), multi-corer (Barnett et al. 1984), Haps-corer (Kanneworff and Nicolaisen 1973), and Craib-corer (Craib 1965). Lightweight bottom sampling devices such as the Craib-corer are inexpensive, easy to operate and can be deployed from relatively small boats. SCUBA diving is also commonly used to extract short sediment cores in waters shallower than 50 m (Sayer 2007; Heine 2011; Eleftheriou 2013). It is a research technique that places the scientist directly within the sampling environment and is especially useful in providing access to seabed sites otherwise inaccessible from surface-deployed equipment (e.g., Nickell et al. 2003). Cores obtained by SCUBA have been used in support of a range of scientific disciplines (Sayer 2007; Heine 2011; Eleftheriou 2013).

The overall lack of validation studies for sediment coring techniques in shallow coastal environments has generated assumptions as to the legitimacy of employing ex situ analyses on samples obtained in this way. There is an obvious need to assess the effects of sample retrieval and the original sampling method. The present study compares the biogeochemistry of sediments measured in situ by instruments attached to benthic landers against the same parameter measurements made ex situ on samples cored from the same sediments by either Craib-coring or by SCUBA and then transported back to the laboratory for subsequent analyses.

## Materials and procedures

Study area

Sediment samples were collected from 20 m water depth in Camas Nathais bay (56°29′2″N, 5°27′25″W) on the west coast of Scotland in early March 2009. The location typically experiences a tidal range of up to 3.5 m during spring tides and is exposed toward SW. The site was selected on the basis of the close proximity to the laboratory and ease of accessibility by SCUBA divers and the research vessel (RV *Seòl Mara*). A SCUBA survey in the days prior to the experiment being conducted confirmed that the sediment consisted of a relatively homogenous cohesive sandy mud with a moderate degree of bioturbation. The bottom water (BW) temperature during all sampling was 7.5°C, BW salinity was 33.2 PSU and air temperature was 3°C at the time of sampling. The dominant macro fauna at the site was comprised of the sedentary polychaete *Nereis* sp. and the epibenthic gastropod *Turritella* sp.

Sediment core collection

Both sampling methodologies were employed on the same day and location under neap tidal conditions. Eight sediment cores were each collected by Craib-corer and by SCUBA diving within a depth range of 18–20 m and randomly along a single transect of approximately 10 m in length.

The Craib-corer (Fig. 1A) is a sediment sampler designed to obtain intact and virtually undisturbed sediment cores (Craib 1965). The corer stand is equipped with a centrally placed Plexiglass core-liner (240 mm long and 59 mm internal diameter) which is driven into the sediment by lowering the corer on a wire down to the sediment surface. Penetration of the core tube into the sediment is hydraulically dampened and the sediment and overlying water is retained in the core tube by a ball closure mechanism. On deck the cores were immediately capped with rubber bungs and transferred to a dark storage tank filled with bottom water to keep the temperature stable. Bottom water was also collected with a 20 L Niskin bottle for the laboratory incubations and for the determination of the BW oxygen concentration by Winkler titration (Strickland and Parsons 1972).

Core sampling by SCUBA diving involved manually driving the same type of Plexiglas core-liners as those employed by Craib-coring (240 mm long and 59 mm internal diameter) very gently into the sediment without disturbing the sediment surface (Fig. 1B). This was carried out randomly along a 10 m ground line reeled out from the bottom weight of a surface mooring. Each SCUBA core was capped with
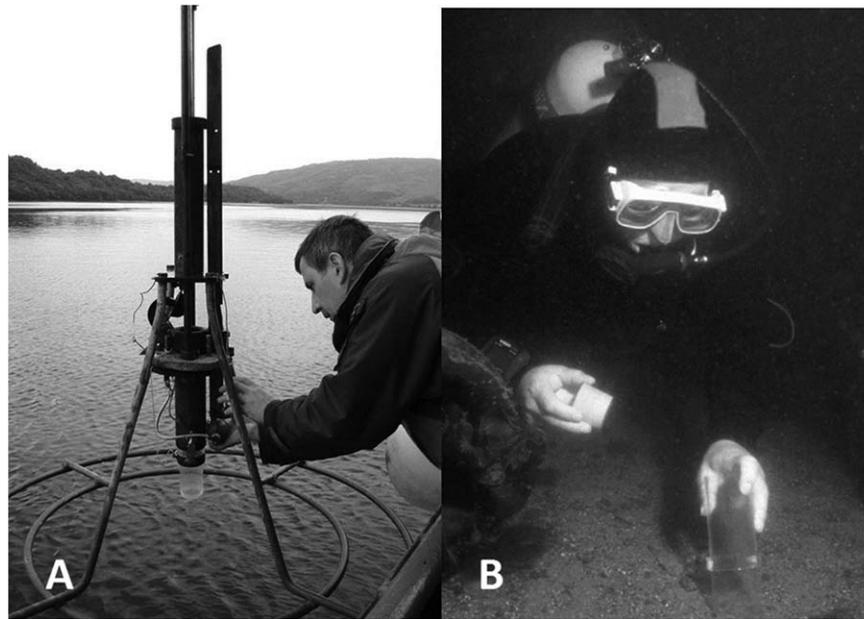
Fig. 1. (**A**) A Craib-corer being prepared for deployment; (**B**) A SCUBA diver manually coring sediments (note the bungs needed to seal the core tube).

