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Reviews and syntheses: Abrupt ocean biogeochemical change under human-made climatic forcing – warming, acidification, and deoxygenation

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Abstract. Abrupt changes in ocean biogeochemical variables occur as a result of human-induced climate forcing as well as those which are more gradual and occur over longer timescales. These abrupt changes have not yet been identified and quantified to the same extent as the more gradual ones. We review and synthesise abrupt changes in ocean biogeochemistry under human-induced climatic forcing. We specifically address the ocean carbon and oxygen cycles because the related processes of acidification and deoxygenation provide important ecosystem hazards. Since biogeochemical cycles depend also on the physical environment, we also describe the relevant changes in warming, circulation, and sea ice. We include an overview of the reversibility or irreversibility of abrupt marine biogeochemical changes. Important implications of abrupt biogeochemical changes for ecosystems are also discussed. We conclude that there is evidence for increasing occurrence and extent of abrupt changes in ocean biogeochemistry as a consequence of rising greenhouse gas emissions.

1 Introduction

Human-induced climate and environmental forcing is affecting the oceans in many aspects. There are three fundamental threats which play a pivotal role for the well-being of marine life – and ultimately also for human societies: warming, ocean acidification, and de-oxygenation (Gruber, 2011; Schubert et al., 2006), that are acknowledged as stressors for marine ecosystems (Bopp et al., 2013). Sudden changes in ocean physical and biogeochemical state variables generate specific threats to marine ecosystems, as they can lead to the crossing of critical thresholds ("*tipping points*" – a tipping point is "*a critical threshold beyond which a system reorganizes, often abruptly and/or irreversibly*", (IPCC 2022)) beyond which regime shifts

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(i.e. the actual tipping events) are triggered (Biggs et al., 2018). However, it is not as yet conclusively quantified , what ecosystem impact these abrupt ocean environmental changes (often of local or regional extent) have versus smoothly monotonically changing conditions, even though there are some studies in which abrupt state variable changes have been recorded together with negative consequences for ecosystems (Bond et al., 2015; Hoegh-Guldberg et al., 2007; Wernberg et al., 2016, 2021; Chan et al., 2008). This paper focuses on the assessment of abrupt ocean changes in warming (temperature), ocean acidification and carbon fluxes (indicators for acidity such as pH value, carbonate ion concentration [CO_3^{2-}], dissolved inorganic carbon (DIC) and alkalinity, and carbonate saturation state), and de-oxygenation (oxygen concentration [O_2], and concentrations of selected nutrients where important for the O_2 cycle). Where needed, further physical factors are also included in our synthesis. We define a change as abrupt (in a system) when it is substantially faster than the typical rate of the changes during a reference period.

Considerable challenges exist in detecting and analysing abrupt changes in the ocean. Inherent problems arise from the short spatial scale and long temporal scale of mesoscale ocean variability as compared to the atmosphere, and the inaccessibility of the ocean as compared to land. In contrast to the atmosphere, fewer marine observational data sets are available and in particular there is a lack of data sets that are sufficiently long to detect abrupt changes. The limited resolution in space and time of large-scale or global ocean and Earth system models puts further restrictions on the detection of abrupt marine changes. Recently, some progress has been made with analysing the occurrence of abrupt marine biogeochemical changes (e.g. through the European project COMFORT, https://cordis.europa.eu/project/id/820989, last accessed 23.09.2022). We structure our paper into the following sections. Section 1 briefly describes the human-induced climate forcing for both physics and chemistry and introduces the key hazards of warming, ocean acidification, and deoxygenation to the reader. Section 2 gives an overview of the types of various abrupt changes that occur in the ocean. For each of these types the development of the key hazards are described: global changes (section 3), regional persistent changes (section 4), regional extremes (section 5), and reversibility (section 6). A discussion of ecosystem impacts follows in section 7, and conclusions are drawn in section 8. There is also additional information in a list of acronyms and a glossary, which may be found useful by non-specialists.

1.1 Human-induced climate forcing

Ocean warming is a direct consequence of the ocean uptake of excess heat from the atmosphere originating from the increased concentrations of greenhouse gases emitted in the course of industrialisation and land-use change over the past two centuries. The molecules of these greenhouse gases resonate with the long-wave thermal radiation emitted from the Earth surface and

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thus heat up the lower atmosphere. The most important excess warming comes from the long-lived greenhouse gases CO_2 (carbon dioxide), next to CH_4 (methane) and N_2O (nitrous oxide). Human-caused CO_2 emissions arise primarily from fossil fuel burning, deforestation, and cement manufacturing (Friedlingstein et al., 2022). Excess CH_4 emissions come from a range of sources including permafrost-thaw, livestock farming, rice cultivation, waste management (landfills etc.), and biofuel as well as biomass burning (Saunois et al., 2020). Anthropogenic N_2O emissions are mainly due to agriculture (direct soil emissions from fertiliser additions, manure left on pasture, manure management and aquaculture), direct anthropogenic sources (including fossil fuel burning and industry, waste and wastewater, and biomass burning), and indirect emissions from anthropogenic nitrogen additions (nitrogen deposition on land and oceans as well as nitrogen leaching and runoff from upstream) (Tian et al., 2020). The anthropogenic greenhouse gas concentration increase is well documented through direct measurements for the historical period and ice core data from the past 800,000 years (Loulergue et al., 2008; Luthi et al., 2008; Lüthi, 2008; Schilt et al., 2010). From 1750 to 2019, atmospheric concentrations of CO_2, CH_4, and N_2O increased by 131.6 ± 2.9 ppm (47.3%), 1137 ± 10 ppb (156%), and 62 ± 6 ppb (23.0%) respectively (Gulev et al., 2021). These changes exceed the difference between interglacial and glacial periods over the last 800,000 years for CO_2 and CH_4 and are of approximately the same magnitude for N_2O (Gulev et al., 2021). Anthropogenic climate forcing further includes aerosols (that can have a cooling or warming effect depending on their properties and origin), short-lived greenhouse gases (including ozone in the stratosphere and troposphere) and biophysical changes such as land-use induced albedo changes. The change in effective radiative forcing of the Earth's surface – ERF (see Glossary) – between 1750 and 2019 amounts to ca. +3.3 W m^{-2} for long-lived greenhouse gases, ca. -1.1 W m^{-2} for aerosols, ca. +0.5 W m^{-2} for short-lived greenhouse gases, and +0.12-0.15 W m^{-2} for biophysical changes from historical changes in land use including albedo changes (Gulev et al., 2021). The effect of a change in solar forcing is small compared to the human-induced greenhouse gas forcing. The respective change in effective radiative forcing due to this solar forcing change increased from -0.12 W m^{-2} at the Maunder minimum (1645-1715) (see, e.g., Usoskin and Mursula, 2003) to +0.15 W m^{-2} in 2019 as compared to the long-term average (Forster et al., 2021). Next to the radiative effect of human-caused climate forcing agents comes their chemical forcing, which is occasionally overlooked. This chemical forcing through greenhouse gases, aerosols, and nutrient additions (in particular through chemical fertiliser) influences the oceanic and terrestrial uptake of CO_2 and modifies the oceanic nutrient budgets and hence the marine biological carbon cycling. The chemical forcing induces feedbacks to the radiative forcing (e.g., Heinze et al., 2019). CO_2 and nutrient forcing (human additions of N and P to freshwater systems and the ocean) also have implications for ocean acidification and ocean deoxygenation.

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1.2 Key hazards: Warming, acidification, deoxygenation

The radiative and chemical forcing of the ocean through human-caused climate forcings induce a number of hazards to the marine environment. Seawater temperature and salinity (the latter due to changes in evaporation minus precipitation and changes in freshwater fluxes under climate change), density stratification, ocean currents, mixing, and sea ice cover alter with implications also for marine biogeochemistry and marine ecosystems. In interplay with the physical changes, chemical forcing affects the cycling of carbon, nutrients, and oxygen in the ocean with respective consequences for the environmental conditions and ecosystems. We focus on three main hazards for the marine environment – warming, acidification, and deoxygenation (**Figure 1**).

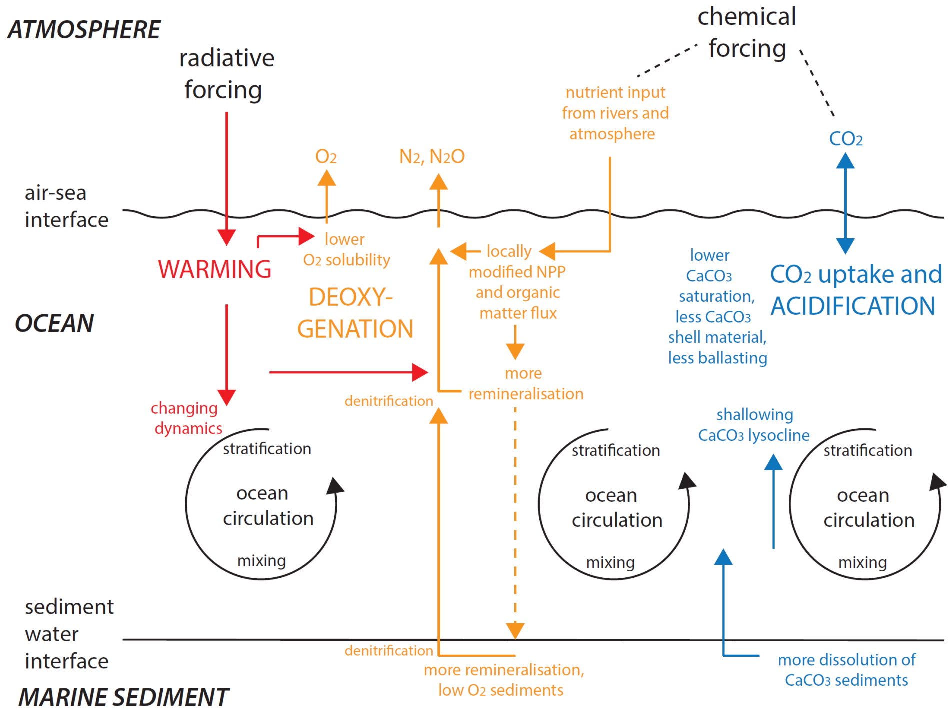

Figure 1: The three key oceanic hazards of human-induced climate change: warming, deoxygenation, and acidification (NPP: Net Primary Production).

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1.2.1 Warming

Based on a combined analysis of direct observations and models, the globally averaged surface temperature has increased from 1850-1900 to 2011-2020 by about 1.09 °C (regardless of whether using the global mean surface temperature (GMST), which is a combination of land surface air temperature (LSAT) and sea surface temperature (SST), or whether using the global surface air temperature GSAT, which is a combination of LSAT and marine air temperature (MAT) – with a global mean LSAT increase of 1.59 °C and an SST increase of 0.88 °C (Gulev et al., 2021). The lower marine value reflects the high heat capacity of the ocean and the downward mixing to subsurface and deeper layers eventually leading to a substantial change in ocean heat content (over all ocean depths) of 436×10^{21} J since 1871 (Zanna et al., 2019). The ocean has accordingly taken up more than 90% of the heat added to the Earth system from human activities (Bindoff et al., 2007; Rhein et al., 2013). Climatic warming induces sea ice loss in both the Arctic and the Southern Ocean. The density stratification of the ocean water column has increased on average (since the surface layer becomes warmer and less dense) and accordingly large-scale ocean overturning and vertical mixing have decreased in intensity (because the increased stratification acts as a barrier to vertical convection and mixing), while – at least in some regions – surface currents have accelerated (Peng et al., 2022). Sea-level rise through increased thawing of land-ice and freshwater transfers to the sea, through thermal expansion of the water column, and through changes of ocean currents causes increasing erosion of coastal areas thus also influencing marine biogeochemical tracer concentrations. Each organism species has an optimal thermal window for growth, which initially increases slowly with increasing temperature and drops sharply after the peak growth rate temperature has been exceeded (Eppley, 1972; Pörtner, 2010). Therefore, a little further warming beyond the optimal growth temperature can induce a sudden deterioration of growth conditions (Cooley et al., 2022). Phytoplankton (photosynthesising plankton), which live in the sun-lit surface layer of the ocean and form the basis of the global marine food web, experience deteriorating community structures due to climate change (Henson et al., 2021). Besides that, an increase of harmful algae blooms is observed (Gobler, 2020; Huisman et al., 2018; Litchman, 2022; O'neil et al., 2012). In addition, the frequency and extent of marine heatwaves, which can cause abrupt and deleterious changes in ecosystems (Wernberg et al. 2016, Smith et al 2023), are very likely to increase under the general background warming of the Earth system (Frölicher et al. 2018).

1.2.2 Acidification and carbon fluxes

The anthropogenic emissions of the key climate driving agent CO_2 do not only generate an additional forcing for the radiative budget of the Earth but also change chemical cycling. Additional CO_2 enters the ocean through air-sea gas exchange. Since the start of the industrial revolution (period 1750-2020), the oceans have taken up ca. 38% of the cumulative fossil fuel

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emissions or ca. 25% of the total anthropogenic emissions (incl. land-use change emissions) (Crisp et al., 2022). The additional CO_2 is acting as a massive forcing of the ocean chemical composition, notably of that of the marine carbon cycle. In general, CO_2 is reactive in the ocean (in contrast to the atmosphere) and dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions (for details about marine inorganic carbon cycling, see Zeebe and Wolf-Gladrow, 2001). The foundation for this reactivity of CO_2 is the presence of cations in excess of the equivalent anions of strong acids in seawater, which is quantified through alkalinity (Rakestraw, 1949; Middelburg et al., 2020; Wolf-Gladrow et al., 2007; Dickson, 1981, 1992). Only a small portion remains as free CO_2, i.e. as carbonic acid and gaseous dissolved CO_2. CO_2 reacts also with water directly, so that for the inorganic carbon equilibrium in the ocean, the dissociation of water itself needs to be taken into consideration. CO_2 addition to seawater causes the CO_2 partial pressure, the free CO_2 concentration, the HCO_3^- concentration, and the H^+ concentration to increase, while the CO_3^{2-} concentration decreases. The rise in H^+ concentration leads to a decrease of seawater pH (pH=-$\log_{10}([H^+])$). Air-sea gas exchange of CO_2 per se does not change alkalinity. Parts of the CO_2 added to the ocean can be neutralised by additions of alkalinity from external reservoirs (e.g. benthic carbonate deposits). Carbon and alkalinity in the ocean are transported along with ocean currents and mixed as passive tracers. Biota keeps the surface ocean carbon concentration low through the formation of organic particles/matter. When marine biota die, these particles sink through the water column and their organic matter is remineralised, resulting in oxygen consumption and release of inorganic carbon. This introduces a gradient with lower inorganic carbon concentration in the surface and higher levels deeper down. In the euphotic zone (the region of the upper ocean where sunlight penetrates), alkalinity is produced in the formation of organic material and consumed in the formation of calcareous ($CaCO_3$) shells, where the latter process often dominates. In the deep ocean, the $CaCO_3$ material becomes re-dissolved when sinking below the $CaCO_3$ saturation horizon, leading to an increase in alkalinity there (Berelson et al., 2007). The salinity-normalised concentrations of total DIC (the sum of free CO_2 concentration, $[HCO_3^-]$, and $[CO_3^{2-}]$) and alkalinity thus follow nutrient-type concentration profiles with generally increasing concentrations from top to bottom (Gordon, 1986; Broecker and Peng, 1982). In order to measure the corrosiveness of seawater with respect to the dissolution of the various polymorphs of $CaCO_3$ (calcite, aragonite, high-magnesium calcite), the carbonate saturation state for calcite (Ω_{calc}) and aragonite (Ω_{arag}) are often used.

For abrupt changes in the ocean carbon cycle, ocean acidification and carbon uptake from the atmosphere are the key processes that are of interest within the climate/environment realm. However, changes in the CO_2 concentration and pH will also affect other chemical systems, their ionic speciation and chemical equilibria, that may have secondary effects on carbon fluxes. One such example is trace metals that are essential for organisms, such as bioavailable iron. The pH variation directly affects trace metals and nutrients and their biogeochemical cycling, through changes that occur in the acid-base, oxidation-reduction,

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solubility-precipitation and complexation equilibria. Many divalent and trivalent trace elements that are strongly hydrolysed in seawater (aluminium, iron, chromium, ferrous and ferric ions) form oxy-anions [MO_x^- $(OH)_n$], hydroxy-complexes [$M(OH)_n$] and carbonate complexes. It is estimated that, due to ocean acidification, the concentration of these anions will decrease by 82% and 77% respectively, in surface waters (Millero et al., 2009), producing changes in the speciation, thermodynamics and chemical kinetics of those metals, increasing their concentration as free ions at lower pH (Byrne, 2002; Millero, 2001). In the case of iron, a decrease in pH will affect the extent of organic chelation of this metal and hence its availability to marine organisms. While a decrease in pH may affect the availability of iron (Fe) to phytoplankton, an increase in CO_2 partial pressure (pCO_2) may also change their Fe requirements. The net result of seawater acidification will be an increase in the Fe-stress for the phytoplankton in many areas of the oceans, especially those regions that experience co-limitation by Fe and light (Shi et al., 2010). When the pH and carbonate ion concentration decreases the labile ferric iron (Fe′) concentration and Fe' bioavailability decrease, and both of those processes lead to a reduction of phytotransferrin-mediated iron uptake (Mcquaid et al., 2018). Other processes affected by high CO_2/low pH conditions will include phytoplankton intracellular pH homeostasis, N_2-fixation rates (Hong et al., 2017), and cellular uptake of inorganic phosphate for metabolism (Xu et al., 2006b) that may also affect iron uptake rates.

1.2.3 Deoxygenation

Ocean deoxygenation, i.e. a decline of dissolved oxygen content over time averaged over larger areas, is due to ocean warming (the O_2 solubility decreases with increasing seawater temperature), a respective slowing down of ocean mixing and increased stratification (increasingly warmer water over cool sub-surface layers), and perturbations of nutrient cycling especially through additions of nitrogen-based artificial fertiliser to the Earth system. Transport of additional nutrient loads to the oceans, especially of human-induced additions of reactive nitrogen (N_r) via rivers, streams, and atmospheric transport/deposition cause regionally increased biological particle production at the ocean surface inducing higher rates of oxygen consumption in sub-surface layers when the organic particles sink through the water column and undergo remineralisation back to the dissolved constituents (Codispoti et al., 2001; Duce et al., 2008). Furthermore, under hypoxic and anoxic conditions (see Keeling et al., 2010) denitrification processes in the water column and sediment can cause an increased production and hence outgassing of the powerful greenhouse gas N_2O (nitrous oxide). Ocean deoxygenation generally has a less pronounced and more uncertain signal than the ocean pH change (Oschlies, 2021). Reasons for this uncertainty are the strong natural O_2 variability (Schmidtko et al., 2017; Stramma et al., 2020; Frölicher et al., 2020; Sharp et al., 2022), the still sparse spatiotemporal coverage of observational data, and difficulties in simulating the marine O_2 cycle (Buchanan and Tagliabue, 2021; Cabré et al., 2015; Kwiatkowski et al., 2020; Andrews et al., 2013; Oschlies et al., 2018; Oschlies et al., 2017).

