1 Modelling impacts and recovery in benthic communities exposed to localised

2 high CO₂

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6 Abstract

- 7 Regulations pertaining to carbon dioxide capture with offshore storage (CCS) require an
- 8 understanding of the potential localised environmental impacts and demonstrably suitable
- 9 monitoring practices. This study uses a marine ecosystem model to examine a comprehensive range
- 10 of hypothetical CO₂ leakage scenarios, quantifying both impact and recovery time within the benthic
- 11 system. Whilst significant mortalities and long recovery times were projected for the larger and
- 12 longer term scenarios, shorter-term or low level exposures lead to reduced projected impacts. This
- 13 suggests that efficient monitoring and leak mitigation strategies, coupled with appropriate selection
- 14 of storage sites can effectively limit concerns regarding localised environmental impacts from CCS.
- 15 The feedbacks and interactions between physiological and ecological responses simulated reveal
- 16 that benthic responses to CO₂ leakage could be complex. This type of modelling investigation can aid
- 17 the understanding of impact potential, the role of benthic community recovery and inform the
- 18 design of baseline and monitoring surveys.

19 Highlights

20 • We parameterised response of zoobenthos to low pH in marine biogeochemical/ecosystem 21 model. 22 A comprehensive range of scenarios was examined revealing complexity of biotic response ٠ 23 to low pH. 24 Precise benthic response is heavily dependent on model parameterisation. • 25 ٠ Levels of impacts depend on both the duration of exposure and magnitude of the pH 26 changes. 27 The impact of a leak is minimal when either the intensity or duration of perturbation is ٠ 28 restricted.

29 Keywords

- 30 Carbon Capture and Storage; CO2 release; pH; environmental impacts; benthic communities;
- 31 biogeochemical modelling

32 Introduction

- 33 Carbon dioxide capture and storage (CCS) provides a credible option for the removal of a significant
- 34 proportion of carbon dioxide (CO₂), primarily from point source fossil fuel and industrial emissions,
- thereby reducing the environmental and economic effects of climate change (Fuss et al., 2014; IPCC,
- 2005). Although the likelihood of CO_2 leakage from CCS is thought to be small (IPCC, 2005) both

- 1 environmental legislation (e.g. EC, 2009; OSPAR, 2007; Dixon et al., 2015) and public interest, require
- 2 operators to assess the potential environmental risks associated with CCS and to employ appropriate
- 3 monitoring and mitigation strategies to detect leakage and reduce the potential for environmental
- 4 damage. Fundamental to achieving these requirements is to understand the possible impacts of CO₂
- 5 leakage on local organisms and ecosystems and the potential for their recovery once any leak has

6 ceased (Widdicombe et al., 2013).

7 In many parts of the world, deep geological storage reservoirs are situated offshore (Nakanishi et al., 8 2009; Senior, 2010). Consequently, benthic faunal communities are expected to be the most likely to 9 be exposed to elevated levels of CO₂ should point-source leakage occur at the sea floor. Given that 10 many of these species are also sessile or have limited mobility and dispersal potential (i.e. no 11 planktonic stage) and that some species have relatively slow generation times, benthic communities 12 are more likely to be affected by CCS leakage. Whilst pelagic biota may also be affected, as the 13 plume of CO₂ disperses up through the water column, the impacts on planktonic communities will 14 likely be less than those for the benthos. This is primarily because planktonic organisms are generally 15 highly dynamic both spatially and temporally and have fast generation times. In addition, the lateral 16 advection of replacement populations, are likely to negate the impact and hasten the recovery for 17 planktonic species, while larger, actively mobile pelagic species, such as fish, may be able to detect 18 and avoid impacted regions altogether. Consequently, most recent CCS environmental impact 19 studies have concentrated on the response of benthic communities and this also forms the focus of 20 the current paper.

- 21 Carbon dioxide is naturally found in sea water and in sediment pore water, providing the substrate
- 22 for photosynthesis and being the product of respiration. However, excess CO₂, beyond natural
- 23 variability, causes significant changes to sea water chemistry, including increased acidity (reduced
- 24 pH) and reduced carbonate content, all of which can impact the health, function and survival of
- 25 marine organisms (Gattuso and Hansson, 2011; Widdicombe and Spicer, 2008). To fully appreciate
- the environmental risks associated with a CO₂ leak requires several variables to be quantified: the
- probability that leakage will occur, the degree of chemical perturbation that would result from the
 leak, the spatial extent over which potentially harmful perturbations would occur and the length of
- leak, the spatial extent over which potentially harmful perturbations would occur and the length of
 time this perturbation would persist. Using model simulations, this study focusses on describing how
- 30 the chemical nature of a CO_2 leak, specifically the severity and longevity of any chemical
- 31 perturbation, will impact upon a representative benthic community, including an estimation of
- 32 recovery potential.
- 33 The impacts of high CO_2 on marine systems have been studied using different approaches, each of
- 34 which has specific strengths and weaknesses (Jones et al., 2015). Manipulative experiments
- 35 conducted in laboratories or mesocosms allow for controlled, short term exposure experiments on
- 36 single species or simplified communities (e.g. Kita et al., 2013; Widdicombe et al., 2013). Natural CO₂
- 37 release sites (also known as natural analogues) can be studied to investigate ecosystem-level
- responses or those of particular species or features in a natural setting (e.g. Calosi et al., 2013; Hall-
- 39 Spencer et al., 2008), but are often geographically limited, sometimes confounded by other
- 40 environmental factors such as temperature and often ecologically and physio-chemically distinct
- 41 from CCS storage sites and possible leakage signals. Controlled leakage experiments performed in
- 42 the field offer a method of conducting more ecologically realistic exposure experiments in conditions
- 43 relevant to real-life CCS activities and with opportunities to assess natural processes such as

- 1 recovery (Blackford et al., 2014; Taylor et al., 2015b). However, these studies can be expensive, lack
- 2 repeatability as well as being restricted to a limited number of exposure scenarios. Models, such as
- 3 that used here, can be used to integrate knowledge and explore a wide range of scenarios including
- 4 processes of recovery, albeit within simplified, idealised ecosystems.