rubber bungs inserted at the top of the core tube and then at the bottom after gently pulling the core out of the sediment. Care was taken to retain the top bung as the bottom bung was being inserted; this resulted in the cored material being moved slightly but gently upwards in the core tube until both bungs were secured. The diver kept the core tubes vertical at all times and secured each sampled tube upright into individual spaces of a holder crate that was weighted to maintain a vertical orientation. When SCUBA coring was completed the crate was retrieved to the surface by gentle lifting on a surface rope (Munro 2013).

In both sampling cases, all cores were assessed on the surface and the only the five best cores with a minimum of 10 cm sediment depth and a visually undisturbed sediment surface with clear overlying water were considered for further analyses. After both collections were completed the cores where immediately transported back to the laboratory (ca. 40 min travel time).

Ex situ core incubations and profiling

Within 30 min after returning to the laboratory all cores were uncapped and triplicate water samples from the overlying water column were extracted and the oxygen concentration determined subsequently by Winkler titration (Strickland and Parsons 1972). Following the initial water sampling, the cores were placed into two incubation tanks filled with bottom water collected from the study area. They were maintained in dark conditions at a constant temperature of 8.0°C and with a continuous supply of air bubbling through the tank to maintain close to 100% air-oxygen saturation. To prevent stratification of the water overlying the sediment in each core, continuous stirring was applied by a small Teflon-coated magnet driven by

a strong rotating external magnet (Glud et al. 1994). The cores were left uncapped in the incubation tanks to acclimatize for 24 h before any measurements were made (Rasmussen and Jørgensen 1992). The total oxygen uptake rate (TOU: mmol m^{-2} d^{-1}) of the sediment was measured by capping five cores from each sampling method (Craib and SCUBA) using rubber bungs, for a period of 4.5 h. Water samples were taken from the overlying water column of each core directly before and after the 4.5 h incubation and the oxygen concentration was determined in each sample by Winkler titration. The cores were then left uncapped to acclimatize for another 24 h to re-establish their initial condition.

Following the 24 h re-acclimation period, vertical distributions ($n = 3$) of dissolved oxygen in the porewater and diffusive oxygen uptake rates (DOU: mmol m^{-2} d^{-1}) were determined in each of the same five cores using a Clark-type oxygen microelectrode, equipped with a guard cathode (Revsbech 1989). The outside diameter of the microelectrode tip was 5–20 μm and it had a stirring effect of $< 1\%$. The microelectrode was positioned in the core by an automated micromanipulator (MM33, Unisense A/S) mounted on a heavy stand with computerized depth control (Profix, Pyroscience), and was set to sample at 100 μm intervals down to 10 mm depth in the sediment, with a resting time of 5 s between steps. The microsensor was connected to a picoammeter (PA2000, Unisense A/S) for amplification of the analog sensor signal. The amplified signal was digitized by an A/D converter (ADC-215, Pyroscience) and transferred to a Laptop using the Profix software package. The picoampere signal from the microelectrodes was calibrated by using a two-point calibration between the known oxygen concentration

in the overlying water and the anoxic part of the sediment (i.e., where the signal was close to zero and constant with depth). Three individual oxygen profiles, obtained at random positions within each core, were obtained and pooled to produce one averaged oxygen profile per core.