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Moreover, there is no significant change in atmospheric O_2 concentrations (in contrast to atmospheric CO_2) that would imprint itself as a forcing on the ocean directly via air-sea gas exchange. It is estimated that the global marine O_2 inventory has decreased by about 2 % since the 1960s (Schmidtko et al., 2017; Ito et al., 2017; Breitburg et al., 2018) and is projected to have decreased by 0-5.5 % relative to pre-industrial time by the end of the century depending on emission scenario (IPCC, 2019; Kwiatkowski et al., 2020). Besides these long-term mean changes, recent studies suggest that low-O_2 extreme events are expected to increase in intensity, frequency, and duration (Gruber et al., 2021). The drawdown of O_2 in the ocean occurs when O_2 consumption (through biological respiration) exceeds O_2 supply, either biologically (e.g., photosynthesis) or physically (e.g., ocean ventilation). The ocean vertical O_2 profile often follows a typical shape with high values at the ocean surface (due to primary production as well as equilibration with the O_2-rich atmosphere), a decline over the first few hundred meters due to remineralisation of sinking organic matter, and elevated values in deep waters due to advection of high O_2 originating from cold polar areas of deep convection. Deviations from this standard profile occur when deoxygenation drops O_2 levels to 20-60 mmol m^{-3}, substituting the oxic respiration process with anoxic ones that imply the reduction of nitrate, manganese, iron, sulphate, and methanogenesis (e.g., Nealson and Saffarini, 1994; Wright et al., 2012) – with positive feedback on climate change due to resulting emissions of N_2O and CH_4. In coastal waters, deoxygenation is intensified by human activities through the addition of nutrients, which can lead to eutrophication and related extremely low-O_2 'dead zones' below the mixed layer (e.g., Malone and Newton, 2020). Eutrophication and the related low-O_2 in coastal zones as well as deoxygenation in the open ocean can have considerable impact on the well-being of marine organisms: Examples are shifts in community structure (Beman and Carolan, 2013; Wishner et al., 2018), habitat compression and changes in distribution (García Molinos, 2016; Köhn et al., 2022; Perry et al., 2005; Wishner et al., 2018; Deutsch et al., 2020), as well as changes in metabolism, aerobic performance and in extreme cases the emergence of anoxic 'dead-zones' (Beman and Carolan, 2013; Diaz and Rosenberg, 2008; Mccormick and Levin, 2017; Wright et al., 2012). The expansion of O_2 deficient zones (ODZs) is of particular concern because many marine species cannot tolerate the low O_2 levels associated with these zones. In general, the impact of low-O_2 waters on a species depends on whether the ratio between O_2 supply and O_2 demand allows for sustaining a viable population of that particular species (Deutsch et al., 2015; Deutsch et al., 2020; Buchanan and Tagliabue, 2021; Clarke et al., 2021; Mccormick and Levin, 2017). However, many factors complicate the effect on organisms and depend on a combination of a) the characteristics of the exposed species (e.g., adaptability, mobility, tolerance levels) (Collins et al., 2021; Pinsky et al., 2013; Vaquer-Sunyer and Duarte, 2008), b) the characteristics of the deoxygenation be it mean deoxygenation or an extreme event (Cheung et al., 2021; Gruber et al., 2021), c) the co-occurrence of other stressors suppressing tolerance windows , d) the different severity levels of impacts – e.g., visual impairments due to hypoxia start to occur at much higher O_2 levels than (near) lethal O_2 physiological stress (Mccormick and Levin, 2017), and e) the co-occurrence of other extremes when considering low-O_2 extreme events (such as low-acidity extremes, heatwaves or low nutrient extremes (Burger et al., 2022; Le Grix et al., 2021). When critical O_2 thresholds relevant for a particular ecosystem or species are crossed either by mean changes or extreme low-O_2 events, an ecosystem can be tipped into a new equilibrium state (Laffoley, 2022).

2 Typology of abrupt biogeochemical changes in the ocean

Before starting an analysis of fast changes in the various climatic variables, we would like to describe the meaning of the term "abrupt change" as used in this paper. We will focus on 3 different archetypes of abrupt change (see also the schematic in **Figure 2**) (based on material from Clark et al., 2016; Jacques-Coper and Garreaud, 2015; and Wernberg et al., 2016) (see also Wernberg et al., 2021): a. Global large-scale changes with respect to long timescales of several 1,000 years or more. b. Regional (local to basin-scale) changes that represent a sudden switch from one value to another value on a timescale of one decade to centuries. c. Regional changes in the frequency of occurrence and extent of extreme events (where normally the value would approach the average level after an extreme event, but also changes in extreme event statistics can be important here). All three types would have implications for ecosystems and potentially can induce ecosystem regime shifts. A further issue of relevance is a consideration of how reversible or irreversible the abrupt changes are.

2.1 Global changes that are fast with respect to variability over geologic time, especially the Holocene

The industrial revolution (the onset of the Anthropocene (Crutzen, 2002a, b)) has brought about fundamental changes in climatic and environmental conditions that had previously been varying only slightly over the course of the Holocene (last 11,700 years following the termination of the last glacial cycle). Radiative forcing has changed suddenly since the early 18th century with respect to heat and also the CO_2 forcing as chemical agent. Some of the reactions of the Earth system to this are equally fast as the imposed forcing (**Figure 2a**) and are expected to have consequences for 100,000 years and possibly even longer. A decline in calcium carbonate ($CaCO_3$) surface sediments on the ocean floor and the alteration of the atmospheric CO_2 concentration (and hence the surface ocean CO_2 partial pressure) are examples of long-term changes that are triggered by only a few centuries of human-caused greenhouse gas emissions. Moreover, dissolved oxygen content is expected to decline in parallel with ocean warming, where also runaway effects on oxygen decline can potentially be already triggered now due to human-made nutrient additions to the ocean (Watson, 2016; Watson et al., 2017). An important abrupt Earth system change without a real palaeo-analogue is the emerging acidification step change occurring over only few decades/centuries that is unprecedented for the past 300 million years (Caldeira and Wickett, 2003).

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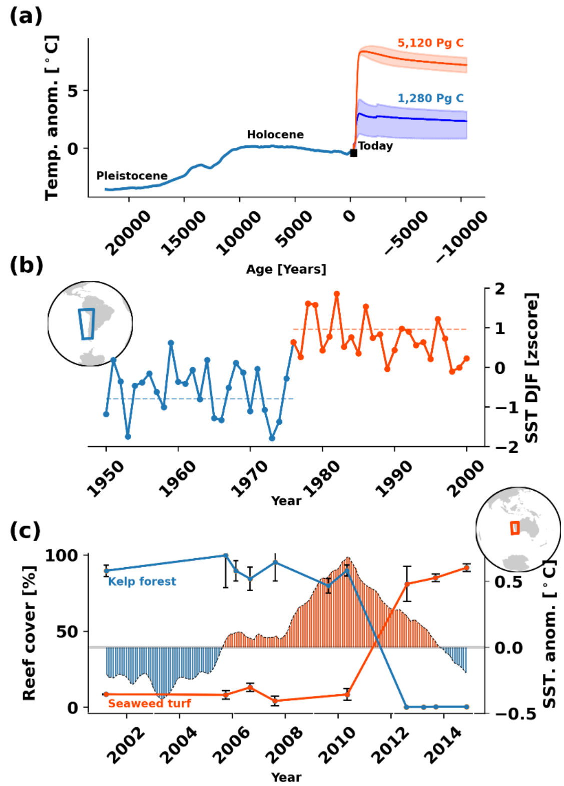

Figure 2: Examples for different types of abrupt change. (a) Global changes that are fast with respect to variability over geologic time, especially the Holocene. Example: Global (surface) temperature anomalies reconstructed from palaeoclimate archive for the past 20 000 years, and two emission scenarios for the next 10 000 years based on temperature increase for the two emission scenarios with 1,280 and 5,120 PgC total CO_2 emissions (following Clark et al., 2016). Reproduced with permission from Clark et al., 2016 (License Number: 5607550239461, Copyright 2023, Springer Nature). (b) Regional persistent changes that are fast with respect to natural variability and human-induced forcing. Example: Standardized composite (DJF) of SST in South Pacific Ocean showing abrupt change in temperature (see map at the left corner for area) (ErSST product: https://www.ncei.noaa.gov/products/extended-reconstructed-sst, last accessed 06.10.2023, Huang et al., 2017) (following (Jacques-Coper and Garreaud, 2015). Reproduced with permission from Jacques-Coper and Garreaud, 2015 (License ID: 1385909-1, Copyright 2023, John Wiley & Sons ltd.). (c) Regional extreme events and their change in extent and frequency such as marine heatwaves. Example: Regime shift from kelp forests to seaweed turfs after the 2011 marine heat wave in east of Australia (see map at the right corner for area) (following Wernberg et al., 2016). Reproduced with permission from Wernberg et al., 2016 (License Number: 5607550239461, Copyright 2023, Science).

2.2 Regional persistent changes that are fast with respect to natural variability and human-induced forcing

Sudden regional changes in ocean state variables (**Figure 2b**) that switch from one stable state to another stable state within only a few years have not yet been assessed sufficiently because of lack of observations. Nevertheless, there is evidence for such changes while many such shifts may have not yet been recognised. Analyses of results from runs with coupled Earth system models under different forcing scenarios can be employed to study such regime shifts in physical and biogeochemical state variables. A shift in physical variables can be decisive for subsequent changes in biogeochemical variables, because many ecosystems and chemical reactions depend on temperature, circulation, and sea ice cover. An example of a respective shift would be the change in dissolved oxygen concentration off the coast of Oregon (Chan et al., 2008).

2.3 Regional extreme events and their change in extent and frequency such as marine heatwaves

Extreme events usually happen over short timescales but can have major impacts for ecosystems and livelihoods that depend on them. Examples would be the marine heatwaves in the northwestern Pacific during 2014-16 (known as the 'blob') (Bond et al., 2015; Piatt et al., 2020) and the Australian heatwave event around 2011 (Kajtar et al., 2021). Though the local ocean state at sites of extreme events may return to quasi-normal values after the event, the extreme event can trigger persistent changes in ecosystems (Wernberg et al., 2016; Wernberg et al., 2013). Marine heatwaves, sudden seasonal acidification events, e.g. due to regionally occurring strong upwelling (Feely et al., 2008; Negrete-García et al., 2019), and temporary drawdown of oxygen, e.g., as in some mesoscale eddies with high surface biological production, (e.g., Karstensen et al., 2015), usually last longer than their atmospheric analogues – from months to multiple years.

Of course, certain abrupt changes in the ocean can be of mixed types covering two or even all types discussed. For example, a basin-scale change in the statistics of extreme events would encompass simultaneously types 2.2 and 2.3. An important question is whether abrupt ocean changes can be reversible (if the forcing is reversed) or not, or only for strong negative forcing. Ideally, a change in seawater properties and ocean dynamics would return to the pristine unperturbed state if a negative forcing is applied (e.g. an extraction of greenhouse gases from the atmosphere to the same extent as they have been emitted in the first place) or if the additional net greenhouse gas emissions to the atmosphere would stop entirely. In many cases, if at all, the systems would not change back along the reversed trajectory of their original abrupt change. A larger amount of negative rather than positive forcing would often be needed to realise a reversal (negative hysteresis). However, occasionally faster recovery than onset can occur as well (positive hysteresis). These considerations are important for aspects of climate mitigation (to avoid damage) and adaptation (to minimise damage, when the forcing already has happened or cannot be effectively reduced).

3 Global changes

3.1 Introduction to global changes

Through geologic time, the global ocean has undergone many changes in biogeochemistry, partly caused by changes in ocean circulation, in sea ice cover, and in other physical factors, such as variations in the solar insolation (Kump et al., 1999; Sundquist and Broecker, 1985; Schlesinger, 1997). In which way does the anthropogenic climate forcing induce abrupt global changes on the background of natural fluctuations? The ocean overturning timescale is of the order of 1000 years (Devries and Primeau, 2011; Khatiwala et al., 2012), therefore, abrupt global ocean changes will manifest on the same (or longer) timescale. The major reference period here is the climatically relatively stable Holocene series/epoch from ca. 11.7 ka BP up to the present (Walker et al., 2012) if the time after the onset of the industrial revolution is excluded. Evidence from palaeoceanographic data and coupled physical-biogeochemical models indicates also relatively stable conditions of the marine carbon cycle, seawater temperature, and ocean overturning circulation (Menviel and Joos, 2012; Segschneider et al., 2018) where the carbonate ion concentration and the dissolved oxygen concentrations are associated with some long-lasting trends. The late Holocene pre-industrial atmospheric CO_2 concentration rose by about 20 ppm from 8 ka BP to the beginning of the industrial revolution due to the still ongoing accumulation of $CaCO_3$ in shallow oceans as a result of the deglacial CO_2 extraction from the ocean (Indermuhle et al., 1999). The trend in atmospheric pCO_2 is in line with reconstructions of respective surface ΔpH and $\Delta[CO_3^{2-}]$ from 8 ka BP to the preindustrial (Foster, 2008). Compared to the last nine glacial cycles (Berger et al., 2016) that are documented by ice core measurements for atmospheric composition of trace gases such as CO_2, the human-caused change in atmospheric CO_2 led to greenhouse gas forcing higher than the last glacial interglacial atmospheric CO_2 amplitude (ca. 140 ppm vs. 90 ppm) and on a shorter timescale (for anthropogenic CO_2 emissions from 1750 to present day over ca. 270 years as compared to the 6000 years from 18 ka BP to 12 ka BP) than for the fast warming events at glacial terminations (while the onset of glaciations worked on even longer timescales) (Marcott et al., 2014; King et al., 1992) (see also https://keelingcurve.ucsd.edu/, last accessed 08.09.2023). Within the glacial cold periods abrupt "unforced" millennial-scale climate fluctuations occurred (Dansgaard-Oeschger events; sudden warming from glacial temperature levels to interglacial levels) (Dansgaard et al., 1993) as well as rapid climate fluctuations triggered by melt water pulses (as shown through the occurrence of ice-rafted debris in sediment cores, Heinrich events) (Bond et al., 1993). For both the "forced" and the "unforced" fluctuations, re-organisations of the Atlantic meridional overturning circulation (Pedro et al., 2022) and possible linkages are still under scrutiny (Mann et al., 2021). These strong and rapid millennial scale climate fluctuations have the same order of magnitude in timing and extent (relative to the respective baseline climate) as the current anthropogenic warming. However, they occurred relative to a much colder base line than today's climate change. Before the stable late

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Holocene climate phase, the rapid deglacial warming to the Bølling-Allerød warm period and the subsequent transient cold Younger Dryas event occurred, with much larger climate fluctuations than during the late Holocene. In the late Holocene, further natural climate fluctuations occurred (e.g., the 8.2 ka BP cold event (Daley et al., 2011) and the Maunder minimum) that were about one order of magnitude smaller than the temperature rise due to the Bølling-Allerød and the Younger Dryas cooling.

While the glacial/interglacial changes in atmospheric greenhouse gas forcing are due to an internal redistribution of matter between the ocean, atmosphere, and land, the anthropogenic climate forcing is caused by an addition of CO_2 (and other greenhouse gases) from a previously locked reservoir to the atmosphere (and afterwards also to the oceans and the land biosphere). Such changes of the chemical and heat inventories of the Earth's surface reservoirs have happened earlier in the Earth's history mainly through catastrophic events (with associated mass extinctions of biota) such as the asteroid impact at the Cretaceous/Tertiary transition 65.5 Ma BP (Schulte et al., 2010) and the PETM (Paleocene Eocene Thermal Maximum) at 55 Ma BP due to a large CH_4 and/or CO_2 release from previously locked reservoirs (gas hydrates, volcanism, permafrost etc.) (Gutjahr et al., 2017; Higgins and Schrag, 2006; Zachos et al., 2003). While the meteorite impact cannot be used as an analogue to human-induced forcing, the PETM is discussed as a potential palaeo-analogue for global warming and ocean acidification. However, the PETM warming occurred with a ramp-up over about 20,000 years and hence is a much less abrupt climate change than that caused through human-induced greenhouse gas emissions to the atmosphere. In addition, the land-sea distribution around 55 million years before present was quite different from the present configuration. While proxies exist for past seawater temperatures (Sarnthein et al., 2003; Shackleton, 1967; Hoche et al., 2021), nutrient concentration (Farmer et al., 2021) and to some degree also for pCO_2 (Witkowski et al., 2020; Rau et al., 1991), $CaCO_3$ saturation (Farrell and Prell, 1989, 1991), and pH (Sanyal et al., 1995; Honisch et al., 2012), reconstructions of dissolved oxygen are hardly available (except for switches to hypoxic or anoxic conditions) and potentially successful proxies are still under discussion (Hoogakker et al., 2015).

How would the future climate and the respective ocean conditions for temperature, carbon cycle (acidification), and oxygen cycle (deoxygenation) look if no human-induced climate change happened? This question is interesting for the framing of human-induced abrupt global change concerning its legacy effect on climate and marine environmental conditions far ahead in the future. The literature on "natural" future climates is mainly focused around the question of potential future ice ages that was quite popular up to the 1990s when the public and scientific discourse was more focussed on global cooling rather than warming. According to the orbital solar insulation forcing variations of climate (Milankovitch cycles, frequencies of

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variability in obliquity, tilt, and precession of the equinoxes, (see Imbrie et al., 1993; Imbrie et al., 1992; Berger and Loutre, 1991)), the natural length of the ongoing interglacial would last for ca. 1,500 years in a world without human-caused greenhouse gases (Tzedakis et al., 2012). Depending on the greenhouse gas emission scenario and the potential melt of the Greenland ice sheet, model projections indicate a delay up to several 10,000s of years or even 100 ka AP until the next glacial inception (Berger and Loutre, 2002; Cochelin et al., 2006; Loutre and Berger, 2000). These studies underpin the importance of the anthropogenic greenhouse gas perturbation to the heat budget of the Earth surface reservoirs over long future intervals.