5 Several modelling studies have been used to explore the spatial and temporal distribution of 6 chemical changes in seawater resulting from a wide range of seabed CO_2 leakage scenarios. For 7 example, Dewar et al. (2013) detailed the fine scale dynamics of bubble plumes arising from smaller 8 scale leak events; Blackford et al. (2013) examined mid-scale leaks within tidal regimes; Blackford et 9 al. (2008) and Phelps et al. (2015) described larger hypothetical leakage events. Whilst the degree of 10 perturbation tends to scale with leak rate, these studies projected considerable variability in 11 individual leak characteristics, suggesting that potential leakage events cannot be simplistically 12 generalised. The magnitude and spatial extent of chemical perturbation in the surface sediments 13 and overlying water during a leak depends on many factors, including the nature of the leakage 14 pathway, the rate of leakage (Paulley et al., 2013), its duration, the physio-chemical composition of 15 the overburden including shallow sediments (Blackford et al., 2014; Queirós et al., 2015c), the 16 properties of any bubble plumes (Dewar et al., 2013) and the degree of hydrodynamic mixing at the 17 leakage site. The latter is driven by tidal mixing, currents, thermal stratification and weather, 18 resulting in temporally and spatially complex plumes of high CO_2 water (Blackford et al., 2013; 19 Phelps et al., 2015). Despite all this variability, modelling studies do uniformly suggest that once 20 leakage ceases, chemical recovery in seawater is very rapid, driven by hydrodynamic mixing, dilution

- and outgassing (Blackford et al., 2013; Phelps et al., 2015). Furthermore, a CO₂ release experiment
- conducted in the field also showed fast chemical recovery in seawater and surface sediments
- 23 (Blackford et al., 2014).
- 24 To date, no modelling studies have incorporated representations of benthic biota within a physically
- 25 and chemically realistic simulation of leakage, although some model studies have investigated
- 26 biological impacts of ocean acidification on pelagic processes (e.g. Artioli et al., 2014; Dutkiewicz et
- al., 2015; Tagliabue et al., 2011). These studies have shown significant interactions and feedbacks
- 28 between ecosystem components arising from relatively simple impact mechanisms, suggesting that
- 29 such modelling at least has a role in developing hypothesis, even if parameterisations and the
- 30 resulting projections remain uncertain, due to our limited spread of observations to date.
- Despite the fact that each individual leak is likely to be unique in the precise nature of its formation,
 development, size and duration, it is possible to generalise that all leaks will produce a gradient of
 chemical change in water and sediments with maximum perturbation occurring at the epicentre
 reducing to zero at some distance from the source of the leak. From a biological point of view the
- degree of perturbation or distance from leakage is the key determinant of impact (Barry et al., 2013;
- 36 Widdicombe et al., 2015).
- 37 In this study we have utilised a comprehensive ensemble of model scenarios that span the expected
- 38 range of chemical perturbations and event durations (exposure scenarios) with an aim to investigate
- 39 the physiological and ecosystem response of zoobenthic communities exposed to low pH due to CO₂
- 40 leaks and the subsequent potential for recovery. We have applied these scenarios to a 1D (vertical)
- 41 setup of an established marine ecosystem model ERSEM (Blackford et al., 2004; Butenschön et al.,
- 42 2015), rather than attempt a more realistic implementation of a limited number of scenarios in a

- 1 computationally demanding 3D model. We have incorporated a parameterisation of benthic fauna
- 2 response to decrease in pH based on published impact responses, as detailed in the following
- 3 section.
- 4

1 Methodology

2 Description and setup of the model

3



4

Fig. 1. Conceptual diagram of ERSEM showing interactions between the model components. Benthic carbonate
chemistry parameters pH, DIC and total alkalinity are represented in the model as mean values in the sediment column
of 0.3 m depth. Suspension-feeders inhabit the top layer of sediments, feeding on organic matter and near-bottom
pelagic material, while deposit-feeders are present deeper in the sediments and feed mainly on organic matter.

9 A coupled 1-D water column model GOTM-ERSEM (e.g. Allen and Clarke, 2007) was implemented to 10 study the impact of CO₂ leakage on zoobenthic communities. ERSEM is a well-tested marine ecosystem model (Fig. 1) configured for temperate shelf seas and can be coupled to a range of 11 12 hydrodynamic host models representing either 1D (water column) or fully 3D marine systems 13 (Butenschön et al., 2015). ERSEM includes a sub-model of the benthic environment capable of reproducing sediment and pore-water biogeochemical processes, biological interactions and the 14 15 resulting benthic-pelagic exchange in an active sediment layer of 0.3 m depth (Butenschön et al., 2015; Ebenhöh et al., 1995). The model splits zoobenthos into three functional groups, based on 16 17 their feeding sources: suspension feeders, feeding mainly on particulate organic matter (POM) at or 18 immediately above the sea floor; deposit feeders, which feed on material within sediments, and

- 19 smaller organisms within the sediment structure, termed meiobenthos (Table 1). The functional type
- approach enables a reasonable formulation of the physical impacts that zoobenthos exert on
- 21 sediment structure and chemistry due to bioirrigation, which enhances diffusivity of solutes in the

- 1 sediments, and bioturbation, which affects the vertical redistribution of POM. Benthic alkalinity and
- 2 concentrations of DIC in sediment pore water are both used to define the typical sediment pH
- 3 profile. For the present study, the existing ERSEM model formulation of pelagic carbonate chemistry
- 4 (Artioli et al., 2012) has been extended to account for fluxes of benthic alkalinity, thereby enabling
- 5 the calculation of mean benthic pH alongside the existing calculation of pelagic pH. Sources and
- 6 sinks of benthic alkalinity include contributions from bacterial and zoobenthic exudation of
- 7 ammonium and phosphate, nitrification and denitrification (Fig. 2). Alkalinity and DIC fluxes across
- 8 benthic-pelagic interface are calculated using equilibrium profile assumptions. A detailed description
- 9 of the implementation of benthic-pelagic fluxes in ERSEM is given in Butenschön et al. (2015).