In situ lander incubations and profiling

In order to evaluate the ex situ core incubations and profiling results, in situ measurements were made using a pair of landers that were deployed in the core sampling area at the same time that the Craib and SCUBA cores were being taken. Both landers were deployed by gently lowering them down on a surface mooring. As DOU and O_2 penetration depths at unirrigated sites vary on scales of 1–2 cm rather than meters (Glud et al. 2005, 2009; Jørgensen et al. 2005), the in situ microprofiling experiment was designed with a single deployment per lander. The microprofiler measurements represented an area of ~ 25 cm^2 and so captured this variability; while a horizontal separation of several cm per measurement prevented auto-correlation.

The first type of lander was a benthic chamber lander (Glud et al. 1993); this was used to measure the in situ TOU. This lander inserted a 30×30 cm chamber into the seabed following which a lid closed and an incubation was started. The lid was equipped with a stirring impeller driven by a DC-motor in a pressure-compensated housing; this mixed the overlying water gently to prevent stratification of the overlying water inside the chamber and to maintain a diffusive boundary layer (DBL) thickness of typically 200–600 μm above the sediment surface (Glud et al. 1995). Two precalibrated oxygen optode sensors (Aanderaa Instruments AS, model 3830) measured the oxygen concentration both inside and outside the benthic chamber at pre-programmed time intervals throughout the deployment. The sensor recording and data logging was controlled by a custom-made on-board computer housed in a pressure cylinder. The on-board computer and stirring motor was powered by a 24 V lead-acid battery (Deep-Sea Power and Light).

Sediment pore water distributions of dissolved oxygen were obtained using a second profiling lander (Glud et al. 1994). This lander was equipped with an array of 10 Clark-type oxygen microelectrodes (as specified above for the ex situ analyses) attached to a pressure cylinder which also housed an on-board computer and data logger. The microelectrode array, attached to the bottom of the pressure cylinder, was driven vertically across the sediment water interface and into the sediment by a stepper-motor in fine resolution steps (100 μm) down to 40 mm while recording the oxygen concentration at each level. The sensors where calibrated with a two-point calibration as described above.

Sediment solid phase analysis

For the solid phase analyses three cores from each ex situ sampling method (Craib core and SCUBA core) were extruded and sliced for porosity, sediment chlorophyll *a*

(Chl *a*) and bulk organic carbon (OC) at 0.5 cm intervals down to 5 cm and at 1 cm intervals between 5 cm and 10 cm. In contrast to the flux measurements, no in situ measurements were available for reference. The sediment cores were extruded with a plunger and sliced using a 0.5 mm thin Plexiglas sheet. Porosity measurements were carried out by drying for 72 h at 60°C. Following drying, sediment samples were combusted at 450°C and the total organic matter content was estimated as ash-free dry weight converted to percent organic carbon content using a conversion factor of 0.4 as per Craft et al. (1991). Sediment Chl *a* was extracted from non-dried 1–2 g aliquots of sediment using 5 mL of buffered acetone and sonication with an ultrasound probe for 1 min. Samples were then centrifuged for 10 min at 3000 rpm at 5°C. An ammonium acetate (0.5 M) buffer was then added to the acetone extracts in the ratio 1 : 3. Chl *a* concentrations were determined using High Performance Liquid Chromatography (HPLC) with a 100 μL injection volume and a two-component gradient elutant protocol modified from Mantoura et al. (1997).

Calculations

The total oxygen uptake (J_t; mmol m^{-2} d^{-1}) was calculated from the slope of the linear concentration change of oxygen (dC) over time (dt) in the overlying water multiplied by the height (h) of the overlying water in the cores (Eq. 1).

$$J_t = \frac{dC}{dt} h \qquad (1)$$

This approach assumes a linear concentration change over time and to both assure this and minimize the effect of changing oxygen conditions within the core/chamber on fauna behavior, oxygen concentrations were never allowed to decrease below 90% of its initial value during incubations. For the chamber data, where more than two data points were available over the time of the incubation, the slope of the concentration change was achieved by least square linear regression.