3.2 Abrupt global changes in warming

When it comes to global fundamental changes of the physical ocean since the onset of industrialisation as compared to the fairly stable Holocene period, several major features stand out: the large change in ocean heat content due to anthropogenic greenhouse gas emissions and a potential slowing down of the overall ocean circulation in parallel with a stronger density stratification especially in the upper ocean layers. In this section we focus on global trends in temperature, while changes in the AMOC (Atlantic Meridional Overturing Circulation) and sea ice are dealt with in section 4.1. Future projected changes in these quantities may be investigated using fully-coupled Earth System Models such as those used in the CMIP6 exercise (Coupled Model Intercomparison Project (Phase 6), Eyring et al. (2016)). Under the high-emission and low-emission shared socioeconomic pathway scenarios (SSP5-8.5 and SSP1-2.6) (O'Neill et al., 2014), the CMIP6 models project an increase in total upper 2000 m ocean heat content of about 4–6 and 2–4 times the observed 1958–2019 increase respectively (Cheng et al., 2022). At the ocean surface in both scenarios, the projections show global sea surface warming and strong northward amplification with multi-model mean warming in the Arctic surface waters surpassing 5°C in SSP5-8.5 and 2°C in SSP1-2.6 by the end of the century. Projected sea surface warming exhibits high regional robustness across the models (Kwiatkowski et al., 2020) that should increasingly resemble real patterns of warming as the ocean heat content increases (Bronselaer and Zanna, 2020).

The extent of globally averaged surface air warming to first order depends linearly on the integrated cumulative human-caused CO_2 emissions to the atmosphere over time (Transient Climate Response to cumulative carbon Emissions, TCRE) (Allen et al., 2009; Matthews et al., 2009; Rogelj et al., 2019), although deviations from this linear relationship have been identified due to the quantification method (Collins et al., 2013, see their Figure 12.45) and also for potential applications of Negative Emissions Technologies (NETs) (Zickfeld et al., 2016). The question is whether there is a substantial committed warming that continues even after human-caused excess greenhouse gas emissions have ceased. Newer analyses indicate that the warming extent levels off after a stop of emissions (Macdougall et al., 2020). However, due to the long ocean overturning

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timescales and the slow mixing of additional heat into the large deep ocean volume, a slight cooling of surface air temperatures and hence SSTs occurs only on several 1,000- to several 10,000-yr timescales (Solomon et al., 2009; Clark et al., 2016), and some continued warming on centennial timescales cannot be ruled out (Frölicher et al. 2014).

Two recent comprehensive model intercomparison projects have been dedicated to identify how the Earth system reacts if greenhouse gas emissions are set to zero at a certain point in time (ZECMIP, Zero Emissions Commitment Intercomparison Project) (Jones et al., 2019), and how it reacts if additionally negative CO_2 emissions can be achieved (CDRMIP, Carbon Dioxide Removal Model Intercomparison Project) (Keller et al., 2018). The first ZECMIP results confirm that the abrupt global surface air temperature rise since the start of industrialisation is only slowly – if at all – attenuated over time even if greenhouse gas emissions swiftly go to zero (Montero et al., 2022; Schwinger et al., 2022b). The picture changes for massive carbon dioxide removals from the atmosphere, where the global mean surface air temperature approaches the preindustrial levels if indeed preindustrial CO_2 concentrations were re-established (Jeltsch-Thömmes et al., 2020; An et al., 2021). The rate of return to pre-industrial global mean surface air temperatures, however, is dependent on how large the climate sensitivity of the Earth system is (Jeltsch-Thömmes et al., 2020). Phasing out carbon emissions can invoke a transient century scale cooling in the northern high latitudes if a significant AMOC slowdown has been caused by anthropogenic climate change. Such climate fluctuations could be amplified by strong carbon dioxide removals in a world with a slow AMOC and lower atmospheric CO_2 concentrations than prevailing at the time when this AMOC slowing down was caused (An et al., 2021; Schwinger et al., 2022a; Schwinger et al., 2022b). Such a transient cooling can significantly disrupt adaptation measures to climate change.

3.3 Abrupt global changes in ocean acidification and carbon fluxes

The ocean is a major long-term sink for anthropogenic CO_2 emissions to the atmosphere (e.g., Caldeira and Wickett, 2005; Maier-Reimer and Hasselmann, 1987; Bolin and Eriksson, 1959; Friedlingstein et al., 2006). While global abrupt changes may occur under certain circumstances, such as with massive negative emissions of atmospheric CO_2 and other greenhouse gases, that would also imply a transient outgassing of human-caused CO_2 from the oceans as a respective rebound effect, the long timescales of oceanic mixing mean that such changes would take several decades to centuries to take place (An et al., 2021; Schwinger et al., 2022b). If no negative emissions are applied and no other effective long-term CO_2 sinks contribute, the ocean will absorb significant amounts of CO_2 from the atmosphere over several tens of thousands of years until it has buffered about 92% of the atmospheric CO_2 perturbation (Bolin and Eriksson, 1959; Egleston et al., 2010; Revelle and Suess, 1957). The impact of shock-like– on geologic timescales – anthropogenic CO_2 emissions on the ocean has been examined for

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varying quantities of CO_2 emissions using impulse response functions (Joos et al., 2013; Maier-Reimer and Hasselmann, 1987). These theoretical experiments have shown that following an initial period of strong CO_2 uptake, a very long tail of the atmospheric retention of human-caused CO_2 persists. The slow uptake response after the initial shock is due to the dissolution of $CaCO_3$ sediment on the ocean floor and terrestrial carbonate weathering cycles that only exhibit effects for the fossil fuel CO_2 neutralisation and hence atmospheric CO_2 reduction on multimillennial timescales (Archer, 2005; Archer et al., 1998; Archer et al., 1997; Jeltsch-Thommes and Joos, 2020). Additionally, the partial loss of $CaCO_3$ sediment, as documented in these studies, is another long-term consequence of the anthropogenic climate perturbation not yet adequately assessed in risk studies. It may also lead to a partial loss of the climate $CaCO_3$ sedimentary palaeo-climate record for a substantial time interval of several tens of thousands of years.

Coupled Earth system models have been used to investigate the effects of historical and future climate forcing on ocean acidification over timescales from the beginning of the industrial revolution to the year 2100. By the end of the century, these models project that the global accumulation of anthropogenic CO_2 in the ocean will reduce the mean sea surface pH by −0.44 ± 0.005 and −0.16 ± 0.002 pH units in the high SSP5-8.5 and low emission SSP1-2.6 scenarios, respectively (Kwiatkowski et al., 2020), with strong agreement across models on both the magnitude and distribution of projected changes (Kwiatkowski et al., 2020; Bopp et al., 2013). Another direct consequence of continued CO_2 uptake is the reduction of the ocean's buffering capacity, which is its ability to absorb further CO_2 (e.g., Sarmiento et al., 1995; Revelle and Suess, 1957). The rate at which the buffering capacity diminishes is strongly linked to the circulation and re-emergence of anthropogenic CO_2 (Rodgers et al., 2020) and upwelling strength at the Southern Ocean (Roy et al., 2021). However, the effects of ocean acidification and buffering capacity reduction are not regionally consistent, as detailed further below; ocean acidification tends to increase towards the poles, with the Arctic experiencing the highest levels due to the combined impact of sea ice loss and low temperatures. Impacts on shelf and marginal seas can be further amplified by circulation change.

Although stabilising ocean pH levels may be achievable through a partial extraction of CO_2 from the earth system using NETs and a cessation of greenhouse gas emission, pH levels would not return to pre-industrial levels due to the ocean's reduced buffering capacity (Schwinger et al., 2022b; Mathesius et al., 2015). However, the feasibility of achieving strong negative emissions through NETs is highly uncertain due to the lack of technical readiness, upscaling perspectives, and understanding of the associated potential negative side effects (Fuss et al., 2018; Minx et al., 2018; Nemet et al., 2018). Alternatively, if greenhouse gas emissions were simply stopped without the use of NETs, pH and Ω_{calc} would only recover very slowly after several centuries, with a somewhat faster recovery for lower cumulative emissions (Caldeira and Wickett, 2005) and slower in the deep ocean than at the surface.

3.4 Abrupt global changes in deoxygenation and relevant nutrient fluxes

Global dissolved O_2 measurements indicate a decline in the O_2 content of 1.1-3.1% in the upper 1000 meters of the ocean over the last ~60 years (Ito et al., 2017; Schmidtko et al., 2017), which should be considered abrupt on the global scale. The spatial pattern is widespread throughout all ocean basins with the most intense decline generally occurring at high and low latitudes, whereas subtropical regions (~20° - 40°N/S) contain the smallest decline. Analysis of O_2 losses indicate that temperature-driven solubility effects explain most of the decline above the thermocline, while reduced ventilation from enhanced stratification dominates the deoxygenation trend in the ocean interior (Schmidtko et al., 2017). Nevertheless, both trends and drivers depend strongly on location and the timescale considered (e.g., Frölicher et al., 2009; Frölicher et al., 2020; Keeling et al., 2010). Projections from global climate models (e.g., those from CMIP6; Kwiatkowski et al. (2020)) underestimate the observed ocean deoxygenation trend by more than a factor of 2 on average (Oschlies et al., 2018) and do not offer consistent results for both sign and magnitude of future change in tropical regions (Cabré et al., 2015; Kwiatkowski et al., 2020). The lack of robust model projections indicates that our comprehensive representation of the full physical transport and biogeochemical processes that contribute to the ocean deoxygenation signal is incomplete and needs to be further investigated. This includes uncertainties in regional projections of NPP (Net Primary Production) (Tagliabue et al., 2021) and the potential in nutrient uptake plasticity (Kwon et al., 2022). Projections of O_2 show a O_2 decline in the subsurface ocean (100 to 600 m) of -13.27 ± 5.28 mmol m^{-3} and -6.36 ± 2.92 mmol m^{-3} in the high SSP5-8.5 and low emission SSP1-2.6 scenarios respectively (2080-2099 mean values relative to 1870–1899 ± the inter-model standard deviation; Kwiatkowski et al. (2020)). Models that simulate a strong NPP reduction in the tropics tend to simulate a too minor O_2 decline or even predict increasing O_2 levels in the low-latitude ocean interior (Kwiatkowski et al., 2020; Stramma et al., 2012). Beyond the 21st century, further modelling shows that even if no additional carbon were emitted beyond the year 2020, the deep ocean has already been committed to experiencing a four-fold rise in O_2 depletion over the next few centuries (Oschlies, 2021).

Regionally increased inputs of reactive nutrients in conjunction with warming and reduced mixing are expected to increase the intensity and extent of oxygen minimum zones (OMZs) which would lead to a substantial increase in production and outgassing of the greenhouse gas N_2O (Codispoti et al., 2001; Hutchins and Capone, 2022; Voss et al., 2013). Through increasing redox processes involving phosphate and iron in ocean sediment, potentially runaway deoxygenation process may trigger mass extinction events on multi-millennial timescales (Meyer and Kump, 2008; Watson, 2016; Watson et al., 2017).

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Attribution of these changes has proven to be difficult: dissolved oxygen in the ocean is highly sensitive to climate change because it is influenced by both air-sea gas exchange, ocean circulation, biological production, and respiration. Thus, as opposed to warming and acidification, there is no direct forcing of the O_2 inventory due to the abundant atmospheric pool. Deoxygenation is nevertheless intrinsically linked to warming through its influence on solubility: global warming reduces solubility in surface waters, lowering air-sea gas exchange and impacting ocean circulation patterns and ventilation, which decreases O_2 supply to the ocean interior. The anthropogenic influence on deoxygenation is even more uncertain: Warming-enhanced stratification likely reduces ocean productivity and subsurface O_2 consumption, while regions with significant eutrophication may experience enhance productivity and subsurface deoxygenation through remineralization of the excess organic matter. Given the challenges of continuously measuring, projecting, and attributing changes in marine O_2 levels, particularly across the world's vast oceans, many studies tend to concentrate on regional deoxygenation when discussing abruptness (Section 4.3). Nevertheless, the observed ~2% decrease in the global ocean O_2 levels over the last ~60 years is considered abrupt on geological timescales. In line with these uncertainties, it is not yet fully established how the decline in ocean O_2 concentrations, and the evolution of changing ocean nutrient budgets develop in the long term under warming scenarios. Sedimentary records from past warm climates (e.g., Cretaceous ~90 Ma) indicate more intense OMZs, particularly near continental shelves in the proto-North Atlantic that may be linked with high temperatures and nutrient levels (Monteiro et al., 2012). However, a recent study from more moderate warm periods in the Eocene and Miocene (Auderset et al., 2022) suggest the opposite trend further complicating any straightforward response to warming. In the more recent Last Glacial Maximum (~21 ka), sedimentary records indicate less intense OMZs in tropical intermediate waters (Galbraith et al., 2013), but at the same time enhanced deoxygenation in the deep ocean (>~1500 m) (Jaccard and Galbraith, 2012). This glacial O_2 trend has been reproduced by a isotope-constrained ocean biogeochemical model and found to be due to a combination of temperature-dependent surface solubility, a more sluggish and shoaled overturning circulation, and enhanced productivity over the Southern Ocean driven by additional iron deposition (Somes et al., 2017). Overall, the sedimentary records paint a complicated picture indicating no simple deoxygenation response to warming and emphasize that all critical processes controlling O_2, both physical and biogeochemical, must be carefully considered in each region and timescale. Recent modelling studies have emphasized the importance of increasing nutrient inputs for global marine biogeochemical change, including deoxygenation. Increased input occurs via atmospheric deposition, riverine input, N_2 fixation, and redox-dependent sedimentary iron release (e.g., Bopp et al., 2022; Ito et al., 2016; Wallmann et al., 2022; Hamilton et al., 2020; Yamamoto et al., 2022). For example, Somes et al. (2016, 2021), have included all these processes together in a warming projection scenario (**Figure 3**). This novel model predicts that these nitrogen and iron source inputs, mostly importantly N_2 fixation and reductive

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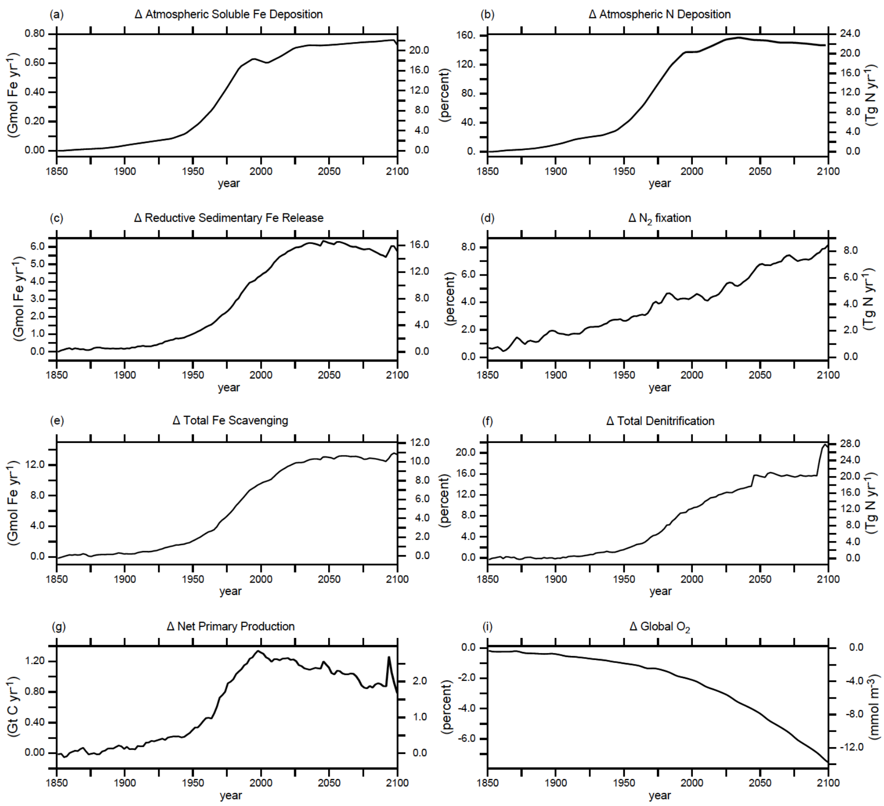

Figure 3: Globally integrated projected changes to marine biogeochemistry relative to the preindustrial (outer axes show unit values and inner axes show percent) in business-as-usual warming scenarios including increasing pollutants in atmospheric soluble iron deposition (Myriokefalitakis et al., 2018) (a) and atmospheric nitrogen deposition (Lamarque et al., 2013) (b) in reductive sedimentary iron release (c), N_2 fixation (d), iron scavenging (inorganic + particle) (e), denitrification (water column + sedimentary) (f), , Net Primary Production (g), dissolved O_2 concentration (h). The Model of Ocean Biogeochemistry and Isotopes (MOBI) includes a prognostic nutrient budget and inventories of the marine nitrogen (Somes and Oschlies, 2015) and iron (Somes et al., 2021) cycles, which are incorporated within the UVic Earth System Model of intermediate complexity (version 2.9; Eby et al. (2009)). The idealized model projections scenario prescribes business-as-usual increasing atmospheric CO_2 concentrations (reaching 830 ppm at year 2100 and atmospheric nutrient deposition based on independent ensemble inter-model averages (a,b).(see Landolfi et al. (2017) for additional model forcing details). Note that we assume the same rate of change for iron deposition as the nitrogen deposition scenario (Lamarque et al., 2013) at each model location since it is not provided and many of the key source processes (e.g., fossil fuel combustion) are the same.

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sedimentary iron release, increase in response to anthropogenic forcings, which significantly contributes to increasing Net Primary Productivity (>2%) and subsequently enhances deoxygenation in the 21st century (**Figure 3g,h**). Expanding OMZs in this scenario further enhanced redox processes in the water column and sediment porewaters (e.g., denitrification and iron reduction, **Figure 3**). In previous model versions where these nutrient source inputs were excluded (e.g., Landolfi et al., 2017; Stramma et al., 2012), the model predicted the opposite trend in the low latitudes, suggesting that increasing nutrient source inputs are an important contributor fuelling tropical marine productivity and deoxygenation in the Anthropocene. A positive feedback, caused by a concomitant increase in organic ligands for iron, has the potential to further amplify the reactions of ocean productivity to these changes (Volker and Ye, 2022).