Fig. 2. Conceptual representation of modelled benthic DIC and alkalinity fluxes required for determination of benthic pH. Benthic zone (shaded area) is represented with three dynamic layers. Processes defining sources (+) and sinks (-) of DIC (left) and alkalinity (right) are indicated. These processes define vertical profiles and the resulting benthic-pelagic fluxes of DIC and alkalinity. For a detailed description of the benthic biogeochemical dynamics and benthic-pelagic fluxes of

15 solutes in ERSEM see Butenschön et al. (2015).

- 17
- 18
- 19

2 Table 1. Contribution of each zoobenthic functional group to key model processes within ERSEM

	Deposit-feeders	Suspension-feeders	Meiobenthos
Uptake of pelagic material	-	Phytoplankton, pelagic medium-sized POM	-
Depth of sediment for uptake of benthic POM	0.0025-0.3 m	0-0.0025 m	0-0.03 m
Predate on	Aerobic and anaerobic bacteria, meiobenthos	Aerobic bacteria (close to sediment surface)	Aerobic and anaerobic bacteria, meiobenthos
Coefficient of contribution to bioturbation	1.0	-	-
Coefficient of contribution to bioirrigation	1.0	-	0.2
Assumed pH dependence	Benthic	30% pelagic, 70% benthic	Benthic

3

4 For the present study, the General Ocean Turbulence Model – GOTM (www.gotm.net, Burchard et

5 al., 1999; Burchard et al., 2006) was used to represent a seasonally stratified water column of 69 m

6 depth in the central North Sea (56°N, 3°E). The model was forced using climatological atmospheric

7 data derived from 20 years (1980-2000) of ECMWF-ERA40 reanalysis data (Uppala et al., 2005). In

8 order to realistically simulate the onset and the duration of stratification in such a dynamic

9 environment as the North Sea using a simple 1D model, the simulated vertical profiles of

10 temperature and salinity were relaxed to their climatology retrieved for the study location from a 3D

11 model covering the same period of time and forced with the same atmospheric conditions (Holt et

al., 2012). ERSEM biogeochemical variables were initialized applying values typical for the study

area. Results of a spin-up simulation of 5 years were sufficient to achieve a steady annual cycle, and

14 these were used as initial condition for all exposure scenarios.

15 Parameterization of zoobenthic response to lowering pH

16 The response of individuals and species to lowering pH is complex. However, much information can 17 be derived from more than a decade of dedicated ocean acidification and CCS impact research. This 18 work suggests that the impacts of lowered pH induced by acute hypercapnia are highly species- and 19 context-specific (Christen et al., 2012), depending on individual-level factors such as whether or not 20 organisms have calcified body structures and their ability for acid-base regulation of internal fluids 21 (Kroeker et al., 2010). Environmental conditions, such as the availability of resources to support the 22 energetically costly stress responses to low pH, are important moderators of response (Thomsen et 23 al., 2013). In addition, at the community level it is important to consider competitive interactions 24 between differently affected predators and prey or competition for a shared food source, as well as 25 behavioural responses such as ability to detect food (Queirós et al., 2015b). More recently, some 26 progress has been made towards a synthesis of survival, calcification, growth, development and

- 1 abundance responses to low pH (Kroeker et al., 2013; Nagelkerken and Connell, 2015) and it is now
- 2 possible to identify groups of animals that are potentially more vulnerable than others.
- 3 The default ERSEM zoobenthic community structure comprises of three functional groups:
- 4 "suspension-feeders", "deposit-feeders" and "meiobenthos" (see Table 1). The first two groups
- 5 describe generic macrofauna (i.e. >1mm, see Ebenhöh et al., 1995) and were specifically
- 6 parameterised for this study to reflect their different degree of dependence on pelagic and sediment
- 7 pore water pH conditions. Specifically, deposit-feeders in the model respond only to the simulated
- 8 pore water pH, while suspension-feeders respond primarily to benthic pore-water pH and
- 9 secondarily to pelagic pH. Arbitrarily, this proportion was set to 70% benthic and 30% pelagic pH.
- 10 This assumption was chosen so that deposit feeders would be solely impacted by low pH within the
- area of actively leaking CO₂ as the escaped gas percolated though the overburden and superficial
- sediments to reach the sediment surface. On the contrary suspension feeders would also experience
- 13 low pH conditions over a wider spatial extent due to the formation of a CO₂-rich plume through the
- 14 water column, above the sediment (Blackford et al., 2014; Widdicombe et al., 2015). To illustrate
- 15 potential differences in sensitivity between species and the effect of interspecific competition for
- 16 resources between these, each of these functional groups were split into two subgroups, i.e.
- 17 sensitive or tolerant to low pH. We assumed that organisms exhibiting tolerant and sensitive
- 18 responses to low pH would have equal representation in the community at the beginning of each
- 19 model simulation, although any combination is likely possible in natural ecosystems.
- 20 The impact of pH on the faunal metabolism was accordingly parameterised using a limiting function
- 21 applied to the metabolic activity of organisms (i.e. the food uptake and the activity respiration). The
- 22 limiting function (Eq. 1, Fig. 3) has been defined by adapting the classical logarithmic dose-response
- curve used in ecotoxicology essays (Calow and Forbes, 2003; Gaddum, 1933), allowing for a more
- stringent constraining of the curve around a response of 1 and 0.
- 25 $f(pH) = 1 exp(-10 * max(pH pH_{thr}, 0)^3)$
- According to the shape of the function, lowering pH causes a decrease in feeding activity and related respiration, ultimately leading to complete metabolic depression at $pH = pH_{thr}$, a "shutting-down" of

(1)

- respiration, ultimately leading to complete metabolic depression at $pH = pH_{thr}$, a "shutting-down" of physiological activity observed in studies where negative response to low pH is identified (e.g.
- Queirós et al., 2015b). Without food uptake, only basal metabolism takes place. A suite of impacts
- representing a first-order response of benthic fauna to lowering pH can be characterised in 3 phases
- representing a mist-order response of bentine radia to lowering pir can be characterised in 5 phases
- 31 (Fig. 3):
- Phase 1) metabolic activity decrease: the metabolic activity and therefore growth start to
 decrease. This occurs starting from sediment pore water pH<7.5 for the sensitive groups or
 pH<6.9 for the tolerant groups.
- Phase 2) metabolic depression: as *pH* approaches *pH_{thr}* (6.7 and 6.1 for sensitive and tolerant
 groups, respectively) fauna minimises any activity and the basal metabolism becomes the
 dominant process.
- 38Phase 3)mortality: $pH < pH_{thr}$ becomes directly toxic for benthic fauna, leading to increasing39mortality rates induced by low pH.