The OPD and the DOU were calculated from the oxygen microprofiles. The OPD was determined directly from the oxygen profile and expressed as the depth after which the microelectrode signal reached a constant low reading of approximately 1% of the BW value (Cai and Sayles 1996). The diffusive oxygen uptake (J_d) was calculated by Fick's first law of diffusion (Eq. 2) from a linear regression fitted to the data points marking the diffusive boundary layer seen within the microprofile as a linear gradient immediately above the sediment surface (Rasmussen and Jørgensen 1992),

$$J_d = -D_0 \frac{dC}{dz} \qquad (2)$$

where D_0 is the diffusion coefficient of oxygen in sea water at a given temperature and salinity and C is the
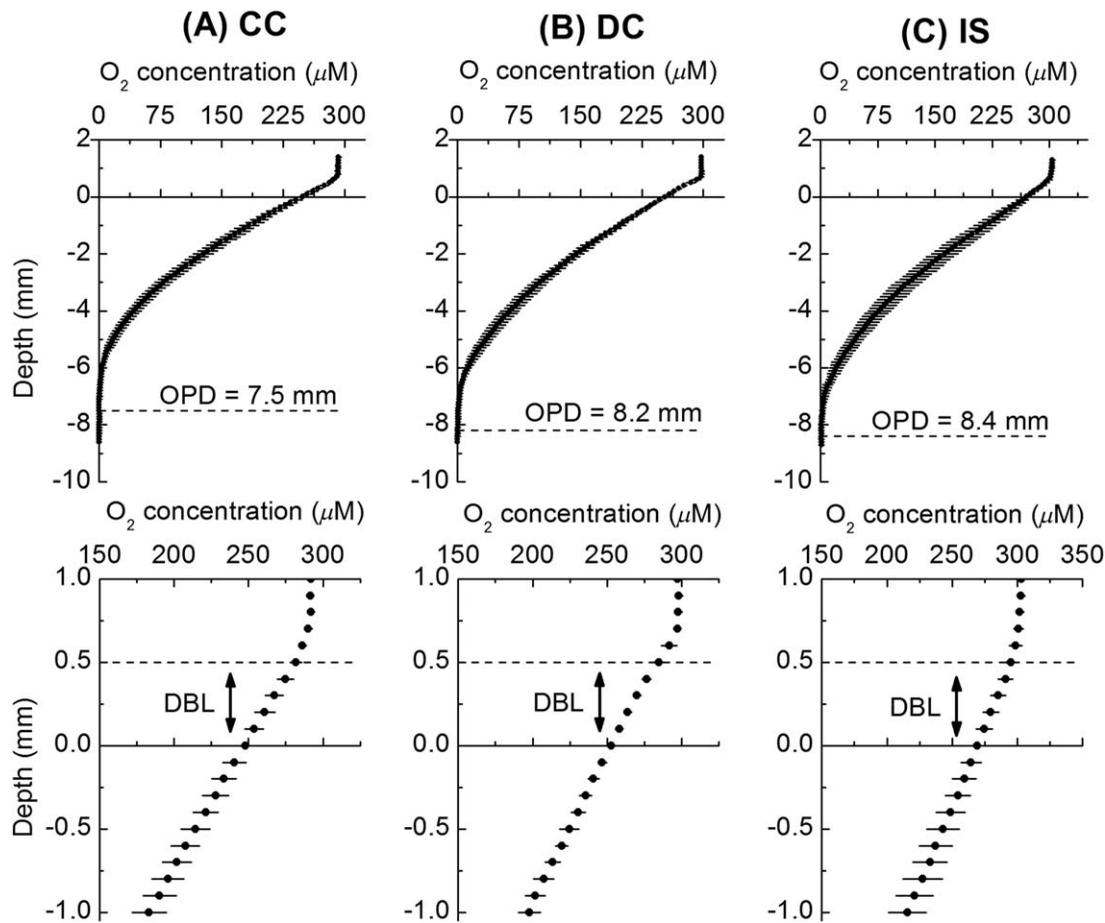
Fig. 2. Representative mean ± SD oxygen microprofiles obtained from (**A**) Craib cores (CC, core 4, $n = 3$ profiles), (**B**) SCUBA cores (DC, core 2, $n = 3$) and (**C**) in situ lander (IS, $n = 10$). X-axis indicates the sediment–water interface; oxygen penetration depth (OPD) is the depth in the sediment where the oxygen concentration first reaches zero. The bottom panels illustrate the approximate location and size of the diffusive boundary layer (DBL). DBL thickness was 300–600 μm.

concentration of oxygen at depth z. Values for D_0 were obtained from tabulated values according to Li and Gregory (1974).