4 Regional persistent changes

We will now look at regional abrupt changes in warming, acidification, and deoxygenation that can be interpreted as regime shifts for the biogeochemical realm. While the timescale for global abrupt changes was in the centennial to millennial category on a multi-millennial background, we deal now with abrupt annual to decadal changes that are faster and significant with respect to the pre-industrial or the historic period for which we have most observations. In contrast to extreme events, we will assess those changes that prevail regionally for a time that is significantly longer than the interval over which the actual abrupt change in state variables occurred.

4.1 Abrupt regional persistent changes in warming and other physical factors

We again start with abrupt changes in warming and other physical factors that have direct implications for marine biogeochemical changes.

4.1.1 Atlantic meridional overturning circulation and North Atlantic region

These changes include two classical tipping elements of the Earth system (Biggs et al., 2018; Lenton et al., 2008; Mckay et al., 2022). The Atlantic Meridional Overturning Circulation (AMOC) is the Atlantic branch of the global ocean conveyor belt circulation and is a critical element of the climate system with implications for the global climate and the efficiency of the meridional heat fluxes from low latitudes to polar regions. It thus has consequences for larger areas than only the Atlantic Ocean domain. Results from global coupled Earth system models as well as stand-alone experiments with large-scale ocean models and also observational evidence indicate consistently that the AMOC can change significantly when the surface

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density forcing through air-sea heat fluxes and fresh water fluxes is altered (e.g., Kuhlbrodt et al., 2007; Buckley and Marshall, 2016). Whether the AMOC will fully collapse in the future as a consequence of anthropogenic climate change is currently an open question. While large international model intercomparison projects estimate a full collapse as being unlikely, the possibility of a strong reduction in the AMOC remains (e.g., Collins et al., 2019; Schwinger et al., 2022a). Most Earth system models project a decrease in the AMOC from ca. 20 Sv (1 Sv = 10^6 m^3 s^{-1}) by several Sv over the 21st century (Collins et al., 2019; Meehl et al., 2007, see their instructive Figure 10.15; Eyring et al., 2021) depending on the strength of the warming scenario applied. While the overall magnitude of the current AMOC overturning is well constrained by observations such as the RAPID array, a comparison of the observed and simulated rate of change of the AMOC is more difficult to achieve because of the short length of the observational time series and also the existence of higher frequency variability (Eyring et al., 2021; Frajka-Williams et al., 2019). Also, while most parts of the North Atlantic surface waters warm under anthropogenic climate change, a "warming gap" in the Atlantic subpolar gyre has been identified that may be linked to AMOC variations (Menary and Wood, 2018). In this region, abrupt cooling events have been found which reveal varying degrees of strength depending on the warming scenario used (Swingedouw et al., 2021; Sgubin et al., 2017).

Recently, a new mechanism was identified that can contribute to AMOC changes. The variability of Labrador Slope Water (LSLW) as it penetrates from the subarctic into the Gulf Stream region has been investigated using a high resolution (1/12°) NEMO ocean model simulation, together with observations from the "Line W" moorings and EN4 climatology (New et al., 2021). The LSLW, which derives from the Labrador Current, was seen to penetrate as a boundary current into the Slope Sea (the region between the Gulf Stream and the eastern US-Canadian shelf-slope), and in particular into the Western Slope Sea (west of about 65°W), bringing it into close proximity with the Gulf Stream. Here, the LSLW interacts strongly with the Gulf Stream through the ejection of small-scale filaments, **Figure 4**. There are periods when the LSLW is fresher and more extensive (thicker) in the Slope Sea (e.g., 2003-2008), and these periods contribute an additional 1.3 Sv to the Gulf Stream transport and AMOC. These periods appear to be controlled by the wind stress curl near the Grand Banks and to alternate with periods of freshening in the North Atlantic. As such, it is possible that the changes in the LSLW offer a new mechanism for decadal variability in the Atlantic climate system, through altering the characteristics of the Gulf Stream and AMOC. Furthermore, the LSLW waters are both rich in nutrients and high in oxygen, and when the LSLW is more extensive, these waters invade the US-Canadian shelf and shelf slope, in particular through the Laurentian Channel, the Scotian Shelf and the Gulf of Maine, and thereby affect the ecosystems on the shelf (e.g., Claret et al., 2018). While currently this process appears to form part of a natural multi-decadal cycle (with potential feedback mechanisms under investigation), it is possible that this

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could contribute to a tipping point in the future if there were to be a suitable long-term shift in the wind stress patterns in the North Atlantic.

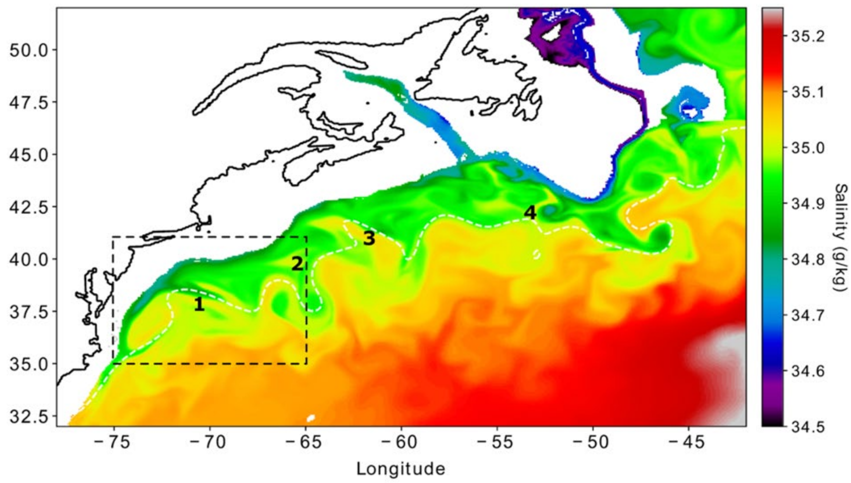

Figure 4: High-resolution (1/12°) NEMO ocean model output (a 5-day mean snapshot) showing the salinity of the Labrador Slope Water (LSLW) penetrating as a boundary current from the subarctic to the Gulf Stream, bringing fresher water as a boundary current near 500 m, and spreading across the Slope Sea. The dashed box, the Western Slope Sea, is a key area in which the LSLW interacts directly with the Gulf Stream through the ejection of small-scale filaments marked 1 and 2, while other ejection events (marked 3 and 4) contribute to the mixing elsewhere in the Slope Sea. The white dashed line shows the position of the Gulf Stream core (figure reproduced from New et al., 2021, under a Creative Commons licence; see New et al., 2021 for more details).

The North Atlantic Current (NAC) is the extension of the Gulf Stream as it crosses the North Atlantic, and may be viewed as marking the southern boundary of the sub-polar gyre. Modifications of this current system under climate warming have striking implications for oceanic tracer transports, as shown through a timeseries from 1985 to present (**Figure 5**).The Icelandic Marine Research Institute (MRI) has made biogeochemical observations quarterly at a time series station in the Irminger Sea (IRM-TS; 64.33°N, 28.0°W). Winter observations (January-March) of silicate in the relatively high salinity Atlantic water show a clear shift in silicate concentration around the year 2000 coinciding with higher salinity and temperature. The average near surface concentration from 1992-2020 is 6.67 mmol m^{-3}, where the first two decades of the observed time series are consistently above this average. Since 2001 the concentrations have been below the long-term average. **Figure 5**

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shows near surface (0-100 m average) concentrations of silicate in the Irminger Sea as deviations from the long-term average of this time series. At these high latitudes the end of winter nutrient concentrations fuel the spring bloom and lower silicate concentrations may shorten the spring diatom bloom. Similar trends have been reported in the Norwegian Sea and the Barents Sea (Rey, 2012; Gundersen et al., 2021) and have been attributed to changes in the position of the sub-polar gyre (Gundersen et al., 2021; Hatun et al., 2017; Fransner et al., 2023).

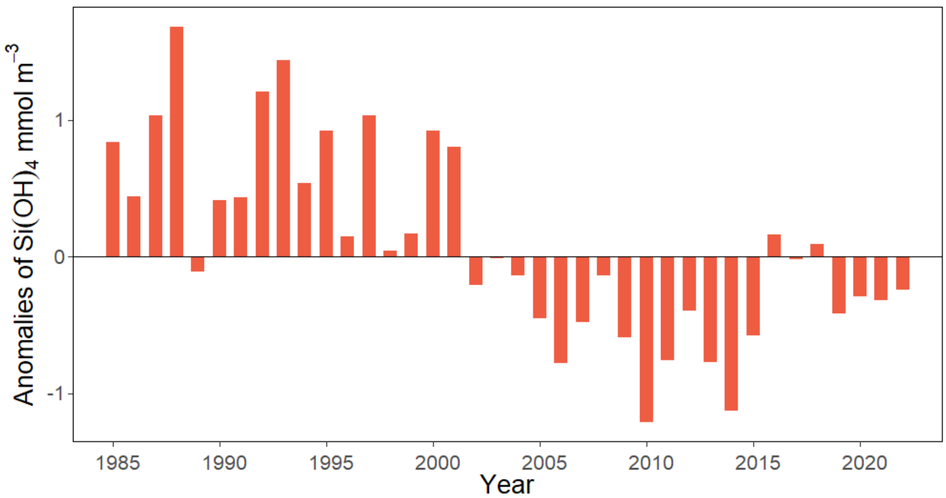

Figure 5: Near surface (0-100 m) anomalies of dissolved silicate concentrations (µmol L^{-1}) in the northern Irminger Sea (deviations from the long-term (1991-2020) average). Data source: For 1983-2013 Ólafsson (2016) and for 2014-2022 Ólafsdóttir et al. (2023).

Changes in the large-scale ocean circulation have down-stream effects on shelf areas as has recently been shown for the North Sea, with quickly occurring changes in the transport of biogeochemical tracers. The North Sea is a part of the North-Western European shelf that is enclosed on three sides by Great Britain and continental Europe, while the Northern side is open to the Atlantic. The main circulation pattern is characterised by an anticlockwise circulation, receiving Atlantic waters from three different currents in the northern boundary (the Fair Isle Current, the East Shetland Current, and the Western Norwegian Trench current, FIC, ESC and WNT in **Figure 6**) and exporting shelf waters to the ocean in the East through the Norwegian

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Trench (NT) mixed with the Baltic outflow. Climate change could significantly affect this pattern under the RCP8.5 scenario, with a progressive slowdown of all currents contributing to the exchange with the North Atlantic (Holt et al., 2018, who use a regional downscaled model forced by an Earth System Model projected into the future). The WNT is projected to experience an abrupt change under RCP8.5 between 2030 and 2060 when the current is projected to reverse its direction and instead of bringing Atlantic waters into the North Sea, will join the main branch of the NT current to export fresher shelf waters north-

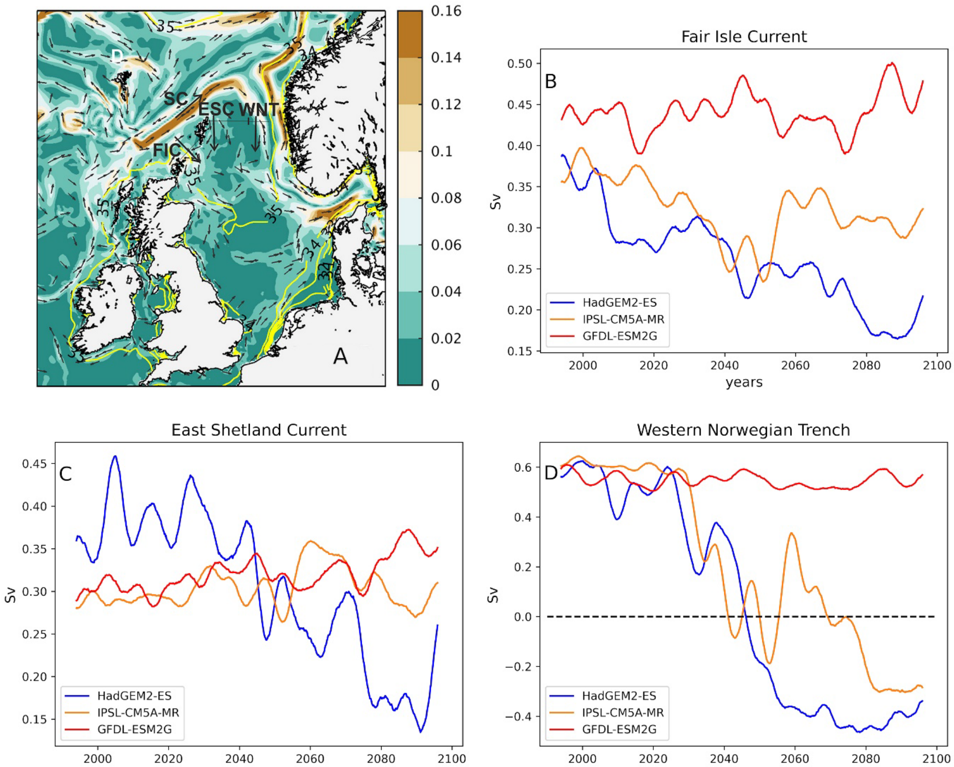

Figure 6: Depth mean currents (0-200m) for the present climate (1990-2020, A: adapted from Figure 1 in Holt et al., 2018) (CC-BY4.0) and future projections of the three main influx currents to the North Sea (B: Fair Isle Current – FIC; C: East Shetland Current – ESC; D: West Norwegian Trench – WNT) in a regional climate model driven by three different ESMs of decreasing ECS under the RCP8.5 scenario.

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wards. The main driver for such a change is a progressive freshening and subsequent increase in stratification in the Faeroe-Shetland channel and in the North Atlantic Current, linked to accelerated Arctic sea ice loss. However, these changes are only projected when the regional model is driven by an ESM of high Equilibrium Climate Sensitivity (ECS). **Figure 6** shows the evolution of the three influx currents (FIC, ESC and WNT) in regional projections driven by three ESMs of decreasing ECS: HadGEM2 (ECS 4.6), IPSL-CM5A-MR (ECS 4.1), and GFDL-ESM2G (ECS 2.4). The abrupt reversal of the WNT current is projected only in the case of the higher ECS model, while it is unstable when driven by the model with intermediate ECS and completely absent in the case of driving by the lowest ECS model. Similar differences are also projected for the other two currents, with the FIC decreasing only in the two models with the higher ECS, and the ESC decreasing only in the projection driven by HadGEM2. (These results are similar to those found by Tinker et al. (2016) who studied changes in the surface salinity of the North Western European shelf and the wider North East Atlantic.) Several consequences follow from the circulation changes shown in **Figure 6**: given that the North Atlantic influx is the major source of nutrients for the northern North Sea (Vermaat et al., 2008), a reduction of available nutrients and production, and impacts on oxygen and carbonate chemistry, would be expected in the future. This is indeed projected by Holt et al. (2018) in the eastern part of the northern North Sea, but it is compensated by an increase in its western part where the influence of fresher and nutrient rich waters from the southern North Sea and the Baltic Sea are important.

The Mediterranean Sea is one of the world's most vulnerable climate change "hot spots" (Cramer et al., 2018). Among the physical impacts of this context-specific warming, Pisano et al. (2020) showed that the Mediterranean Sea is warming 3.7 times faster than the global ocean. In particular, over the 2005-2020 period, the vertically integrated ocean heat content in the upper 700 m of the basin has increased considerably, with an acceleration of the subsurface warming being documented even during the past decade (Escudier et al., 2021). Despite its relatively small size, representing only 0.32% of the volume of the global ocean, the Mediterranean Sea constitutes one of the main reservoirs of marine biodiversity, being also characterized by the highest rate of endemism in the world (Bianchi and Morri, 2000). Furthermore, the warming signature is not exclusively confined to the sea surface and subsurface but can also propagate deeper into the water column, with implications for ocean circulation at basin scale and even larger, i.e. North Atlantic water mass formation. In fact, drastic thermohaline changes in the Mediterranean outflow into the Atlantic are being documented from 2013 onwards at the Strait of Gibraltar (García-Lafuente et al., 2021), where a marked warming rate of 0.339 ± 0.008°C decade^{-1} has been measured in the deepest layer of the outflow, which is one order of magnitude higher than any other found in any Mediterranean water mass. Climatic data analysis reveals diminished buoyancy fluxes to the atmosphere during the considered time frame, which in turn reduces the rate of formation of cold waters in the Western Mediterranean leading ultimately to a larger contribution of warmer

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intermediate waters to the outflow (García-Lafuente et al., 2021). Considering that the outflow may contribute to buoyancy loss at high latitudes in the North Atlantic, which preconditions the formation of the NADW and contributes boosts to the AMOC (Reid, 1979), the accelerating warming of the Mediterranean may indeed result in drastic changes in circulation at global scale.

4.1.2 High latitude warming and sea ice

Arctic Ocean warming is one of the most prominent climatic changes over the past few decades (Collins et al., 2019; Meredith et al., 2019) with a warming of the upper ocean (upper 2000 m) of up to 2.3 times the global mean rate, a phenomenon referred to as "Arctic Ocean Amplification" (Shu et al., 2022). This accelerated warming of the Arctic Ocean is mirrored in the Arctic atmosphere with the "Arctic Amplification" (Manabe and Stouffer, 1980), which consists of a warming of the lower atmosphere that is up to 4 times faster than global temperatures (AMAP, 2021; Rantanen et al., 2022) and changes in the wind patterns (Henderson et al., 2021; Simmonds and Li, 2021). While the causes of these "Amplifications" are still debated and very likely due to a complex combination of local and remote positive feedback loops in the atmosphere-sea ice-ocean system, the implications are clear and are not limited to the Arctic region (Previdi et al., 2021). In association with the loss of summer ice extent (Li et al., 2022), the summer sea surface temperature (SST) in the Arctic Ocean shows a linear warming trend (Steele et al., 2008; Timmermans and Labe, 2022) of 0.3 °C per decade while the linear warming trend in the global ocean annual mean SST is 0.1 °C per decade (Huang et al., 2022). The northeast Barents Sea and its atmosphere are now the most rapidly warming place on earth (Isaksen et al., 2022). The warming of the Arctic Ocean can be attributed to increased poleward heat and mass transport of warmer (temperate) water masses from the North Pacific or Atlantic which eventually overcomes winter surface heat losses to the atmosphere (Shu et al., 2022). This phenomenon, also referred to as "Borealization" or "Atlantification/Pacification" (Ingvaldsen et al., 2021; Polyakov et al., 2017) is expected to carry on and even intensify until the end of the century (Shu et al., 2022), keeping the heat in the ocean and altering the ability of the Arctic Ocean to work as a 'cooling machine' (Shu et al., 2021; Skagseth et al., 2020). Indeed, the "Borealization'' also relates to an intensification of currents (Wang et al., 2020b; Oziel et al., 2020; Woodgate and Peralta-Ferriz, 2021; Polyakov et al., 2020) and mesoscale activity (Armitage et al., 2020; Wang et al., 2020a) due to an increase in both buoyancy fluxes and wind stress (Timmermans and Marshall, 2020). Correspondingly, the advection potential for heat (Smedsrud et al., 2022), biogeochemical tracers (Oziel et al., 2022), and plankton organisms (Neukermans et al., 2018; Vernet et al., 2019; Wassmann et al., 2019; Kelly et al., 2020; Oziel et al., 2020) is enhanced.