- 1 The increased mortality is parameterised using a parabolic equation (Eq. 2) that ensures rapid
- 2 extinction of the affected fauna when pH is lower than the physiological limit pH_{thr} :
- 3 $mort(pH) = \alpha * (min(pH, pH_{thr}) pH_{thr})^2$ (2)
- 4 where α is 0.07 for sensitive groups and 0.17 for tolerant groups as well as for meiobenthos.

5 The specific thresholds implemented are based on current evidence, but are not intended to be

6 comprehensive, because different species living in different habitats will exhibit different

7 sensitivities (Jones et al., 2015).

- 8 The third functional group within the benthos represents meiofauna (i.e. fauna smaller than 1 mm
- 9 but larger than 0.063 mm). This group was parameterised so that it does not experience the first two
- 10 phases of response, but does experience mortality (phase 3). This follows from our more limited
- 11 understanding of meiofauna physiology in the context of exposure to high DIC/low pH conditions,
- 12 where mortality is more frequently the response investigated (Dashfield et al., 2008; Meadows et al.,
- 13 2015). In contrast to filter feeders and deposit feeders, which are known to occur in environments
- 14 with highly variable pH conditions influenced by pelagic and in-burrow pH, but for which we can
- 15 constrain known ranges, much less is known about the specific responses of meiobenthic
- 16 communities, which include a mixture of many, generally interstitial species able to exploit variety of
- 17 microhabitats. Therefore, modelled meiofauna were not split into two subgroups. For the purpose of
- 18 this study, it was assumed that meiobenthos explicitly responds only to benthic pH variations.



Fig. 3. Response of sensitive (thick solid line) and tolerant (thick dashed line) zoobenthos to pH conditions, applied as
 coefficients of total food uptake and activity respiration rates of zoobenthic groups. Zoobenthos is not impacted at pH >

- 23 decreased as a function of uptake. Uptake entirely ceases at pH = 6.7 for sensitive groups and pH = 6.1 for tolerant ones
- 24 (as indicated by solid and dashed thin vertical lines, respectively).

 ^{22 7.5.} At lower pH, total food uptake is decreased proportionally to the value of response function. Activity respiration is

1 Description of exposure scenarios

- 2 A leak of CO₂ will produce two types of impact zone. With leakage from geological storage, CO₂ will
- 3 initially enter the marine environment from deeper sediments and the first biota to be exposed will
- 4 be the sediment dwelling fauna. Away from the area of leakage, impacts will be mediated *via*
- 5 advection of CO₂ rich plumes in the water column. The latter type of impact zone is also expected if
- 6 there is a breach in the transport pipeline, where CO₂ would enter the water column directly. In this
- 7 case the sediment surface dwelling fauna will be impacted first.
- 8 In order to account for both types of impact, two 100 member series of 20-year model runs were
- 9 conducted: one increasing the dissolved inorganic carbon (DIC) concentration within the sediments
- and the other adding DIC to the bottom layer of the water column, respectively simulating CO₂
- 11 permeating through sediments (in the vicinity of the epicentre of a leak, henceforth referred to as
- 12 "benthic exposure") and a laterally advected CO₂ plume (away from the epicentre, henceforth
- 13 referred to as "pelagic exposure"). The DIC additions were chosen to produce a graduated series of
- 14 reductions in pH with a maximum change of -2.0 pH units, sufficient to cover the range of
- 15 zoobenthic response parameterisations (Fig. 3).
- 16 The range of pH values considered here also approximately corresponds to the range identified in
- 17 modelling studies of dispersion of DIC leaks. For example, in the small-scale simulations of CO₂
- 18 plumes by Dewar et al. (2013) a maximum ΔpH of -2.51 was achieved with a leakage rate scenario of
- 19 1 kg s⁻¹, within a 15 m² leakage area.
- 20 Zoobenthic recovery was studied by repeating the above set of simulations limiting the period of 21 simulated leak to 1 day, 1 week, 1-11 months, 1, 3 and 5 years. Natural baseline conditions were 22 obtained from a 20-year simulation run without imposing additional DIC (hereafter referred to as the 23 reference run). Results from the reference run were used to define the degree of perturbation as a 24 result of added DIC (and low pH) exposure scenarios, as well as to determine the establishment of 25 "normal" conditions in post-leak estimates, which enabled the calculation of recovery times for the 26 impacted zoobenthic communities. Recovery is defined as the time taken for re-establishment of 27 90% of the reference zoobenthic functional group biomass, post-exposure (following Allen and 28 Clarke, 2007).
- 29 Although the precise time taken for CO₂ to return to background values post-leakage would, in 30 natural communities, strongly depend on prevailing hydrodynamic conditions, as well as the physical 31 characteristics of a particular leakage and sediment structure, it has been shown by both models and 32 experiments that this will be generally rapid in most instances (Blackford et al., 2014; Blackford et 33 al., 2013; Phelps et al., 2015; Queirós et al., 2015c). For example, a recent experimental study has 34 shown that pH levels of muddy and sandy sediments exposed to a high CO₂ plume for 3 days are restored within 24 hours, but the specific dynamics of the recovery depends on sediment type and 35 the initial depth of pH perturbation observed within the sediment (Queirós et al., 2015c). 36
- 37 Background minimum values of 1.0 mg C m⁻² were applied to each zoobenthic functional group, as a
- 38 proxy for lateral re-colonization which is not explicitly accounted for in the present model structure.
- 39 This also avoids numerical issues related to zoobenthic recovery after complete extinction.