Statistical analyses used Student's t-test (Minitab v13) following Minitab's Test for Equal Variances. The analyses were based on assuming all samples were statistically independent within the context of comparing the different sampling methodologies and not attempting to accurately represent the biogeochemical profiles of the experimental area as a whole. Although the lander profiles were made at one location, results were obtained from 10 microprofilers and there is often significant patchiness in O$_2$ penetration, DOU, and TOU in sediments at relatively small scales. DOU and O$_2$ penetration depth at sites unaffected by irrigation vary at scales of 1–2 cm caused by POC deposition, rather than on meter scales (Glud et al. 2005, 2009; Jørgensen et al. 2005). The in situ microprofiling measurements represented an area of ∼ 25 cm^2 and so would be assumed to capture this variability. Microprofile measurements separated by a few cm

are, therefore, not spatially auto-correlated; TOU and DOU vary on different spatial scales (*see*, for instance, Glud and Blackburn 2002). Patchiness at these scales would also convey relevant replication for the diver and Craib samples obtained randomly over scales of many meters.

Assessment

Oxygen profiles and penetration depth

Representative average oxygen profiles obtained from the three different sampling methods (Craib-corer, $n = 3$; SCUBA corer, $n = 3$; and in situ lander, $n = 8$) are shown in Fig. 2. The bottom water oxygen concentration ranged from 292 μM to 303 μM in the ex situ samples and the in situ measurements and was distributed homogenously above the DBL, indicating a well-mixed water phase both in the ex situ setup as well as in situ. The DBL thickness varied between 300 μm and 500 μm in the Craib and SCUBA samples, which was similar to the DBL thickness (300–600 μm) obtained by the lander in situ. The oxygen profiles showed a typical
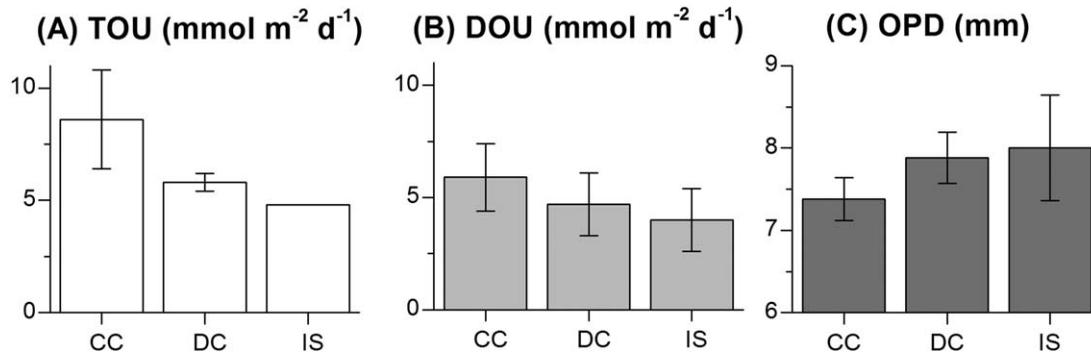
Fig. 3. (**A**) Total oxygen uptake (TOU, mean ± SD; $n = 5$ for CC and DC, $n = 1$ for IS), (**B**) diffusive oxygen uptake (DOU, mean ± SD; $n = 15$ for CC and DC, $n = 10$ for IS), and (**C**) oxygen penetration depth (OPD, mean ± SD; $n = 15$ for CC and DC, $n = 10$ for IS) for the Craib cores (CC), SCUBA cores (DC) and the in situ lander (IS).

exponential decrease in the oxygen concentration with sediment depth and with little variation between individual cores.

The average OPD, derived by pooling the total, individually calculated microprofiles (three spatially distinct microprofiles from each of the five Craib and SCUBA cores, $n = 15$; and eight spatially distinct in situ samples, $n = 8$) was shallowest in the Craib samples (7.38 ± 0.26 mm; mean ± SD, $n = 15$) and deepest in the in situ samples (8.0 ± 0.64 mm, $n = 8$) with the SCUBA samples in-between (7.88 ± 0.31 mm, $n = 15$) (Fig. 3). Although not statistically different from the in situ OPD values (Craib $p = 0.11$; SCUBA $p = 0.37$), the difference between the OPD of the two ex situ methods was significant ($p < 0.05$). A homogeneous distribution of oxygen and/or aerobic activity in the sediments would have to be assumed in order to suggest that the slightly shallower OPD value for the Craib cores could indicate a degree of core compression. However, there may be significant variations in the distribution and consumption of oxygen in sediments, even over very small scales (Glud et al. 2009). This variation may be reflected by the higher uncertainties recorded in the IS profiles that would potentially have been sampled over a broader range of microtopography.