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Under such climatic warming, Arctic Sea ice extent and thickness are affected (Stroeve and Notz, 2018; Thomas, 2017) and abrupt changes in sea ice distribution may occur (Drijfhout et al., 2015). Once a critical warming level of seawater and the overlying air are reached, even winter ice cover may vanish eventually (Bathiany et al., 2016; Hezel et al., 2014). While some negative feedbacks may delay the occurrence of an ice-free Arctic Ocean (Notz and Marotzke, 2012; Bitz and Roe, 2004; Hezel et al., 2012; Tietsche et al., 2011) in spite of the positive ice-albedo feedback (Curry et al., 1995; Holland et al., 2006), the already reduced summer ice extent can lead to critical changes in air-sea carbon and oxygen fluxes as well as changes in marine ecosystems (Wassmann et al., 2011; Steiner et al., 2021). In a Eulerian framework, the binary states of "sea ice on" and "sea ice off" can trigger regime shifts in the physical, chemical, and ecosystem realms (Loose et al., 2011).

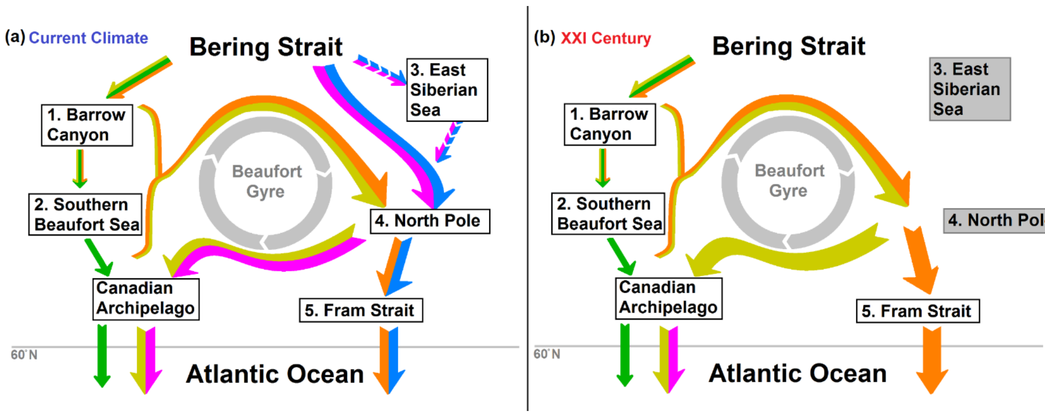

Figure 7: Schematics of the (a) current and (b) future (21st century) pathways of Pacific water across the Arctic Ocean. The direct route, in the current climate, from the Bering Strait to the North Pole and Fram Strait disappears in the future climate in CMIP6 projections with the UKESM model under SSP5 scenarios. (The figure is updated from Kelly et al. (2020) in agreement with the license CC BY 4.0.)

In addition, in future projections with UKESM (SSP5 scenarios), Atlantic water pushes Pacific water towards the North American coast, shortening Pacific water pathways, and pathways to the west disappear (e.g., the pathway from the Bering Strait via the North Pole to the Fram Strait), see **Figure 7**. These changes in the circulation pathways lead to the intrusion of new, invasive species of marine organisms from both the Atlantic and Pacific into the Arctic (Kelly et al., 2020).

Currently, the Southern Ocean (SO) contributes disproportionally to the uptake of excess heat from the atmosphere (Frölicher et al., 2015; Bourgeois et al., 2022), and its contribution to global heat uptake has increased over the recent past (Meredith et

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al., 2019). Over the last three decades, subsurface waters and surface waters north of the Antarctic Circumpolar Current (ACC) have warmed, while surface waters south of the ACC have cooled (Armour et al., 2016). Until 2100, the surface SO is projected to warm everywhere for all emission scenarios (by up to 2.1°C relative to preindustrial times for the SSP5-8.5 scenario) (Gutiérrez et al., 2021; Iturbide et al., 2021). In contrast to a projected 21st century decrease in SO sea ice extent (Roach et al., 2020), this has generally increased over the satellite era, but abruptly decreased to record-lows in 2017 (Parkinson, 2019; Meehl et al., 2019) and 2022 (Fetterer et al., 2017), possibly hinting at a persistent change (Eayrs et al., 2021). Concurrently, surface freshening of the SO over the past decades was mainly attributed to enhanced wind-driven northward freshwater transport by sea ice (Haumann et al., 2016). As a result of the changes in temperature and salinity distributions and of intensifying westerly winds, the ACC has accelerated over the last three decades, and this trend is projected to continue into the future (Shi et al., 2021). Surface freshening and warming also lead to stronger stratification which reduce the efficiency of the Southern Ocean in sequestering excess heat and carbon from the atmosphere to the deep ocean (Bourgeois et al., 2022). On the high-latitude continental shelves in the SO, precursors of Antarctic Bottom Water (AABW) have warmed and freshened over the observational record (e.g., Menezes et al., 2017; Strass et al., 2020), overlying substantial interannual variability in their water mass properties (Abrahamsen et al., 2019; Silvano et al., 2020; Gordon et al., 2020). For the highest-emission scenario, climate model projections suggest shelf bottom waters may warm by up to ca. 0.6°C by 2100 (Purich and England, 2021). Already today, coastal winds have systematically changed in some sectors of the high-latitude SO (from easterly to neutral or westerly winds), and this change is possibly sustained under on-going climate change (Holland et al., 2019). Ultimately, combined with changes in subsurface density gradients across the continental shelf break, these changes affect shelf-open ocean exchange (Thompson et al., 2018). The projected freshening of shelf waters due to enhanced glacial and ice-shelf basal melt contributes to the erosion of cross-shelf break density gradients, and to a reduction in the export of AABW precursors from the continental shelves to the abyss (Nissen et al., 2022). Furthermore, an eroded cross-shelf break density gradient facilitates a sudden increase in the on-shelf flow of warmer waters from offshore (Hellmer et al., 2017; Naughten et al., 2021; Nissen et al., 2023a; Haid et al., 2022). Notably, for the SSP5-8.5 scenario, bottom-water warming is projected to surpass 1°C on the Weddell Sea continental shelves as a result of a reversal in the density gradient (Nissen et al., 2023a), thereby exceeding even the local rate of warming in the atmosphere. Altogether, the persistent changes in water mass properties on the continental shelves directly affect ice-shelf basal melt, with some sectors already showing accelerated melt today (Amundsen Sea; Rignot et al., 2019).

4.1.3 ENSO and Monsoon

Large-scale modes of climate variability and seasonal climate patterns such as the El Niño Southern Oscillation (ENSO) in the Equatorial Pacific and the Monsoon systems in the Indian Ocean may change under climate warming and develop new persistent characteristics in their variability (Cai et al., 2021; Hsu et al., 2012; Xu et al., 2006a). Both mechanisms influence oceanic upwelling systems and hence biological production, the oxygen cycle, and air-sea carbon fluxes. During El Niño events, outgassing of CO_2 from the ocean is reduced temporarily (Keller et al., 2015; Jones et al., 2001). Although it has been unclear in earlier studies in which way ENSO will change under human-induced climate forcing (Collins et al., 2010), more recent results indicate a rising variability of future ENSO sea surface temperature and hence a higher ENSO magnitude under climate warming (Cai et al., 2021). On the other hand, Monsoon- induced seasonal upwelling events such as the Somalian upwelling in the Indian Ocean count among the strongest upwellings in the ocean and changes in the strength of these events can have substantial effects on local biological organic matter production, particle fluxes, and related interactions with the marine oxygen cycle (Bakun, 2017; De Verneil et al., 2022).

4.1.4 Greenland Ice Sheet, West Antarctic Ice Sheet, coastal erosion, and Arctic rivers

Firstly, we remark that freshwater discharge from the Greenland ice sheet melting processes (Sejr et al., 2017; Weijer et al., 2012) and a potential instability of the Antarctic coupled shelf-ice and ice sheet system (Nakayama et al., 2020) are directly affecting the ocean currents and mixing in the vicinity of these land masses and thus will also have an effect on marine biogeochemistry (in addition to that on sea level rise). Furthermore, changes in the matter content of the ocean (carbon, nutrient, and trace metal reservoirs) through increased or decreased coastal erosion in connection with sea ice retreat and wind changes can happen (Barnhart et al., 2014).

In more detail, rates of Arctic coastal erosion were calculated from wave undercutting and the associated fluxes were obtained for a historical simulation covering 1979-2015 (Rynders and Aksenov, 2022b; Rynders and Aksenov, 2022a). There is a high spatial variability of erosion and associated carbon and nutrient fluxes due to the geomorphology of the coast. The components of variability are a seasonal cycle imposed by the significant wave height, multi-annual variability associated with the Arctic Oscillation (AO) and a long-term trend associated with sea ice decline (Grigoriev, 2019; Nielsen et al., 2020). Years of extreme high or low erosion are caused by the sea ice distribution in the Siberian Seas. The Siberian coastline is transitioning from a lower to a higher coastal erosion regime, which may be considered a change point due to regional sea-ice decline. The currently observed accumulated erosion volumes are increasing in hotspots in Alaska and Siberia (Terhaar et al., 2021c; Nielsen et al., 2022) and such erosion overall dominates over the coastal build-up of sediments (Philipp et al., 2022). Arctic coastal erosion fluxes may impact the biogeochemistry and primary production in the North Atlantic, and there is a net export of phosphorus from the Arctic to the North Atlantic. For the Arctic, this net export is partially balanced by the Arctic coastal

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erosion flux which adds phosphorous to the Arctic from the land. However, the system is affected by the AO, and a positive AO state is associated with reduced connectivity between the Siberian Shelves and Fram Strait (Wilson et al., 2021), which means that in this case the highest erosion fluxes may not reach the North Atlantic. This interaction with the circulation pattern needs to be investigated further.

Turning now to the effect of rivers in the Arctic, the riverine flux of nutrients can support about one third of the Arctic NPP (Net Primary Production) (e.g., Terhaar et al., 2021c). The main region of increase in the NPP due to the riverine nutrient sources (in a 1° simulation with the NEMO ocean model coupled to the MEDUSA biogeochemical model) is in the coastal areas and the Arctic shelf seas (**Figure 8**). The flux of riverine nitrates to the Arctic is currently increasing in the American rivers and decreasing in the Siberian rivers (ArcticGro database, https://arcticgreatrivers.org/, last accessed 06.10.2023; Zolkos et al. (2022)), which suggests a differential change in the Atlantic and Pacific ecosystem provinces in the future.

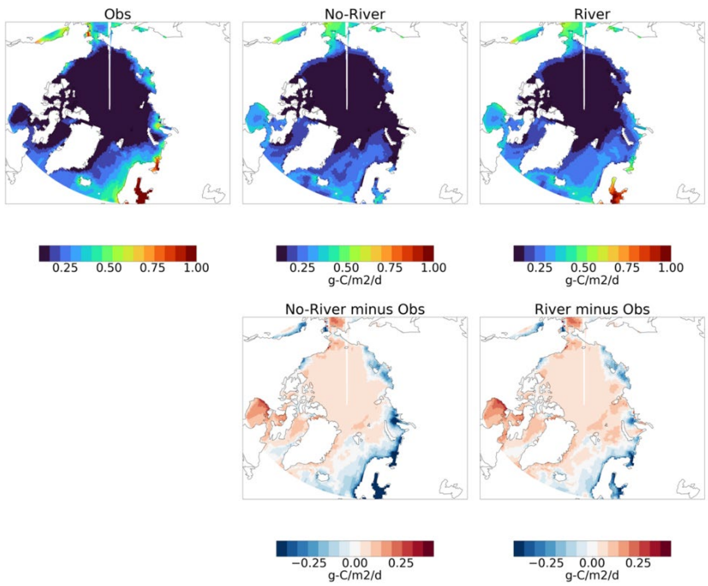

Figure 8: Impact of including riverine nutrient inputs to the ocean on the Arctic Net Primary Production (NPP) in NEMO-MEDUSA 1° historical integration, showing the observed (satellite-derived) values (Obs) and those in the model both with and without the riverine inputs of nutrients ("River" and "No-River" respectively).

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4.2 Abrupt regional persistent changes in ocean acidification and carbon fluxes

A review of trends and variability in oceanic CO_2 uptake has recently been conducted (see, Gruber et al., 2023). Gradual changes in ocean pH and carbonate saturation are tied to the net uptake of anthropogenic CO_2 from the atmosphere, while abrupt changes occur when additional forcings come into play. For example, the impact of vertical water exchanges on dissolved substances, such as CO_2, occurs in ocean upwelling regimes and in deep-water production areas. The northern North Atlantic is a hot spot for human-made CO_2 uptake per unit area (Sabine et al., 2004), meaning a decrease in deep-water production through overturning circulation change can lead to a sudden increase in upper ocean dissolved inorganic carbon concentration and a drop in pH (Fröb et al., 2016; García-Ibáñez et al., 2016). The Nordic Seas' fast flushing time means that its entire water column is expected to become undersaturated with respect to aragonite by the end of the 21st century (under a strong RCP8.5 warming scenario) (Fransner et al., 2022). The low buffering capability of cold water, which corresponds to a high Revelle Factor (Sabine et al., 2004), serves as an additional magnifying factor for pH changes in this region. Due to its vast area, the Southern Ocean is an overall strong sink for atmospheric carbon, with anthropogenic CO_2 absorbed and submerged during production of Antarctic Intermediate Water (AAIW), Subantarctic Mode Water (SAMW), (Sallée et al., 2010; Morrison et al., 2022), and Antarctic Bottom Water (AABW) formation (Orsi et al., 1999; Marinov et al., 2006). The subduction regions in the midlatitude Southern Ocean very likely dominate anthropogenic heat and carbon uptake (Ríos et al., 2012; Frölicher et al., 2015; Khatiwala et al., 2009; Zanna et al., 2019), although relevant processes for AABW formation on Antarctic shelves are not usually resolved in the models underlying this assessment (Heuze et al., 2013; Heuze, 2021). AABW can efficiently sequester anthropogenic carbon on much longer timescales, i.e., for several centuries compared to decades for intermediate and mode waters (e.g., Rodgers et al., 2003; Hauck et al., 2018) until the large-scale upwelling areas in the northern Pacific are reached by admixtures of AABW. AABW together with North Atlantic Deep Water formation dominates the volume transport into the ocean interior and reach the deep and abyssal global ocean (Morrison et al., 2022). However, the Southern Ocean is also a strong open ocean upwelling area, where "old" waters with a high CO_2 partial pressure emerge at the sea surface. Model results and observational evidence suggest that the Southern Ocean air-sea CO_2 fluxes switch from net release to net uptake as atmospheric CO_2 gradually rises (Le Quere et al., 2007; Gruber et al., 2023; Hoppema, 2004). Critically, carbonate saturation and pH are critically declining in the Southern Ocean, likely leading to detrimental conditions for calcifying organisms in the decades to come (Mcneil and Matear, 2008). In the following sections, we will examine these regions in more detail.

4.2.1 Arctic Ocean

Polar regions exhibit the greatest sensitivities to rising atmospheric CO_2 concentrations, with projected buffer capacity changes and acidification far outstripping those of lower latitudes (decline in surface pH by up to 0.45 in the Arctic and 0.4 in the Southern Ocean, respectively until 2100) (Bindoff et al., 2019; Fassbender et al., 2017; Kwiatkowski et al., 2020). This is due to their oceanographic and climatic specificities: the addition of CO_2 into seawater is facilitated by its high solubility at the typically low temperatures (Weiss, 1974); and these regions already have high concentrations of dissolved inorganic carbon and low concentrations in carbonate ion [CO_3^{2-}] leading to naturally low saturation states of calcium carbonate [$CaCO_3$] polymorphs (Steinacher et al., 2009). In addition, there is evidence for the support of persistent acidification in East Siberian Arctic Shelf regions through degradation of terrestrial organic matter and river run-off with high CO_2 concentrations (Semiletov et al., 2016). Ocean acidification thus threatens marine calcifying organisms in these regions by expanding areas undersaturated with respect to biogenic forms of $CaCO_3$ such as calcite and aragonite (Bates and Mathis, 2009; Orr et al., 2005; Bednaršek et al., 2014; Bednaršek et al., 2012; AMAP, 2018). As sea ice becomes thinner and easier to deform and crack during storm events in winter (Graham et al., 2019), leads open in the Arctic ice cover and increase the potential for ocean CO_2 uptake and vertical mixing (Fransson et al., 2017). Melting sea ice induced by global warming has multiple consequences for ocean acidification including (1) the release of aragonite-undersaturated meltwater which is low in carbonate ions and alkalinity (Chierici and Fransson, 2009; Fransson et al., 2009; Ericson et al., 2019; Ericson et al., 2023; Qi et al., 2022), (2) more favourable conditions for the upwelling of subsurface aragonite-undersaturated waters, (3) the extension of ice-free areas facilitating CO_2 uptake, and (4) the enhancement of organic matter production at the surface and respiration in bottom waters (Yamamoto et al., 2012; Yamamoto-Kawai et al., 2009; Cai et al., 2010; Qi et al., 2020). Rapid ocean acidification in the Arctic basins is reportedly due to meltwater-induced CO_2 uptake on decadal scales (Qi et al., 2022; Ulfsbo et al., 2018). For example, aragonite saturation has decreased faster in western Arctic Ocean basins (3-4 times) and in the Canada basin (10 times) than in other global open ocean regions (between 2003-2007) (Qi et al., 2022; Zhang et al., 2020). In the Chukchi Sea, the period of aragonite undersaturation has been estimated as more than twice as long as during pre-industrial conditions (Yamamoto-Kawai et al., 2016), and calcium carbonate undersaturated surface waters were already observed on freshwater-influenced shelves in the Arctic Ocean in 2005 (Chierici and Fransson, 2009; Fransson et al., 2015; Meire et al., 2015). Climate projections suggest that the Arctic ocean $CaCO_3$ lysocline will shoal at a rate of 18–25 m yr^{-1} (Orr et al., 2005; Skogen et al., 2014): for aragonite, the upper 1000 m are projected to be undersaturated before 2100 regardless of the chosen emissions pathway and in the 2050s under the high-emissions scenario (**Figure 9**) (Terhaar et al., 2021b), whereas for calcite, undersaturation is projected to occur before 2100 only under the high-emissions scenario. Shifts in the timing of the sea surface pCO_2 seasonal cycle have been identified under mid-to-high emissions scenarios, potentially leading to a worsening of Arctic summer acidification (Orr et al., 2022). In general, the seasonality of surface water carbonate chemistry of the Arctic Ocean and Barents Sea is highly affected by CO_2 drawdown

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through primary production, leading to increased aragonite saturation and undersaturation of CO_2 in the growth season (Ericson et al., 2023; Fransson et al., 2017). Yet, in laboratory experiments, Arctic phytoplankton assemblages have shown strong resistance capacities to ocean acidification (Hoppe et al., 2018b; Hoppe et al., 2018a; Wolf et al., 2019). Finally, increasing terrestrial organic carbon inputs from rivers and coastal erosion combined with increasing freshwater content, are expected to contribute significantly to Arctic Ocean acidification (Carmack et al., 2016; Semiletov et al., 2016).