1 Results and Discussion

2 Dynamics of pH depending on exposure type



3

Fig. 4. Model simulation results showing (a) near-bottom and (b) pore-water pH in the case of benthic exposure and (c)
near-bottom and (d) pore-water pH in case of pelagic exposure. Y-axis denotes simulation number (n=100), X-axis
indicates time since beginning of simulation (years).

- 7 The temporal response of pH in the sediment and near-bottom waters to elevated CO₂ is strongly
- 8 influenced by whether it is introduced into the sediment from below (i.e. CO₂ leaking up through the
- 9 overburden) or from above (a plume of CO_2 enriched seawater spreading out from the leak centre).
- 10 In the case of benthic exposures (Fig. 4a and b), pore-water pH decreases due to a build-up of DIC
- 11 within the sediment. Diffusion into the water column is limited and any excess DIC is effectively
- 12 mixed in the water column and is degassed into the atmosphere, which results in near-bottom water
- 13 pH remaining almost unaffected until sediment pH decreases below ~7.0. Despite pore water pH
- 14 reducing to <5.5, the lowest pelagic pH achieved is ~ 7.5. In the case of pelagic exposures (Fig. 4c and
- d), accumulation of DIC in the water column first leads to a moderate decrease in near-bottom pH
- and the subsequent decrease of pH in sediments. Stronger exposures lead to similar pH values in
- 17 both sediments and the overlying water. At the very beginning of the pelagic exposure scenarios,
- 18 there is a very short time lag before pore-water pH decreased, due to DIC diffusion into the
- 19 sediments. Pelagic exposure showed strong seasonality in benthic pH due to stronger DIC
- 20 accumulation in the bottom waters and the consequent stronger diffusion in the benthos during
- 21 stratified periods.

22 Impacts of low pH on zoobenthos

- 23 The relative change in the biomass of the five functional groups (tolerant and sensitive suspension
- 24 feeders, tolerant and sensitive deposit feeders, and meiofauna) in response to low pH was
- 25 determined and expressed as the percentage difference between the biomass obtained from each
- 26 continuous 20-year exposure simulation and the reference run. The level of exposure is expressed as
- 27 the mean pH experienced by zoobenthos over the simulation period for each individual scenario
- 28 realization.



2 Fig. 5. Response of zoobenthic biomass under continuous benthic exposure over 20 years: (a) sensitive and (b) tolerant

3 deposit-feeders; (c) sensitive and (d) tolerant suspension-feeders; (e) meiobenthos. The response is shown as the % 4

difference in biomass between exposure scenario and reference runs (i.e. without leakage). X-axis: time (years), y-axis:



Fig. 6. Response of zoobenthic biomass under continuous pelagic exposure over 20 years: (a) sensitive and (b) tolerant
 deposit-feeders; (c) sensitive and (d) tolerant suspension-feeders; (e) meiobenthos. The response is shown as the %
 difference in biomass between exposure scenario and reference runs (i.e. without leakage). X-axis: time (years), y-axis:
 mean benthic pH.

6 The responses of the sensitive groups in both the benthic (Fig. 5a and c) and pelagic (Fig. 6a and c)

7 exposure scenarios were similar. The smallest biomass decrease was projected in simulations where

8 the benthic pH did not fall below 7.3. However, as expected, decrease in biomass of the sensitive

9 zoobenthos with time was projected, due to chronic exposure to sub-optimal pH values. With a

- 1 further decrease of benthic pH to approximately 6.7, the biomass of sensitive groups rapidly
- 2 dropped in the first year due to reduced activity. In the simulations where sedimentary pH was
- 3 allowed to drop even lower, zoobenthic mortality increased, leading to the extinction of the
- 4 sensitive zoobenthic communities within the first few months of the simulation. A slightly lower
- 5 impact was observed in the pelagic exposures because sediment pH was relatively higher at the
- 6 beginning of the simulation period.
- 7 Any decrease of sensitive deposit or suspension-feeders at benthic pH levels above 6.5 was
- 8 accompanied by compensation of total biomass by the corresponding tolerant subgroups (see Fig.
- 9 5b and d and Fig. 6b and d for benthic and pelagic exposure scenarios, respectively). Even though

10 tolerant groups exhibited a slight reduction in food uptake rates, they benefit from an increase in

- 11 available food resources due to the decline in biomass of the corresponding sensitive groups.
- 12 Below a threshold marked by pH of 6.5, tolerant groups experienced a rapid decline in biomass and
- 13 became quickly extinct because the pH induced metabolic depression was stronger than the
- beneficial effect of increased availability of resources. At a mean pH < 6.1 the effect of enhanced
- 15 mortality on tolerant groups is strongly evident. In a similar way as for sensitive groups, additional
- 16 morality had a slightly lower effect in the pelagic exposure case at the very beginning of simulations,
- 17 when sedimentary pH was still relatively high.
- 18 Tolerant suspension-feeders exhibit a contrasting behaviour in the two exposure scenarios for pH <
- 19 6.5: while in the pelagic exposure scenario, they go rapidly extinct (Fig. 6d), in the benthic exposure
- 20 scenario their biomass decreased gradually in the pH range from 6.5 to 6.1. This reflects the
- 21 suspension-feeders' partial dependence on pelagic pH. In contrast to the pelagic exposure, overlying
- 22 water pH remained relatively high during the benthic exposure as DIC accumulated within the
- 23 sediment, only slowly diffusing into the overlying water (Fig. 4).
- 24 Meiobenthos responded in a very similar way in both the benthic and pelagic exposure (Fig. 5e and
- 25 6e, respectively). At pH values higher than 6.5, the biomass of fast-growing meiobenthos slightly
- 26 increased at first, when the biomasses of pH-sensitive macrozoobenthic groups decreased but were
- 27 not yet fully compensated by tolerant groups (Fig. 7). The reduction in total macrofauna allowed for
- the increase of meiobenthic biomass due to reduced predation and increased food availability.
- 29 When tolerant groups fully compensated for the decrease of sensitive group biomass, meiobenthos
- 30 biomass decreased again to values close to reference conditions.
- 31 At sedimentary pH lower than 6.7, meiobenthos biomass increased, reaching more than 200% of the
- reference values at pH lower than 6.5. Only when pH was lower than 5.6, did a quick decline in
- 33 biomass and subsequent extinction of meiobenthos occur due to increased mortality.