Diffusive and total oxygen uptake rates

Linear regression analysis, based on the assumption that all core water would have originally had the same oxygen concentrations as measured in the BW samples, showed that from the time of being collected in the field to being initially sampled in the laboratory Craib samples had estimated TOU rates of 12.3 mmol m^{-2} d^{-1} compared with 5.1 mmol m^{-2} d^{-1} for the SCUBA cores. During the 4.5 h incubations, TOU measured in the Craib and SCUBA cores were reduced on average to 92.5% and 95.4%, respectively, from their initial 100% saturation concentrations whereas the oxygen concentration in the in situ samples was reduced to 98.3%. The Craib samples produced the highest oxygen uptake rate (8.6 mmol m^{-2} d^{-1}), compared with the

SCUBA samples (5.8 mmol m^{-2} d^{-1}) and in situ measurements (4.8 mmol m^{-2} d^{-1}).

TOU values for the Craib samples corresponded well with the values of 8 mmol m^{-2} d^{-1} obtained by Loh et al. (2002) using the same core extraction methodology at the same site between January and March 2001. However, comparing these values with the in situ results suggests that the present and previously published TOU rates from cores obtained by Craib coring are probably over-estimates that may have been influenced by the sampling method. If these observations are caused by physical disturbances induced as a result of the sampling technique then it is important to learn that the TOU results from Craib cored samples are immediately much higher but also continue to be higher over a following 48-h period, even when maintained at in situ equivalent temperatures in water with 100% air-oxygen saturation. Glud et al. (1994) found that the appropriate pre-incubation time is a balance between allowing the sediment cores to recover from the induced disturbances and avoiding changes in bacterial populations and other factors caused by prolonged storage.

The results from the present study suggest two things with respect to the observations: either that the pre-incubation time was insufficient or, alternatively, the disturbances caused by the extraction method were sufficient to prevent in situ conditions from being achieved even after 48 h. The fact that the results from the SCUBA samples, which were treated identically to the Craib ones once extracted, were closer to the in situ lander TOU rates would suggest that extraction methodology is the primary cause of the differences. The objective of a surface-deployed corer, such as the Craib corer, is to achieve the desired penetration into the sediment but with negligible disturbance of the surface layer and minimal compression of the core sample being taken. The Craib corer slowly pushes the sample tube into the sediment under the control of a hydraulic damper. Even though this action is controlled, the results from this present study would suggest that Craib coring might result
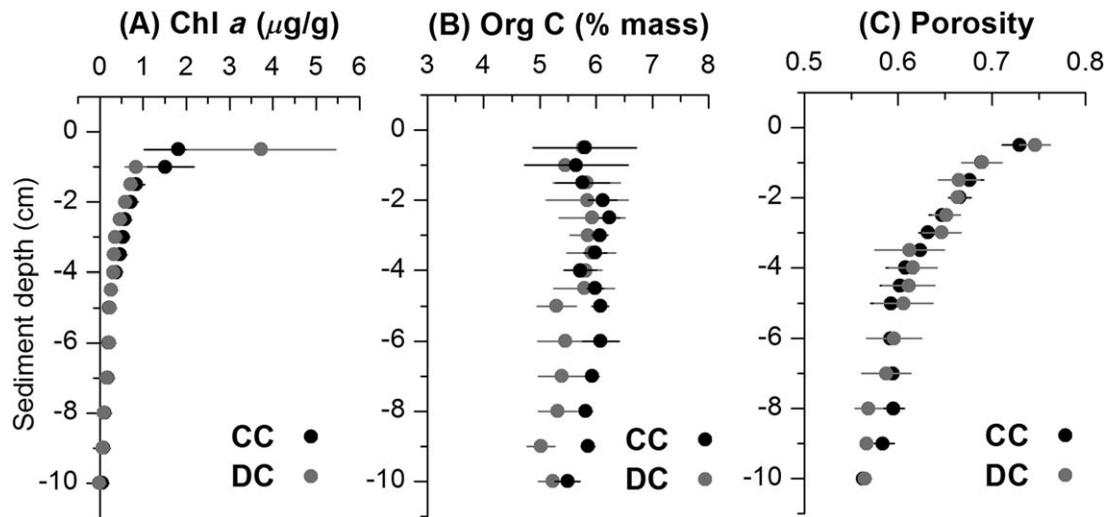
Fig. 4. Depth profiles (mean $\pm$ SD; $n = 3$) for (**A**) Chl *a*, (**B**) organic carbon (OC), and (**C**) porosity, for samples collected by SCUBA (DC) or Craib-corer (CC).