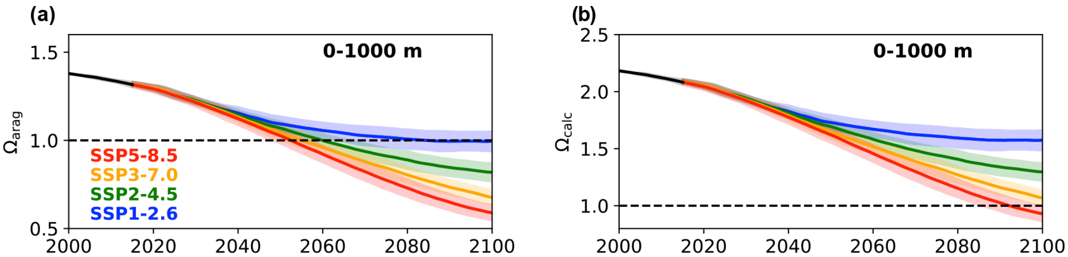

Figure 9: Arctic Ocean calcium carbonate saturation states over the 21st century. Time series of CMIP6 multi-model mean saturation states of (a) aragonite and (b) calcite from 2000 to 2014 (black) and from 2015 to 2100 for SSP1-2.6 (blue), SSP2-4.5 (green), SSP3-7.0 (orange), and SSP5-8.5 (red) averaged from 0 to 1000 m with ±1 SD (n=12–14) shown as a shaded area. (Figure cropped from Terhaar et al., 2021b; Creative Commons Attribution 4.0 License).

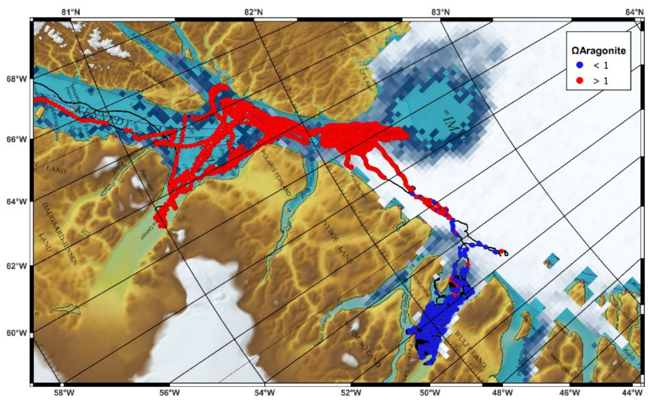

Figure 10: Near-surface (8 m) saturation state of aragonite (Ω_{arag}) computed from underway measurements of seawater pH and total alkalinity along the cruise track of the Ryder Expedition with Icebreaker Oden August-September 2019. The sea ice concentration is a snapshot from 1 September 2019 (AMSR-E, 89 GHz, 3.125 km, University of Bremen). (Modified following Stranne et al., 2021, Creative Commons Attribution 4.0 International License).

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Recent observations from the Arctic Ocean demonstrate how acidification can be amplified through ocean-ice dynamics. Record-high air temperatures were observed over Greenland in the summer of 2019 and melting of the northern Greenland Ice Sheet was particularly extensive (Stranne et al., 2021). In situ observations acquired from the Sherard Osborne Fjord showed that these extreme atmospheric conditions had a strong impact on ocean temperature and chemistry. Observed near-surface temperatures reached 4 °C, which is close to 3 °C higher than previously recorded in any ocean waters off northern Greenland. Thick multi-year sea-ice at the entrance of Sherard Osborn Fjord trapped the surface waters inside the fjord, forming a warm and fresh surface layer. Due to low near-surface salinities, the near-surface water of the fjord was highly corrosive with respect to the calcium carbonate polymorph aragonite (**Figure 10**) and twice as sensitive to ocean acidification from the uptake of atmospheric CO_2 compared to outside the fjord (Lincoln Sea, Nares Strait) and the adjacent Petermann Fjord. Nearly corrosive (aragonite saturation states below 1.2) surface water was also observed in Dijmphna Sound, North-East Greenland at 79°N in late summer 2012 and 2016, when the amount of meltwater was highest (Fransson et al., in review). In 2012, decreasing aragonite saturation due to freshening was counteracted by biological CO_2 consumption, which was not clearly observed in 2016 (Fransson et al., in review). Moreover, aragonite undersaturation has been observed in the East Greenland and West Greenland fjords in surface waters due to meltwater additions from the Greenland Ice sheet (Henson et al., 2023).

4.2.2 Destabilisation of sub-seabed permafrost and gas hydrates

Very few Earth System processes can cause large carbon transfer from land/ocean to the atmosphere during this century – top candidates are thawing land plus subsea permafrost and collapsing methane hydrates in and around the Arctic Ocean. Transformative progress depends on field-based science since compartments such as subsea permafrost, methane hydrates, sediments and subsurface water cannot be observed from space. There are huge uncertainties regarding inventories and functioning of these "Sleeping Giants" of the global carbon system – the prerequisites for understanding the present system and meaningful predictions of future releases. Most investigations of Arctic CH_4 and CO_2 have so far been focused on inland permafrost (e.g., Schuur et al., 2015; Keuper et al., 2020), yet there is growing concern about the effects of the coastal washout of permafrost-released organic matter (incl. on ocean acidification), and destabilization of Arctic Ocean subsea permafrost and methane hydrates. These systems are hard to access and associated with huge observational deficits, yet may be more vulnerable and more likely to hold tipping properties than gradually thawing land permafrost.

Marine sediment records are now accumulating to suggest that the abrupt increase in atmospheric CO_2 during the latest deglaciation was associated with rapid increases in remobilization of permafrost carbon to the Arctic Ocean, from both fluvial

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discharge and coastal erosion (e.g., Tesi et al., 2016; Martens et al., 2020). The adjunct land-ocean-atmosphere carbon couplings during these abrupt events is a frontier that will demand a combination of marine records and biogeochemistry-climate system modelling. The recent advent of the open-access Circum-Arctic Sediment Carbon Database (CASCADE, Martens et al. (2021)) facilitated the revelation that over 80% of recent terrestrial carbon input to the entire Arctic Ocean is released from the permafrost-covered Eurasian Arctic sector (Martens et al., 2022). An observations-constrained understanding of circum-Arctic regional differences in input and vulnerability of land carbon to the ocean will guide assessments also of changing ocean acidification (e.g., Semiletov et al., 2016) and nutrients driving productivity.

Some 60-80% of global subsea permafrost is located underneath the East Siberian Arctic Ocean (ESAO), the World's largest shelf sea system formed by sea-level rise after the ice age. The subsea permafrost system may have recently tipped to start releasing CH_4 as methane seawater concentrations are 10-100 times elevated over extensive scales throughout the overlying shallow water columns (average shelf depths of ca 50 m) (e.g., Shakhova et al., 2010; Steinbach et al., 2021). Investigations on sub-seabed drill cores retrieved from the Laptev Sea have revealed that subsea permafrost has warmed up, has passed the freezing threshold and is now thawing >10 times faster than genetically-related land permafrost (Shakhova et al., 2017). The subsea permafrost can be said to be more vulnerable than its nearby land sibling as studies demonstrate that carbon from subsea permafrost is thawed out 15 times faster (Wild et al., 2022). A first study using triple-isotope source fingerprinting of methane escaping the seabed suggest that, for the study area in the other Laptev Sea, the main source of the methane is from a deep thermogenic pool escaping from the thawing subsea permafrost, rather than from methane hydrates or from the subsea permafrost itself (Steinbach et al., 2021). Furthermore, The Eurasian Arctic Ocean margin has long been pointed to as a hotspot for potentially massive methane hydrates (e.g., Max et al., 2013). Warm Atlantic water inflow (e.g., Ivanov et al., 2016; Polyakov et al., 2017) may destabilize these hydrates, yet published observational data are so far lacking. Taken together, there are strong motivations to expect abrupt changes in release of carbon/methane from cryosphere carbon reservoirs in the coastal and subsea Arctic system, with potential for cascading effects on regional ocean-atmosphere carbon balances, ocean acidification and many other ocean biogeochemical systems (e.g., Wunderling et al., 2023).

4.2.3 Southern Ocean

In addition to contributing disproportionally to uptake of excess heat, the SO also plays a significant role in the uptake (Frölicher et al., 2015) and storage (Gruber et al., 2019b) of anthropogenic carbon, which is expected to continue through the 21st century according to model projections (e.g., Kessler and Tjiputra, 2016; Hauck et al., 2015; Terhaar et al., 2021a; Bourgeois et al., 2022). Due to its physical setting and its chemical characteristics the SO is a naturally low-Ω_{arag} environment

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(Orr et al., 2005) meaning that wide-spread aragonite undersaturation can also be expected here (McNeil and Matear, 2008; Hauri et al., 2016; Negrete-García et al., 2019; Fontela et al., 2021) Shallow saturation horizons may emerge suddenly before the year 2050 on a seasonal scale for specific forcing scenarios (McNeil and Matear, 2008) and even for an emission-stabilization scenario (Negrete-García et al., 2019). Coastal SO regions are generally considered to be a strong sink of anthropogenic CO_2 (Arrigo et al., 2008), mainly due to strong summer-time biological activity (Monteiro et al., 2020; Ogundare et al., 2021; Ingrosso et al., 2022). On the continental shelves, spatio-temporal variability in Ω_{arag} is large and mainly controlled by the complex interplay between strong primary productivity (increasing Ω_{arag}) and freshwater input from sea ice, glaciers, and ice shelves (decreasing Ω_{arag}), with episodic aragonite undersaturation already observed in some regions (Hauri et al., 2015; Ogundare et al., 2021; Lencina-Avila et al., 2018). The future evolution of carbon cycling in the SO coastal regions will critically depend on changes in the combined physical-biological system. Projections with a physical-biogeochemical model with high grid resolution on the Antarctic continental shelves suggest a) strong acidification trends over the 21st century throughout the water column in the coastal regions, with shelf bottom-water pH declining at down to -0.0075 units yr^{-1} in a high-emission scenario in the Weddell Sea (Nissen et al., 2023a) and aragonite undersaturation being ubiquitous in all high-latitude regions by 2100 for the three highest-emission scenarios (Nissen et al., 2023b), and b) abruptly attenuated deep-ocean carbon sequestration under the highest-emission scenario in the Weddell Sea due to a shift of shelf water masses to lighter densities as a result of a strong local warming and freshening (Nissen et al., 2022).

Further, while the SO is an essential sink of CO_2 and excess heat (Frölicher et al., 2015; Fung et al., 2005; Khatiwala et al., 2009; Gruber et al., 2019a), model projections still indicate a large uncertainty in the future sink of anthropogenic CO_2 (Bourgeois et al., 2022). Simulated SO changes under the high emission scenario include but are not limited to, sea ice loss, ocean acidification, and a decrease in CO_2 buffer capacity (Fassbender et al., 2022; Fassbender et al., 2017; Moore et al., 2018; Kwiatkowski et al., 2020; Chikamoto and Dinezio, 2021; Hauck et al., 2015) While emergent constraints have shown success in constraining uncertainty in the SO CO_2 sink projections in recent years (e.g., Bourgeois et al., 2022; Terhaar et al., 2021a), nevertheless, changes in future mechanisms remain poorly understood. Understanding how climate change alters the SO's ability to regulate the CO_2 and heat exchanges, and their governing mechanisms remain a crucial endeavour to strengthen confidence in future projections. A recent study demonstrated that the anthropogenic forcing leads to a major shift in the mechanism, position, and seasonality of the carbon uptake under the high emission scenario in the SO (Mongwe et al., 2023, in review. The region of dominant CO_2 uptake shifts from the Subtropical to the Antarctic region by the end of the 21st century. In the subtropics, the reduction of kinematic CO_2 solubility in summer seasons as the ocean warms reduces CO_2 uptake in the future climate despite higher atmospheric CO_2. Thus, the annual mean CO_2 sink only increases by ~ 43% in the subtropics although atmospheric increases by over a factor of 2.5 in the high emission scenario (Mongwe et al., 2023, in review; Chikamoto and Dinezio, 2021; Lovenduski and Ito, 2009). However, in the Antarctic region (south of the Polar Front), the warming-driven sea ice melt, increased ocean stratification, and mixed layer shoaling, a weaker vertical carbon gradient reduces the seasonal DIC entrainment while enhancing seasonal warming and cooling rates (dSST/dt). Together, these trigger the shift from mixing-driven outgassing to a solubility-driven uptake during winter seasons in future climate. By the end of the 21st century, the Antarctic operates in a hybrid mode between biologically driven summertime and solubility-driven wintertime uptake with further amplification of biological uptake by the increasing Revelle factor. This poleward shift in the CO_2 sink region initiates between 2040-2050 when the sea-ice loss exceeds 5 -10%. The annual mean CO_2 sink increases by nearly 450% in the Antarctic region with respect to the present climate by the end of the 21st century (Mongwe et al., 2023 submitted).

4.2.4 North Atlantic and Nordic Seas

The subpolar North Atlantic is a key area for anthropogenic carbon uptake. In this region, advection of intermediate water depleted in anthropogenic carbon into the surface provides a large potential for carbon dioxide uptake (Ridge and Mckinley, 2020) while deep convection transports waters high in CO_2 away from contact with the atmosphere (Halloran et al., 2015; Rhein et al., 2017; Lee et al., 2003; Goris et al., 2023; Anderson et al., 2000). The cooling in the subpolar gyre over the past decade ("warming hole") has increased the solubility-related uptake of CO_2 in this area (Fröb et al., 2019). In the future climate, models projects that as the Arctic Ocean loses more sea-ice, early sea-ice retreat and greater surface warming will eventually weaken the solubility CO_2 uptake in summer and reversing the seasonal cycle of pCO_2 (Orr et al, 2022). In the northern Barents Sea, sea ice loss and a greater influx of Atlantic waters have led to higher surface water fCO_2 (corresponding to pCO_2 but taking deviations from an ideal gas into account) between 1997-2020 (Ericson et al., 2023), but limited effects on pH due to their compensatory effects (Fransner et al., 2022). For the overall Nordic Seas, the mean decrease in pH over the last four decades is slightly larger (0.0025 yr^{-1}) than the global mean for surface water (ca. -0.0018 yr^{-1} or -0.0017 yr^{-1}, Lauvset et al. (2015), Chau et al. (2023), Pérez et al. (2021), see also the reprocessed data product between 1985 and 2021, from Copernicus: https://data.marine.copernicus.eu/product/GLOBAL_OMI_HEALTH_carbon_ph_area_averaged/description; last accessed 06.07.2023). However, there are large regional differences, and the Norwegian Sea shows almost twice the annual pH decrease (0.0034 yr^{-1}) compared to other time series stations (Fransner et al., 2022; Skjelvan et al., 2022). In the Irminger and Iceland seas, observations recorded increasing trends in hydrogen ion concentration [H^+] of more than 40 pmol kg^{-1} yr^{-1} both at the surface and below 600 m (Pérez et al., 2021) and a decline in Ω_{arag} of up to -0.0052 ±0.0007 yr^{-1} since 1991, which corresponds to a shoaling of Ω_{arag} isolines by 6-34 m yr^{-1} (García-Ibáñez et al., 2021). Similar rates of acidification have been

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observed between 1994-2021 in the Norwegian Sea (Skjelvan et al., 2022) and off the Iberian Peninsula (Flecha et al., 2019; Fontela et al., 2020). Together, these rates of acidification threaten the habitat of cold-water corals in the area (Fontela et al., 2020; García-Ibáñez et al., 2021). At the position of the Irminger Sea time Series (IRM-TS; 64.33°N, 28.0°W) station, north of "warming hole", the weak stratification allows warming, salinification and CO_2 uptake to reach down to ca. 1000 m. The acidification trends are even stronger in the deep layer than in the surface layer (44.2 ± 1.0 and 32.6 ± 3.4 pmol kg^{-1} yr^{-1} of [H^+]$_T$, respectively; Pérez et al. (2021)). For the surface layer, the driver analysis showed that warming contributes up to 50% to the increase in [H^+]$_T$ with low effect in $CaCO_3$. The anthropogenic CO_2 increase is the main driver of the observed acidification in the whole column of water.