Fig. 7. Difference in total biomass (%) of deposit-feeders and filter-feeders under continuous 20-year pelagic exposure, relative to reference run (i.e. without leakage). X-axis: time (years), Y-axis: mean benthic pH.

1 Post-exposure recovery of zoobenthic communities

2 One of the most important considerations for assessing the potential environmental risks associated 3 with CCS leakage is how long it will take communities to recover should leakage occur. Although the 4 chemical recovery of the benthic system can take place at a relatively fast rate (Phelps et al., 2015; 5 Queirós et al., 2015c; Taylor et al., 2015a), it is assumed that the recovery of benthic communities, in 6 terms of re-establishing biomass and abundance that were present prior to the exposure, will be 7 longer. This recovery period will depend not only on potential lateral re-colonization, but also on 8 seasonal recruitment patterns (e.g. Kaiser et al., 2006). The current knowledge gap regarding the 9 potential for benthic community recovery dynamics post-leakage can be informed by benthic 10 trawling research (e.g. Collie et al., 2000; Dernie et al., 2003). However, the physical disturbance 11 caused by trawling may lead to alterations in sediment structure, which is not the case for chemical 12 disturbance. Similarly, benthic recovery following organic pollution (e.g. Pearson and Rosenberg, 13 1978) may also lead to residual impacts in the sediment which will affect benthic organisms long 14 after the source of disturbance has ceased. Given the relatively rapid recovery of the sedimentary 15 chemical environment when compared to other types of benthic disturbance, we can be confident 16 that our model estimates of recovery following CCS leakage will not underestimate the time 17 required for benthic systems to recover. In terms of duration of recovery, we do not differentiate 18 between sensitive and tolerant groups, but focus on the total biomass of macrozoobenthic 19 functional groups.

- 20 In general, the time required for recovery of zoobenthic functional groups increased with the
- severity and duration of the exposure (Fig. 8). In the benthic scenarios, for exposures up to 4 months
- 22 with benthic pH remaining above 6.5 and exposures of up to 1 year with benthic pH remaining above
- 23 7.0, zoobenthos biomass did not decrease below the 90% threshold. For very small perturbations
- 24 both sensitive and tolerant subgroups maintained near normal biomass, otherwise the decrease in
- 25 biomass of sensitive subgroups was compensated for by an increase in the biomass of tolerant
- subgroups. These pH thresholds were slightly different in the pelagic scenarios (Fig. 8c and d): for
- 27 suspension-feeders around pH 7.0 for exposures of up to 1 year, and for deposit feeders around pH
- 28 6.8 for exposures of 1-6 months and around pH 7.0-7.3 for exposures of 7 months to 1 year.
- 29 During short-term exposures of less than one month duration, the decrease in zoobenthic biomass 30 was relatively stronger in the benthic exposure scenarios, as lower pH values were achieved due to 31 higher pore water DIC content, whilst for the pelagic exposures these periods were too short to 32 allow significant amounts of DIC to diffuse into the sediments from the water column. Nevertheless, 33 larger pelagic exposures of one week duration were already sufficient to have detectable impacts on 34 suspension-feeders, but not deposit-feeders, as the latter depend only on benthic pH. Due to the 35 period of time required for DIC to diffuse into sediments, for the strongest pelagic exposures of up 36 to 1-year duration, suspension-feeders experienced lower pH than deposit-feeders and hence 37 required longer recovery times.
- 38 In the case of long-term exposures (3 years and over), no impact (denoted on Fig. 8 by hatched and
- 39 white regions) was seen to extend to lower pH values than for shorter, 1-year exposures. This
- 40 initially counter-intuitive finding is explained by the exposure period lasting more than one seasonal
- 41 cycle, so that increase in biomass of tolerant subgroups during the main growing season takes place
- 42 during the exposure. A further counter-intuitive result is seen in the benthic exposure scenario, for

- 1 exposures to very low pH exceeding 11 months, deposit-feeders are found to recover slightly faster
- 2 than at higher (i.e. approximately 5.7-6.0 units) pH levels. This can be explained by the extinction of
- 3 meiobenthos due to pH-induced mortality: additional benthic food resources therefore became
- 4 available for deposit-feeders post-exposure, which supported their faster recovery (Fig. 8b). In the
- 5 pelagic exposure case, pH levels experience more seasonal variability, so that the total extinction of
- 6 meiobenthos did not take place, which prevented the relatively faster recovery of deposit-feeders at
- 7 lowermost pH values (Fig. 8d).





Fig. 8. Recovery in the benthic exposure case ((a) suspension-feeders and (b) deposit-feeders) and in the pelagic exposure case ((c) suspension-feeders and (d) deposit-feeders)). Each column represents results from a series of 100 3 simulations with exposures of certain duration (1 day (1d), 1 week (1w), 1-11 months (1m- 11m), 1, 3 and 5 years (1y, 3y, 4 5y). In each case, exposure started at the beginning of simulation period. Y-axis indicates mean benthic pH of a period 5 from the beginning until termination of exposure. Colour saturation indicates the time (years) required since the end of 6 the exposure, for each functional group (as a sum of both sensitive and tolerant subgroups) to regain 90% of its biomass 7 found under reference conditions. Hatched areas indicate conditions where no recovery time was required because 8 none of the subgroups decreased below 90% compared to reference biomass, while white areas indicate conditions 9 where a decrease in the biomass of the sensitive subgroup was compensated for by an increase in the tolerant 10 subgroup.