in processes that lead to a slight artificial increase in O_2 consumption either in the sampled near-seafloor waters or the surface sediment. Resuspension may have been caused during Craib sampling, introducing additional particulate organic matter into the near-seafloor waters, with the additional POM translating into increased TOU. Alternatively, or in addition, compression of the cores, which would cause pore water to be squeezed out, and/or disturbance of the surface layers during the sampling process, could result in buried carbon and/or reduced compounds moving into the waters overlying the sediment sample. Enhanced aerobic degradation activity and/or chemical oxidation would translate into an increase in oxygen uptake. Although caused by an initial pulsed input the effects could continue for days following the disruption, especially for carbon, for example, in accordance with observations on its degradation kinetics (e.g., Westrich and Berner 1984; Kristensen and Holmer 2001).

TOU rates can differ when measured in small diameter cores compared to larger in situ benthic chambers because of a reduced representation of macrofauna irrigation (Devol and Christensen 1993; Glud and Blackburn 2002). The faunal component of the TOU is typically calculated as the difference between the TOU and DOU (Rasmussen and Jørgensen 1992), with a small difference indicating a small faunal contribution. Faunal compositions and densities were not analyzed in the present study but the good agreement between the TOU values estimated from the SCUBA samples to the in situ lander rates would suggest that any faunal influence, if any, was small.

The DOU calculated from the linear oxygen decrease in the DBL, were greatest in the Craib samples (5.9 ± 1.5 mmol m^{-2} d^{-1}; mean $\pm$ SD), followed by the SCUBA samples (4.7 ± 1.4 mmol m^{-2} d^{-1}) and the in situ measurements

(4.0 ± 1.4 mmol m^{-2} d^{-1}). The Craib DOU values were significantly greater than the in situ measurements ($p < 0.01$); there were no significant differences between the Craib and SCUBA, or the SCUBA and in situ results ($p > 0.05$ in both cases). One potential reason for these results could be a greater faunal contribution to oxygen uptake in the Craib samples. However, although this possibility cannot be excluded, it would be somewhat unrealistic to assume this was the case as the differences were prevalent within most replicate samples and randomization procedures were employed throughout. A more robust hypothesis would be that the disruption induced through the different sampling methodologies increases the efflux of oxygen-demanding reduced chemical species (e.g., Fe^{2+}, Mn^{2+}) and carbon from the reduced oxygen layers of the sediment to the overlying water column through sediment compression and migration of pore-waters. This may in part be inferred by the difference in sediment porosity between the Craib and SCUBA samples at 6–10 cm depth (Fig. 4C). The ability to gently penetrate the sediment when using SCUBA may be enough to reduce this efflux in comparison to the Craib-corer technique.

Solid phase analyses

Chl *a* concentrations decreased with depth in both the Craib and SCUBA samples (Fig. 4A). Profiles expressed a non-linear, gradual decrease down to approximately 0.0 μg g^{-1} Chl *a* at 10 cm. The SCUBA samples produced significantly different values between the topmost two sections decreasing from $\sim$ 3.5 μg g^{-1} at the surface to $\sim$ 0.9 μg g^{-1} between 0.5 cm and the 1.0 cm in the sediment ($p = 0.01$). Contrastingly in the Craib samples the stratification is greatly reduced within the same depth interval, decreasing from $\sim$ 1.8 μg g^{-1} to $\sim$ 1.4 μg g^{-1} ($p = 0.64$), suggesting a more

homogenized top 1.0 cm in comparison to the SCUBA samples. The BW Chl *a* concentration was 0.22 μg L^{-1}.

Depth profiles of OC content displayed a relatively homogeneous down-core distribution irrespective of coring method, with the largest standard deviation observed within the upper most few centimeters (Fig. 4B). However, no significant difference between the profiles was measurable over the top 1.0 cm ($p = 0.79$).

The porosity-depth profiles for Craib and SCUBA samples showed no significant differences within the top 0.5 cm and 1.0 cm sections (0.5 cm $p = 0.34$; 1.0 cm $p = 0.68$) (Fig. 4C). Differences were most noticeable within the SCUBA samples at the 6–10 cm depth band and significantly different from the Craib samples at 8–10 cm ($p < 0.01$).