The subpolar North Atlantic region is characterised by a strong "biological carbon pump" that draws down surface carbon levels driving atmospheric CO_2 uptake through primary production and the subsequent export of biologically-fixed CO_2 to the deep ocean (Sanders et al., 2014; Henson et al., 2022). Proxy data indicate a decline in Net Primary Production (NPP) in the subarctic Atlantic corresponding to a decline in subpolar gyre strength (Osman et al., 2019). CMIP6 models project, a global decrease in NPP, which is most pronounced in the North Atlantic and western equatorial Pacific and is expected to occur during the 21st century (Kwiatkowski et al., 2020). The cause is thought to be increased stratification leading to decreased euphotic zone nutrient, but NPP might additionally be affected by sudden changes in temperature and mixed layer depth. Abrupt cooling in the north Atlantic subpolar gyre accompanied by a significant shoaling of the mixed layer is projected to occur in both CMIP5 (Sgubin et al., 2017) and CMIP6 models (Swingedouw et al., 2021), with a 36% probability of this occurring by 2030 in the latter. This would directly affect regional CO_2 uptake by increasing the solubility of CO_2 but negatively impacting biological activity. In addition to magnitudes of NPP and phytoplankton biomass, the seasonal timing, i.e., its phenology, is also projected to change potentially impacting the entire ecosystem via a mismatch between higher trophic levels and food availability (Durant et al., 2007; Asch et al., 2019), thereby affecting carbon uptake and transfer to depth in the region. Such shifts have already been observed in the North Sea (Chivers et al., 2020; Edwards and Richardson, 2004) and simulated in models (Henson et al., 2018; Yamaguchi et al., 2022; Hieronymus et al., 2023 in review). In the latter, the earlier bloom onset and peak were attributed to shallower mixed layers early in the growth season and colder temperature and reduced nutrient supply, respectively (Yamaguchi et al., 2022). Examining variability and changes in the North Atlantic Bloom based on observations, a decrease in the Chl-a seasonal mean and maxima is found from the 2000s to 2010s over 3 hot-spot regions: the Northern UK region, Southwest Greenland and North of Iceland. Over the rest of the North Atlantic (28 and 66°N), Chl-a shows a decrease in the seasonal maxima and an increase in the seasonal mean, indicating that the bloom

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has a longer duration in 2010s. Extremes in Chl-a are found more frequently in the 2010s in the Labrador Sea, likely due to changes in deep-water convection.

4.2.5 Mediterranean

Furthermore, future acidification trends can be exacerbated by the continuous contribution of the acidified Mediterranean outflow through the Strait of Gibraltar, as deep layers of the Mediterranean Sea display a noticeable temporal decrease of pH (Flecha et al., 2019). The relatively higher acidification rates in deep water masses are attributable to specific features of the basin i.e. an increased buffering capacity of the carbonate system due to a high alkalinity, that leads to a large absorption of anthropogenic CO_2 that is efficiently transferred to the Mediterranean Sea's interior (Hassoun et al., 2022). The fast overturning time of Mediterranean waters allows a complete renewal of water in the basin in a short period of time in relation to the global ocean and consequently, highly acidified surface waters transport this signature to deep layers in a shorter time frame (Hassoun et al., 2022). High resolution model projections forecast for the RCP8.5 scenario a pH decrease at the end of the century of about -0.25 and -0.2 units in upper and intermediate waters respectively, whereas under a more conservative scenario (RCP4.5) the decline in pH significantly slows down during the second half of the century, yielding an end-of century pH change of -0.08 units (Reale et al., 2022). The analysis also shows profound alterations in nutrient contents, Net Primary Production, phytoplankton respiration and carbon stock under both scenarios along with uniform surface and subsurface reductions in the oxygen concentration driven by the warming of the water column and by the increase in ecosystem respiration (Reale et al., 2022).

4.2.6 Equatorial upwelling/ENSO

After the Southern Ocean, the equatorial ocean is expected to become the second most important oceanic region for anthropogenic CO_2 uptake (integrated over the entire respective region) towards the end of this century (e.g., Roy et al., 2011). The increasing atmospheric CO_2 partial pressure reduces the air-sea CO_2 gradient there preventing outgassing of older CO_2 coming from the ocean interior (with avoided outgassing serving as a net sink). High interannual variability governs the equatorial air-sea CO_2 flux with a persistent trend towards increasing variability with climatic warming, primarily due to ENSO activity and increasing Revelle Factor (Gruber et al., 2023) in parallel with a mean overall decline in surface water pH (Sutton et al., 2014). Acidification can accelerate the destruction of warm water coral reef systems that are already under temperature stress and associated bleaching through additional negative effects on the coral physiology (Hoegh-Guldberg et al., 2007; Anthony et al., 2008; Cornwall et al., 2022).

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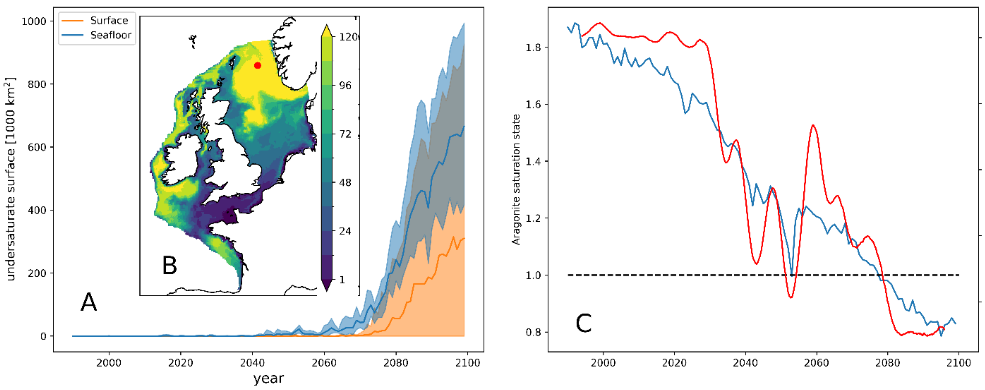

Figure 11: A Extension of aragonite undersaturated area in surface (orange) and bottom waters (blue)showing the annual average (solid line) and seasonal minimum/maximum (shaded). B: Frequency in months of aragonite undersaturation at the seafloor between 2080-2099, with yellow areas permanently undersaturated. C: Seafloor aragonite saturation state (blue line; left y axis) in the Eastern part of the Northern North Sea (red dot in panel B) compared to the intensity of the Western Norwegian Trench current (red line; right y axis).

4.2.7 Coastal and shelf sea changes

Coastal areas are prone to acidification events due to changes in circulation and the interaction between the open ocean and shelf waters through estuarine exchange and upwelling flow patterns (Walsh, 1991). Upwelling of older water and onshore advection in particular can contribute to progressing acidification in continental margin, shelf sea areas, and estuarine systems (Feely et al., 2008; Feely et al., 2010).

Shelf seas (water depth ⩽ 200m) are particularly susceptible to seasonal bottom layer acidification during summer (Rippeth et al., 2005), as thermal stratification limits vertical exchange, preventing the CO_2 produced in organic material respiration from outgassing to the atmosphere (Bates et al., 2009; Zhai, 2018). As increased atmospheric CO_2 uptake preconditions winter waters with higher CO_2 content, bottom waters become more susceptible to crossing critical acidification thresholds during summer. This is exemplified by regional climate projections for the northwestern European shelf under the RCP8.5 scenario projecting aragonite undersaturation in bottom waters starting around 2050, and in surface waters about 20 years later (**Figure 11a,b**). While higher temperatures and primary production are likely to keep surface waters oversaturated in summer, undersaturation in bottom waters is projected to cover a minimum of about 420,000 km^2 (39%) of the surface area of the shelf

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sediments by the end of the century (**Figure 11 a**). In the northeastern region of the North Sea climate change-induced circulation changes (see section 4.2) are projected to exacerbate acidification: a reduction in the influx of oceanic water in the North Sea and the reversal of the Western Norwegian Trench current allow for fresher water masses from the Baltic Sea to expand in the region. As they are characterised by lower total alkalinity, they reduce the buffer capacity and increase acidification (see **Figure 11c** for the close link between the bottom-water aragonite saturation state and the weakening and a reversal of the Western Norwegian Trench current).

4.2.8 Lysocline/Calcium carbonate compensation depth changes

Surface waters are most susceptible to decreasing $CaCO_3$ saturation states and pH values as a consequence of anthropogenic carbon from the atmosphere as documented by Eulerian time series measurements (Bates et al., 2014). However, ocean acidification signals are also already being observed in the ocean at deeper levels such as in the Iceland Sea (Ólafsson et al., 2009) and in the North Atlantic (Vázquez-Rodríguez et al., 2012; Pérez et al., 2021). In some areas of the Nordic Seas, a pH drop can be detected down to depths of 2000 m (Fransner et al., 2022). The shoaling of both the$CaCO_3$ lysocline (the depth interval over which a sudden corrosiveness for $CaCO_3$ is encountered) and the calcium carbonate compensation depth (CCD; the point at which $CaCO_3$ dissolution and $CaCO_3$ from particle fluxes out of shallower layers compensate; below the CCD, no $CaCO_3$ sediments would be found) have a strong impact on deep-sea ecosystems including cold water corals (Fransner et al., 2022; Gehlen et al., 2014; Guinotte and Fabry, 2008). A rapid shoaling of the $CaCO_3$ lysocline can also occur as a result of secondary saturation horizons with corrosiveness at surface and at depth with only an intermediate water depth being a non-corrosive refuge as documented for the Southern Ocean aragonite saturation horizon under human-induced CO_2 forcing (Negrete-García et al., 2019; Hauck et al., 2010).

4.2.9 Changes in iron biogeochemistry

The effects of ocean acidification, surface warming and the contribution of organic matter in certain areas (tropical Atlantic, eastern boundary upwelling regions and the Arctic) have direct impact on the processes that control iron (Fe) biogeochemistry. The persistence of Fe, both as Fe(II) and Fe(III), in the ocean, is a function of various physicochemical parameters (pH, T, as well as S) and the amount/quality of organic matter present (Santana-Casiano et al., 2022). Fe(II) tends to oxidize to Fe(III), and over 99% of the soluble fraction of Fe(III) is complexed with organic ligands. However, Fe(II) can also be found in oxic conditions in the ocean, and both Fe(II) and Fe(III) can be complexed with organic ligands and involved in different redox reactions. These effects, both individually and as part of a complex system, impact different chemical and biological processes that take place in the ocean and which are themselves affected by climate change.

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While a warming scenario tends to favour Fe(II) oxidation and affects the ionic interactions of trace metals in the marine environment, acidification favours the persistence of Fe(II) as when pH decreases Fe(II) oxidation processes slow down and Fe(III) solubility increases. Moreover, deoxygenation will also slow down the Fe(II) oxidation process. With a doubling of pCO_2 by the end of the 21st century leading to a pH decrease of 0.3 units and a temperature increase of 2ºC, the half-life time, $t_{1/2}$, for Fe(II) will increase by 138% in temperate waters (~20º) and by 129% in Arctic waters (~2ºC) (Gonzalez-Santana et al., 2021).

Organic matter also plays an important role in both Fe(II) and Fe(III) availability, and can cause the rate of oxidation of Fe(II) to increase, decrease, or not change at all in processes affected by the pH changes, depending on the type and nature of the functional groups present on the organic compounds (Santana-Casiano et al., 2000). It can also reduce Fe(III) to Fe(II), and increase the solubility of Fe(III) in the ocean (Liu and Millero, 2002). Ocean acidification effects (particularly on the acid-base chemistry of the chelating ligands) combined with multi-stressor environmental challenges thus alter the availability and mobilization of dissolved Fe (depending on the organic ligand characteristics, see Shaked et al. (2020)) that can impact its availability to phytoplankton and have knock-on effects on the biological carbon pump (Ye et al., 2020). The binding of Fe to organic ligands is also a major determinant of its solubility in the ocean. The fact that these ligands themselves are a product of biological activity creates the potential for feedbacks, both positive and negative, which can act to amplify or mediate climate-related changes in iron availability. These feedbacks have been studied in a global box model of the oceanic iron cycle (Volker and Ye, 2022). In this study it was first shown that including a description of the cycling of organic ligands similar to the one in Volker and Tagliabue (2015) into the model improved its fit of the phosphorus and iron cycle to data. Although the nutrient data did not completely suffice to constrain all parameters describing the ligand cycling in the model, it was shown that the overall feedback caused by the biological production of ligands is likely positive, albeit not very strongly so. This means that changes in the availability of iron caused by external, climate-related factors could be somewhat stronger than extrapolated based on constant ligands.

4.3 Abrupt regional persistent changes in deoxygenation and relevant nutrient fluxes, recent findings

A number of review papers on deoxygenation include a discussion about respective regional hotspots (Limburg et al., 2020; Stramma et al., 2010; Gruber, 2011; Keeling et al., 2010; Breitburg et al., 2018; Zhang et al., 2010). Following the observed widespread global O_2 decline, several ocean regions now exhibit persistent O_2 loss. This O_2 loss is evident through enlarging OMZs such as found in the Arabian Sea, the Eastern tropical South Pacific Ocean, and the Eastern tropical North Pacific Ocean (Beman and Carolan, 2013). Many populated coastal zones that receive large inputs of nutrient enrichments from rivers

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(e.g., eutrophication zones of the Baltic Sea, Gulf of Mexico, etc.) suffer accelerated O_2 consumption and therefore enhanced deoxygenation (Zhang et al., 2010; Diaz and Rosenberg, 2008). The un-populated high latitudes experience increased stratification due to the warming of the upper ocean combined with the climate change-induced freshening, which reduce the recirculation of O_2-rich surface waters (Oschlies et al., 2018). The latest ensemble of Earth system models from CMIP6 project detectable deoxygenation throughout most of the upper 2000 m prior the end of the 21st century (Tjiputra et al., 2023).

4.3.1 Development of OMZs

The main spatial structure of marine dissolved oxygen concentrations is tied to the production of organic matter in the euphotic surface layer (O_2 production during photosynthesis), air-sea gas exchange, and remineralisation of organic matter in sub-surface regions and the ocean interior (Sarmiento and Gruber, 2006). Oxygen utilisation, accordingly, is largest where the strongest attenuation of the vertical organic carbon flux takes place, i.e. in the depth range of ca. 100-750 m depth (Keeling et al., 2010; Martin et al., 1987). The associated oxygen minimum zones (OMZs) are particularly vulnerable to become ODZs when the O_2 concentration becomes lower than respective physiological thresholds for organisms. The spreading of OMZs is a useful indicator for progressing ocean acidification because enhanced remineralisation of organic matter under oxygen consumption increases the DIC concentration locally further (Keeling et al., 2010; Limburg et al., 2020). In upwelling areas, OMZs are particularly likely to occur as already "old" water with low oxygen concentrations is lifted towards the upper ocean and the associated nutrients stimulate further the organic matter production at the sea surface (Engel et al., 2022). However, open ocean low O_2 concentrations are not limited to widespread OMZs, but can occur also in mesoscale eddies that are embedded in the mean flow (Karstensen et al., 2015).

4.3.2 Changes at high latitudes and ocean ventilation sites

Oxygen is brought into the ocean interior through gas exchange and subsequent transport and mixing by the ocean circulation. Of special importance are (1) thermocline ventilation in sub-polar and subtropical areas, where water mixes into the ocean interior from outcrop areas of isopycnals along layers of equal density into the ocean interior (Jenkins, 1998; Reverdin et al., 1993) and (2) areas of active deep-water production (deep convection) (Kortzinger et al., 2004; Rhein et al., 2017). During ongoing convective events in winter, water may only be in contact with the atmosphere for short periods and hence full dissolution equilibrium may not be achieved (Wolf et al., 2018). In contrast, newer results suggest that bubble mediated gas exchange can even lead to an enhanced O_2 uptake during convection (Sun et al., 2017; Atamanchuk et al., 2020). A weaker AMOC and a decline in deep-water production can potentially even lead to an ocean deoxygenation signal far away from the source water areas. However, regionally transient increases in interior ocean O_2 concentrations can also occur as documented

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for the southern hemisphere where thermocline oxygen increased in the 2000s following stronger wind forcing and respective ventilation (Talley et al., 2016). In the future, a reduction of deep water formation on Antarctic shelves may not only strongly affect local ecosystems (Nissen et al., 2023b), but also the entire abyssal ocean (Matear et al., 2000; Frölicher et al., 2020).

During the past five decades, the Arctic Ocean represented about 8 % of the global ocean O_2 content changes despite occupying only 1 % of its volume (Schmidtko et al., 2017), therefore contributing disproportionally to deoxygenation relative to its size. Recent studies show that the Arctic Ocean will experience deoxygenation rates within the 200–3000 m layer of 0.3–3.7% by 2100 (Bindoff et al., 2019; Sweetman et al., 2017). This general result is however an average and hides large regional contrasts in the highly heterogeneous Arctic environment (Brown et al., 2020). Arctic coastal areas and continental shelf seas may remain almost unaffected by deoxygenation or may even experience an increase in oxygenation in the future (Gong et al., 2021), however, open ocean areas and deep interior Arctic basins are among the most affected regions of the global ocean (Breitburg et al., 2018; Gong et al., 2021), showing some of the largest decreases in O_2 concentrations of the global ocean (>5 % / decade) (Oschlies et al., 2018). Therefore, the open ocean areas of the Arctic Ocean seem particularly vulnerable to future deoxygenation (Kwiatkowski et al., 2020). Recent results from FESOM2.1-REcoM simulations in a high-resolution Arctic Ocean set-up suggest that most of the O_2 decrease may occur in the meso-pelagic zone (200-1200m) after the 2030s, with the exception of the low emission scenario SSP1-2.6 (**Figure 12a**). In the benthy-pelagic zone (1200-3000m), the O_2 concentration follows the current increasing trend until an eventual inflexion point in the 2060s with an O_2 decrease, again excepting the low emission scenario (**Figure 12b**). This Arctic Ocean vulnerability, particularly at the sub-surface, may be due to a combination of several environmental factors. The first factor is the Arctic Ocean geography: a semi-enclosed sea surrounded by land with poor connectivity with the global ocean through narrow gateways (Timmermans and Marshall, 2020), a specificity that makes it difficult for the Arctic Ocean to redistribute low-oxygenated water to adjacent seas. The second factor is the strong increase in stratification in the Arctic central basins (Carmack et al., 2016) due to surface freshening in the Pacific-influenced Amerasian basin (Solomon et al., 2021), while the Atlantic-influenced Eurasian basin is rather impacted by increased heating from advective sources (Polyakov et al., 2017). In both cases, increased stratification affects O_2 levels at depth (Lévy et al., 2022), which result from the balance between respiration processes (sink) and vertical mixing that replenishes surface O_2-rich waters (source). The freshwater accumulation and warming at the surface increase stratification, reduce mixing, and decrease O_2 solubility, while warming at depth enhances respiration processes (Brewer and Peltzer, 2016). Another reason that makes the Arctic Ocean particularly vulnerable to deoxygenation is the continuous increase in primary production (e.g., Lewis et al., 2020) as well as increasing terrigenous inputs of both organic and inorganic carbon and nutrients from rivers (Holmes et al., 2012) and permafrost thaw (inland and coastal erosion) (Fritz et al., 2017; Mann et al., 2022) that

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lead to increased remineralisation and hence oxygen consumption sub-surface. Therefore, the increase of organic matter (either produced through photosynthesis or directly discharged from land) can induce enhanced microbial respiration and exacerbate emerging deoxygenation (Robinson, 2019).