11 Post-exposure zoobenthic community structure

- 12 Here we analyse long-term changes in zoobenthic community structure following exposure scenarios
- 13 by looking at community compositions at the end of the 20-year simulation. Although initial
- 14 distribution of tolerant and sensitive groups in the modelled zoobenthic community was equal,
- 15 impacts of exposure to low pH introduced changes in community structure, generally leading to a
- 16 decrease in the proportion of sensitive organisms' biomass. Since re-immigration from adjacent less
- 17 impacted locations is not explicitly taken into account in the model, the degree of deviation from the
- 18 initial distribution reflects the maximum potential disturbance to community composition depending
- 19 on duration and strength of exposure (Fig. 9).
- 20 The general pattern confirmed initial expectations that shorter periods and smaller intensities of
- 21 exposure would lead to smaller changes in the composition of zoobenthic communities. The biomass
- 22 of sensitive subgroups remained close to 50% of the total in cases of short term exposure (<1 week)
- 23 for all pH perturbations. In addition, sensitive subgroups were also resilient to pH perturbations of
- 24 less than -0.5 units, irrespective of the exposure duration. Significant changes in community
- 25 structure are seen for perturbations exceeding approximately 1.0 pH units and 1 month and for
- 26 perturbations exceeding approximately 0.5 pH units and one year. These patterns are similar for
- 27 both benthic and pelagic exposure scenarios.
- However, a fundamental difference in the structure of zoobenthic communities between benthic 28
- 29 and pelagic exposure scenarios arose at the most extreme perturbations in terms of both pH and
- 30 duration. In benthic exposure scenarios, the recovered community is composed of about 50%
- 31 tolerant and 50% sensitive subgroups, similar to initial distributions. However, in pelagic scenarios
- 32 tolerant subgroups still dominate with sensitive subgroups comprising only 20-30% of total biomass.

- 1 These results are a consequence of the dynamics of pH restoration, where high DIC in pelagic
- 2 bottom water (in the pelagic exposure scenario) or sediment pore water (in the benthic exposure
- 3 scenario) were imposed and consecutively restored to reference conditions to terminate exposure
- 4 to low pH. In the benthic exposure scenarios restoration of pore water DIC led to very fast
- 5 restoration of overall pH conditions both in sediments and in the water column, where pH always
- 6 remained relatively high. However, in the pelagic exposure scenarios after restoration of bottom
- 7 water conditions residual DIC remained in sediments for up to several months in the most severe
- 8 cases, thus keeping pore water pH lower, until it was eventually diffused to the water column and
- 9 degassed to the atmosphere. This explains the slower rate of carbonate system restoration in pelagic
- 10 exposure scenarios which, in turn, allowed for more favourable growth conditions for tolerant
- 11 subgroups immediately after exposure, and led to the suppression of sensitive subgroups' biomass.
- 12 Although these observed restoration patterns arise from peculiarities of the applied model setup,
- 13 they underpin the importance of temporal dynamics of post-exposure chemical recovery, which
- 14 would highly depend on the sediment's capacity to store DIC. A release experiment, where CO₂ was
- 15 injected into shallow sediments, demonstrated that certain sediment strata were capable of
- 16 retaining high concentrations of DIC for several weeks and possibly much longer, whilst overlying DIC
- 17 returned rapidly to normal values (Cevatoglu et al., 2015). The model results suggest that residual
- 18 CO₂ may have a longer term impact in certain circumstances, but this would be strongly dependent
- 19 on sediment characteristics.





Fig. 9. Proportion of biomass of sensitive subgroups in the total zoobenthic biomass at the end of 20-year period. Benthic exposure scenario: (a) suspension-feeders and (b) deposit-feeders. Pelagic exposure scenario: (c) suspensionfeeders and (d) deposit-feeders. Each column represents results of a series of 100 simulations with exposures of certain 4 duration (1 day (1d), 1 week (1w), 1-11 months (1m- 11m), 1, 3 and 5 years (1y, 3y, 5y). Y-axis indicates mean benthic pH 5 of a period from the beginning until termination of exposure.

1

1 Advantages and limitations of the modelling approach

- 2 The application of a computationally efficient 1D modelling approach allows us to examine a
- 3 comprehensive range of exposure scenarios that could be brought about by a leak from CO₂ storage
- 4 or transport pipeline. Such a comprehensive set of scenarios could not be realised by experimental
- 5 or analogue based studies, or by fully 3D simulations of explicit leak scenarios. This work, to our
- 6 knowledge, is the first attempt to generalize and parameterise zoobenthic response to low pH using
- 7 numerical modelling.
- 8 Modelled ecosystems and their impact responses are simplified representations of reality, which
- 9 exhibit some level of uncertainty due to the aggregation of functional types and parameterisation of
- 10 responses. Hence, the model formulation applied here is not intended to be comprehensive or final,
- 11 but sums up best available knowledge and expert opinion in a format appropriate for
- 12 implementation in a coupled biogeochemical model. Consequently, we believe that a qualitative
- 13 rather than strictly quantitative interpretation of the presented results is appropriate.
- 14 Indeed, further refinement of some model processes and assumptions may be important to consider
- 15 in future work. For example, reallocation of energy resources between maintenance, reproduction
- 16 and growth in response to stress (including hypercapnia), i.e. individual level trade-offs, are
- 17 important mechanisms for coping with adverse conditions (e.g. Kooijman and Bedaux, 1996;
- 18 McNamara and Buchanan, 2005), but are not explicitly accounted for in the model formulation
- 19 applied here. Better refinement of benthic functional types, including their bioturbation potential as
- 20 well as physical sediment properties may also be beneficial (Queirós et al., 2015a). Furthermore, our
- 21 results on recovery only indicate the time scales required for local zoobenthic community biomass
- 22 recovery without directly accounting for recolonization or migration. However, in natural
- 23 environments, following the re-establishment of favourable biogeochemical conditions, immigration
- of fauna from adjacent and connected areas not impacted by a leak may take place and recovery
- time could be quicker. Consequentially, the re-established community could consist of a more
- 26 homogenous mixture of sensitive and tolerant groups than shown in our results. The size and
- 27 characteristics of the area impacted by the leak would be an important consideration in these
- 28 processes, due to the lateral distance between impacted and non-impacted source areas and the
- 29 governing physical dynamics affecting advection of individuals.
- 30 Nevertheless, a modelling approach such as the one presented here allows for an upscaling of the
- 31 physiological responses observed in single species experiments or mesocosm exposures to a
- 32 simplified, but realistic model ecosystem, including ecological competition for food resources, as
- 33 well as the seasonality of physical, biological and life-cycle processes. It also allows us to develop
- 34 hypotheses that can be tested in new manipulation experiments either in the laboratory or in the
- 35 field. Thus, models and experiments are seen as complementary methods and key sources of
- 36 information for each other.
- 37 Whilst ocean acidification studies have informed, to an extent, the parameterisations presented
- 38 here, the extrapolation of these results to ocean acidification impacts should be made with caution.
- 39 Not only is the range of potential pH exposures much larger for CCS events, but ocean acidification is
- 40 also a multi-decadal process, the response to which may involve adaptation of species over many
- 41 generations (e.g. Stillman and Paganini, 2015), or migration in species able to track optimal habitats