The significant differences in the topmost 1.0 cm of the Chl *a* profiles between the heterogeneous SCUBA and the homogenous Craib results, suggest that the upper portions of the cores were better preserved when samples were collected by SCUBA. The mechanisms that have most likely contributed to this are the effects of the hydraulic shock wave ("bow wave") in front of the orifice which may have washed away or resuspended flocculant sediments, and/or rotation and tilting of the sampler upon impact (Blomqvist 1991). While likely to be prevalent in the Craib samples, the effects of these mechanisms were largely controlled during the extraction of the SCUBA samples.

Discussion and recommendations

The development of tube coring as a method for benthic sampling was based on the principle that the sediment samples obtained were minimally disturbed and so were accepted proxies of the in situ environment (Eleftheriou 2013). Previous studies have assumed that sediment samples obtained using various types of mechanical corer will have an undisturbed sediment-water interface (e.g., Loh et al. 2002) or undisturbed sediment profiles (e.g., Mulsow et al. 2006). The required depth of the core, the acceptable degree of disturbance to its profile and the relative importance of the integrity of the sediment–water interface, will all vary depending on the disciplinary focus of the related studies (Eleftheriou 2013).

In the present study, there were significant differences recorded between the two coring methods used to obtain samples for the ex situ analyses. Compared with samples taken by a Craib corer, the ones collected by SCUBA produced biogeochemical values that were closer to those obtained in situ. Importantly, aspects of the biogeochemical stratification in the topmost 1 cm of the sediment seem to have been better preserved in samples obtained by SCUBA. This may be attributed to the ability to exercise care when penetrating the sediment and extracting sediment samples while using this method, and in transferring the sample back to the surface.

The obvious advantage with using SCUBA is that it places the scientist within the sampling environment; this can be essential when having to locate the sampling accurately over small-scale specific areas of interest (e.g., obtaining sediment cores in or close to a controlled subseabed release of carbon dioxide: Lichtschlag et al. 2015; Taylor et al. 2015; Tsukasaki et al. 2015). Having divers present provides the opportunity to make informed decisions related to the methodology being applied and can deliver near instant feedback to the topside team regarding the sampling conditions. For example, the state of the sediment during the extraction process can be continually monitored and any sampling errors can be adjusted for in real-time (e.g., rejecting cores where there is obvious resuspension during the penetration, extraction or when the core ends are being sealed). The diver can also make real-time adjustments to their sampling protocol. For example, the diver can swim past or away from any areas of surface sediment disturbance, areas of obvious resuspension, areas that can't be cored, or places of heightened sediment surface animal activity. It is always preferable for divers to core when there is a slight bottom current and to work into that current. This ensures that any sediment being redistributed into the water column during the coring process is moved away from the sampling site. Similarly, this means that any impacts caused by the presence of the diver (e.g., finning close to the seabed; movement of the core crate) are also kept away from the sampling site. There could be criticism that giving the diver an element of choice over where the sample is taken will make the method non-random. This can be adjusted for by employing methods such as counting fin strokes between samples or by working along gradated ground lines but with either sampling increment determined using a randomly generated number series.

The drawbacks of SCUBA are that most science-based diving is limited to relatively shallow waters ($<$ 50 m) either through national occupational diving regulations or because of the physiological challenges of working at greater depths. Irrespective of those limits, diving time, and thus the number of cores per diving operation, may become reduced at greater depths because of increased decompression obligations for the divers and so the maximum depth for optimal sampling may be shallower than 30 m. That said, a number of studies (Dias et al. 2008; Felden et al. 2010; Van Gaever et al. 2010; Jackson et al. 2017), have used push cores mounted to remotely operated vehicles (ROVs) to sample sediments at depths in excess of a thousand meters.

Although there were differences between the two ex situ sampling methods, this present study was limited to a single sediment type from a single sampling location and it is possible that these results may only be pertinent to this one example, irrespective of whether spatial heterogeneity had any influence. It would, therefore, be a recommendation for any larger or more long-term study to undertake preliminary evaluations that could identify any differences in the results

attributable to sampling methodology. However, even in a shallow coastal environment, where there may be less impact expected from decompression and temperature changes, the assumption that extracted sediment samples are representative of in situ conditions should not be made. This is particularly the case when estimating fluxes of chemical species, as these are likely to be sensitive to even minimal disturbances.

Measurements and recordings taken in situ still remain the preferred choice for a variety of reasons but, where this is not possible or feasible, employing divers to take the samples would appear to be a better option than surface-based gravity coring. The possibility to employ divers to position in situ sampling equipment would combine the strengths of both techniques.

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Conflict of Interest

None declared.