- 1 through range shifts (Queirós et al., 2015b). Conversely, leaks are comparatively fast-paced events
- 2 where stress responses and avoidance are the expected primary drivers of community response.

3 Conclusion: Summary of results and their relevance in the context of CCS

- 4 In the present study we have applied a comprehensive ensemble of model scenarios spanning the
- 5 potential range of chemical perturbations that could arise if CO₂ leaked from offshore geological
- 6 storage. Conforming to the formulation of the impact parameterisations, the model results have
- 7 shown a clear trend of increasing impact and recovery time with escalating exposure strength and
- 8 duration. However, there are emergent properties from the model that also reveal the potential for
- 9 interactions between physiological and ecological responses that introduce a degree of complexity
- 10 to the outcomes. Broadly five categories of exposures and corresponding impacts could be
- 11 distinguished (Fig. 10):



12

Fig. 10. Summary of impacts on benthic fauna depending on duration of exposure (X-axis) and pH decrease (Y-axis).
 Categories of minimal impacts due to short-term exposures (a), (b) minimal impacts due to low levels of pH
 perturbations (b), intermediate impacts leading to changes in community structure (c), exposures leading to selective

tolerance-depending mortality (d) and severe impacts leading to general mortality (e), are indicated (see further
 explanation in the text).

- 18 a) Short-term exposures lasting less than one growing season.
- b) Exposures with small pH decrease. Both a) and b) are characterized by minor zoobenthic
 community changes, with neither sensitive nor tolerant group biomass decreasing
 significantly.
- c) Intermediate exposures, leading to changes in community structure. More significant shifts
 in community structure occurring as a result of decline in biomass of sensitive groups, which
 are replaced by tolerant groups.
- d) Exposures leading to selective mortalities. Selective mortality takes place as sensitive
 suspension-feeders become extinct quicker than tolerant ones, during benthic exposure (see
 Fig. 5c and d).

e) Severe exposures. Biomasses of both tolerant and sensitive groups decline significantly due
 to reduced assimilation and mortality. After restoration of normal pH conditions, tolerant
 groups tend to recover faster due to a larger residual biomass.

These results clearly demonstrate that in addition to concentrations of DIC, it is critical to consider
the duration of exposure: short-term exposures, even to large pH perturbations may be relatively
inconsequential, whilst long term exposures to even moderate perturbations could have comparably
larger impacts on zoobenthos physiology and reproductive success.

- 8 In addition to direct physiological responses, our results clearly show the importance of ecological
- 9 dynamics, with tolerant groups able to compensate negative physiological effect thanks to
- 10 decreased interspecific competition. Post-exposure dynamics of chemical recovery is another
- 11 important driver for composition of the recovered zoobenthic community. For very strong exposures
- 12 and total extinction of benthic fauna, faster pH restoration leads to equal growth conditions for both
- 13 sensitive and tolerant subgroups, resulting in the restored community composition being more
- similar to the reference scenario. Otherwise, if pH restoration is slow, tolerant groups have a
- 15 competitive advantage over sensitive groups during the re-establishment of the zoobenthic
- 16 community.
- 17 In order to make any prediction as part of an environmental impact assessment it is crucial to scale
- 18 these qualitative results to the spatial footprint of a given leakage scenario. This may necessitate
- 19 consideration of many processes superfluous to this study such as overburden flow pathways,
- 20 sediment geomorphology, bubble formation and plume characteristics, as well as 3D hydrodynamic
- 21 flow. So far, the few existing modelling (e.g. Dewar et al., 2013; Blackford et al., 2013; Phelps et al.,
- 22 2015), analogue studies (Caramanna et al., 2011) and release experiments (Blackford et al., 2014)
- 23 indicate that most plausible CCS leakage scenarios would have a restricted spatial footprint and,
- 24 therefore, minor regional impact. Our model results also concur with the only existing field-study to
- 25 date, which suggested that recovery from small leaks may be relatively rapid in situations with
- reasonable hydrodynamic mixing (Blackford et al., 2014; Widdicombe et al., 2015).
- We conclude that the applied modelling approach employed here provides a useful insight into the complexity of zoobenthic response to low pH. Our modelling results concur with experimental and
- analogue studies, emphasising the dependence of impacts on both the duration and magnitude of
- 30 the pH changes, as well as both physiological and ecological processes and feedbacks represented in
- 31 the model. The work presented here qualitatively describes the potential impact of CO₂ leakage, but
- 32 requires coupling with an appropriate understanding of the spatial degree and persistence of
- 33 perturbation for a full impact analysis. We underline the need to consider community structure,
- 34 habitat characteristics, and temporal dynamics when undertaking impact assessments or conducting
- 35 baseline surveys. This study shows that the impact of a leak can be minimised whenever this is
- 36 limited in intensity and duration, highlighting the importance of efficient monitoring, early warning
- 37 systems and consideration of leakage mitigation strategies.
- 38

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