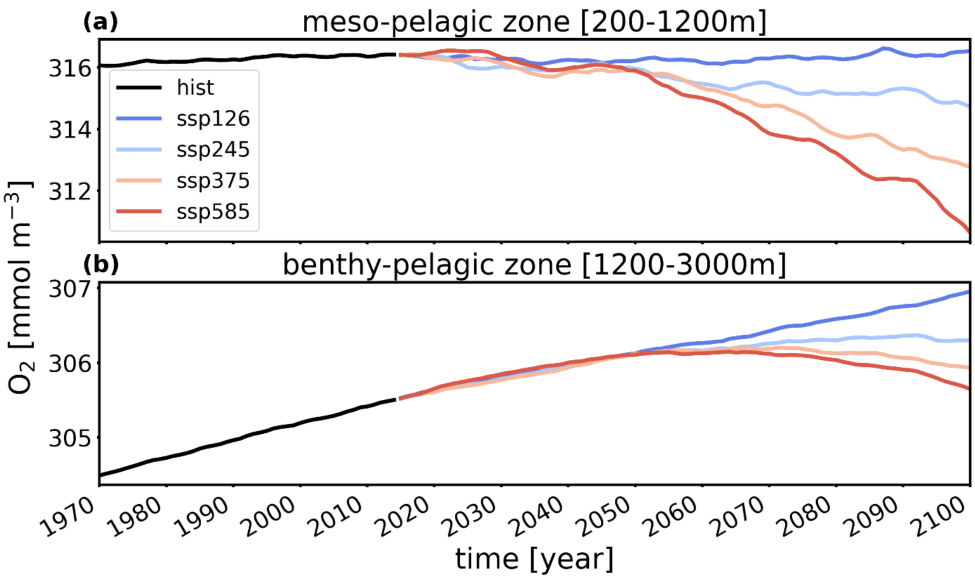

Figure 12: Hindcast and forecast (under different SSP scenarios from 2015 on) FESOM2.1-RecoM3 simulated dissolved O_2 concentration in the (a) meso-pelagic (200-1200 m) and (b) benthy-pelagic zones (1200-3000 m). The simulation is tuned for the Arctic Ocean, offers eddy-resolving horizontal resolution, and includes dynamical coupling of terrigenous inputs of carbon and nutrients (from river and coastal erosion). The simulation has been spun-up for 50 years prior to the historical run.

For the subpolar North Atlantic, available data allow the compilation of O_2 fields for almost every 2nd year for the period 1995-2018, based on the GLODAPv2.2020 data set (Olsen et al., 2020). Typically, the O_2 trends in this dataset are of the order of -0.5 to -1.0 mmol m^{-3}yr^{-1} in the upper water column, and below -0.5 mmol m^{-3}yr^{-1} in the overflow waters from the Greenland Scotland Ridge. They are in general slightly more pronounced when analysed along isopycnals compared to depth levels. This underlines the role of water mass ventilation and spreading for the O_2 anomalies. Almost basin wide, uniform O_2 trends are mainly found in the density layers of Labrador Sea Water (LSW, **Figure 13**). In the upper LSW (ULSW), the O_2 concentration increased between 1995 and 2018, especially away from the formation region towards the eastern Atlantic. This

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is due to the eastward spreading of ULSW that has been formed after the decrease of convection at the end of the 1990s (Kieke et al., 2006). In contrast, the deepest LSW layer (27.78 kg m^{-3} < σ_θ < 27.8 kg m^{-3}) shows the strongest O_2 decline (**Figure 13**). Starting in 2014, the convection in the Labrador Sea became more intense and reached depths of 1500 m and below). Consequently, O_2 in LSW is increased in general, but this increase did not penetrate the densest part of this water mass (Rhein et al., 2017). The LSW formed after 2014 was less dense than the LSW formed between 1987 and 1994 (Yashayaev and Loder, 2016). The O_2 concentrations in the deepest part of the LSW (around 2000 m) have decreased in the formation region and along the main export pathways (southward and eastward crossing the Mid-Atlantic Ridge) for more than 20 years. As 42 % - 71 % of the O_2 consumed in the Upper North Atlantic Deep Water north of the equator is provided by the export of newly formed LSW (Koelling et al., 2022), the long-term O_2 decline along the southward LSW pathway might have impacts on ecosystems in the tropics and subtropics over longer timescales.

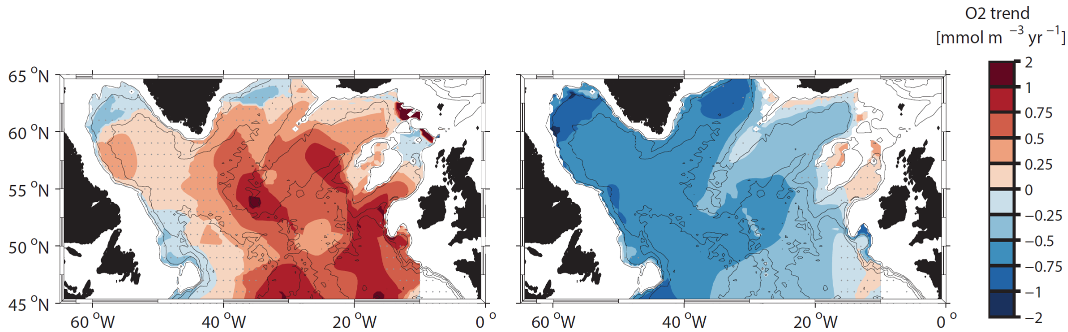

Figure 13: O_2 trend between 1995 and 2018 for isopycnic layers within the LSW (left: 27.7 < σθ < 27.72, right: 27.78 <σθ < 27.80). Stippled areas denote insignificant trends.

4.3.3 Coastal hypoxia increase, estuarine hot spots, shelf sea circulation changes

Oxygen cycling along the continental margins, on shelf seas, in (semi-)enclosed seas and estuarine systems can be extremely variable and heterogenous. Fluctuations in regional circulation can, e.g., lead to advection of low oxygen water onto the shelf and a drastic ecosystem shift in consequence (Chan et al., 2008). In a more general way, shallow seas can more effectively react to warming with a solubility decline and hence O_2 loss. Shallow seas are also are directly affected by increased N_r from river loads and land-derived N_r deposition on the sea surface (Breitburg et al., 2018; Diaz and Rosenberg, 2008). In (semi-)enclosed sea basins such as the Baltic Sea or the Black Sea, a strong density stratification (fresher water from runoff over more saline water from communication with adjacent seas) and only intermittent or very slow deep-water renewal (e.g., through salt water intrusions) can more easily lead to hypoxic or anoxic oxygen bottom waters (Neumann et al., 2017; Krauss and Brugge, 1991; Ozsoy et al., 2002).

Recently, the evolution of near-bed O_2 in the North-Western European Shelf has been studied exploiting a 3-member ensemble of a coupled physics-biogeochemistry regional model driven by three Earth System models of increasing Equilibrium Climate Sensitivity (Galli et al., 2023). It was found that near seabed O_2 consistently declines across all ensemble members and throughout the shelf, by an amount that is proportional to the intensity of climate change projected by each member. A spatially uniform component of change (around −0.3 mg L^{-1} averaged over the shelf; 1 mg O_2 per Liter corresponds to 31.25 mmol O_2 per m^{-3}) is largely attributed to atmosphere-driven warming negatively affecting O_2 solubility. At the same time, in the two models showing the most sustained change, hot-spots of near-bed O_2 decline (with O_2 declining by up to 1 mg L^{-1} by 2100 in the most affected areas) emerges in some areas, namely the Norwegian Trench and the Eastern North Sea, which under the most extreme scenarios also see an enlargement of areas affected by near seabed oxygen deficiency (O_2 < 6 mg L^{-1}) by the end of the 21st century (**Figure 14,** right panels). Here, the onset of the development of low-O_2 hotspots matches an abrupt change in the regional circulation, e.g., a progressive weakening and reversal of the Western Norwegian Trench current (Holt et al., 2018) that is responsible for delivering ocean water to the Northern North Sea (**Figure 14**, left panels). This change happens rather abruptly in both ensemble members and is accompanied by a conspicuous increase in stratification in the affected areas (**Figure 14**; Potential Energy Anomaly, PEA, is an indicator of stratification), which strongly limits O_2 transport from surface to bottom waters. At the same time, increased Net Primary Production due to longer growth season and increased bloom efficiency (Holt et al., 2016) and nutrient availability (Holt et al., 2018) translates into enhanced near-bed bacterial respiration thereby consuming O_2 (Wakelin et al., 2020). The ensemble member that shows the smallest climate change (**Figure 14c**), on the other hand, does not project a significant expansion of near seabed O_2 depletion hotspots (Galli et al., 2023).

4.3.4 Increase in open ocean nitrogen deposition

Though human-induced reactive nitrogen additions have their strongest effect per unit area in coastal seas, the open ocean is meanwhile also affected by deposition of anthropogenic N_r (Duce et al., 2008; Jickells et al., 2017; Altieri et al., 2021). This N_r addition may enhance the oceanic uptake of anthropogenic CO_2 from the atmosphere by ca. 10% (Duce et al., 2008), but this effect on the Earth's radiative forcing is offset largely (two thirds of the 10% uptake increase) by enhanced release of N_2O due to denitrification (Duce et al., 2008). Episodic N_r deposition over oligotrophic ocean areas may contribute to significant biological organic carbon production in otherwise nutrient depleted regions (Owens et al., 1992).

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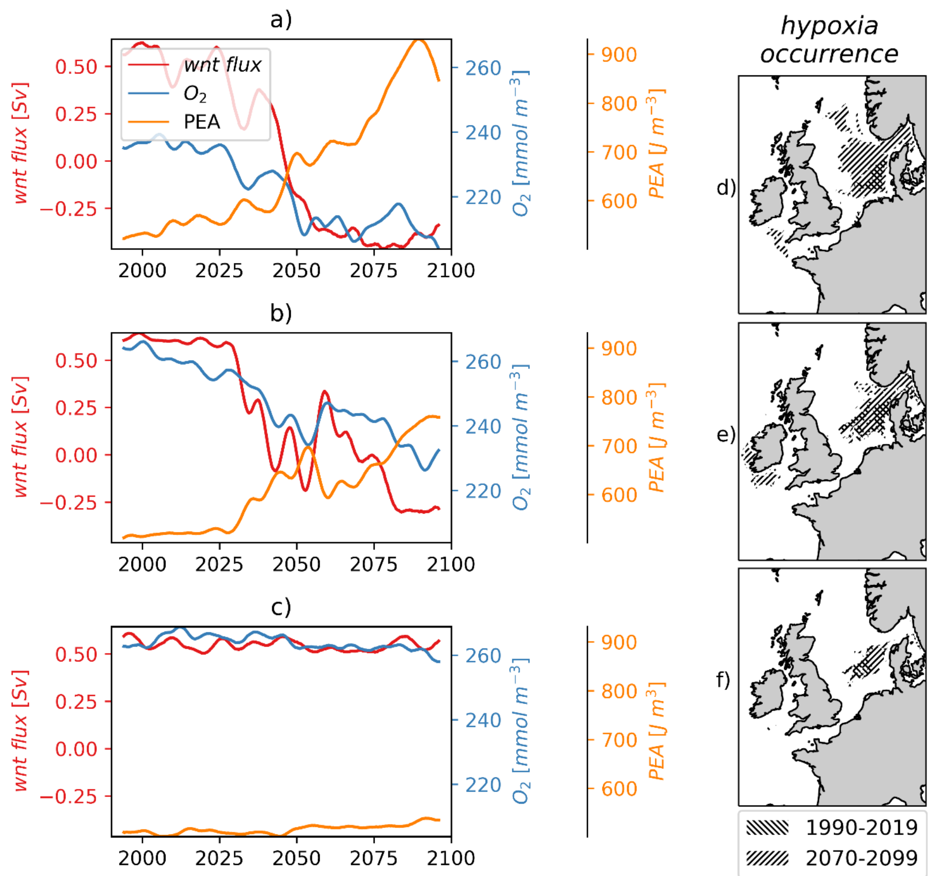

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Figure 14: Left panels: Timeseries of near seabed O_2 and potential energy anomaly (PEA) average over the Norwegian Trench area and Western Norwegian Trench current flux (WNT flux) in three regional climate projections (projections are forced with lateral and atmospheric boundaries from projections with three CMIP5 ESMs: a, HADGEM2-ES, b, IPSL-CM5A-MR, and c, GFDL-ESM2G under the RCP8.5 scenario) with progressively more intense climate-change c) to a). In a) and b) near-
1295 bed O_2 decline is strongly correlated with an abrupt change in local circulation patterns (Western Norwegian Trench current) and with an increase in stratification in the area (PEA), while the member showing the least change c) does not show a significant expansion in hypoxia. Monthly values are smoothed with a gaussian filter. Right panels a), b) and c): occurrence of monthly mean O_2 below the hypoxia threshold of 6 mg/l under present day and end of century conditions in climate projections. O_2 values are bias-corrected against present day climatological values.

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5 Regional extreme events

A special case of abrupt changes in the ocean are extreme events such as marine heatwaves, but also transient high or low concentrations of oxygen, hydrogen ions (pH), or carbonate saturation. A review of biogeochemical extreme events is given by Gruber et al. (2021). A review on marine heatwaves is provided by Oliver et al. (2021) and one on related biological impacts by Smith et al. (2023). The field of extreme events in biogeochemistry is still young with the number of studies rapidly increasing over the past decade. Extreme events are transient in nature, however, they can – next to transient impacts on ecosystems and ocean health – trigger regime shifts in ecosystems causing long-term persistent damage and biodiversity loss (Wernberg et al., 2016; Wernberg et al., 2013; Frölicher and Laufkötter, 2018; Genin et al., 2020; Oliver et al., 2019). Recurrence of extreme events can have an accumulative effect that can exceed the sum of effects from the single events (Gruber et al., 2021; Eakin et al., 2010) but also adaptation and increased resilience to extreme events over time can occur (Hughes et al., 2021). Extreme events can be defined through different metrics such as percentiles of certain state variables (e.g., 10^{th} and 90^{th} percentiles of natural variability in ocean state variables) or through ecological threshold values for organisms and ecosystems (Gruber et al., 2021). One can furthermore distinguish between extreme weather events ("an event that is rare at a particular place and time of year") and extreme climate events ("a pattern of extreme weather that persists for some time, such as a season") (Seneviratne et al., 2021), where the distinction between the two may get blurred somewhat within the ocean due to the long timescales and small spatial scales of oceanic motion and its variability as compared to the atmosphere. Co-occurrence of extremes in several climate and ocean state variables, so-called compound extreme events, have attracted attention due to their potentially strong impact on socioecological systems (Zscheischler et al., 2018; Gruber et al., 2021; Seneviratne et al., 2021; Burger et al., 2022; Le Grix et al., 2021).

5.1 Regional extremes – marine heatwaves

The long-term trends of marine heatwaves have been described for the surface ocean through remotely sensed data and through Earth system models, where increasing trends under anthropogenic climate warming have been identified (Frölicher et al., 2018; Oliver et al., 2019; Ciappa, 2022). The number of marine heatwave days per year has doubled over the period 1982 to 2016 (for a 99^{th} percentile criterion) (Frölicher et al., 2018). Likewise, Earth system models consistently simulate increases in MHW occurrence since pre-industrial times almost everywhere (**Figure 15a**), with the largest increases in the tropical oceans (see also Frölicher et al., 2018). Since the 1980s, the intensity of marine heatwaves has also increased and the duration and intensity of prominent observed marine heatwaves may be attributed to human-induced background warming with high probability (Laufkötter et al., 2020). Marine heatwaves will continue to increase under progressing climatic warming (with

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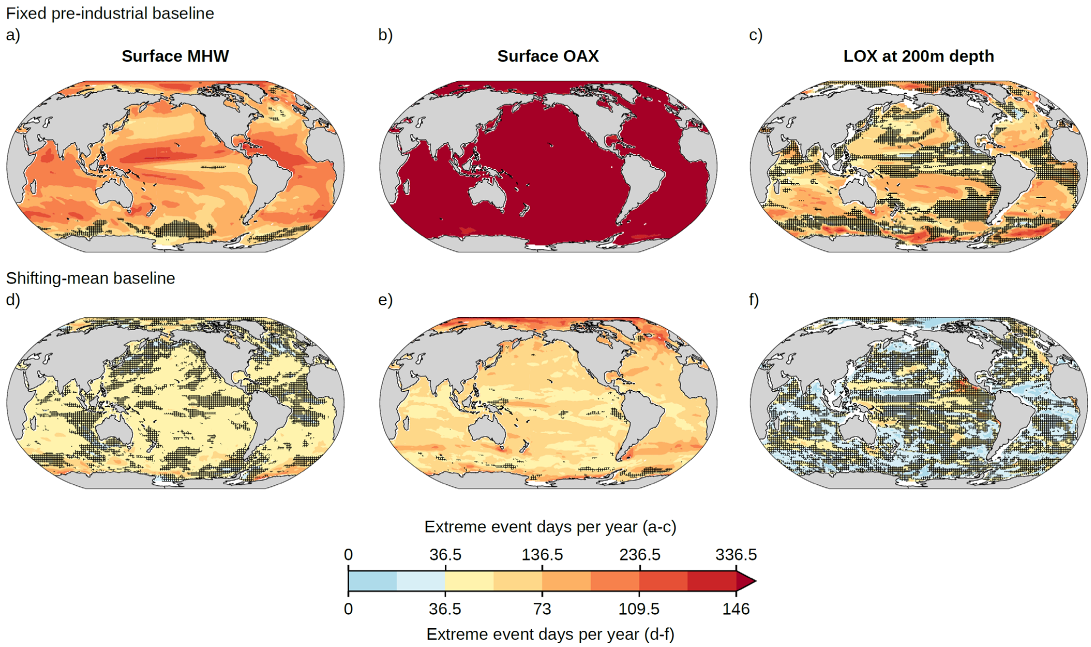

Figure 15: Ensemble mean number of extreme event days per year over the period 2001-2020 in the 6-model COMFORT ensemble for marine heatwaves (MHW; panels a, d), sea surface hydrogen ion concentration extremes (OAX; panels b, e), and low oxygen concentration extremes at 200m depth (LOX; panels c, f). Extremes were defined based on 1850-1900 seasonally varying 90th (T and [H^+]) and 10th (O_2) percentile thresholds (panels a-c) as well as based on a shifting-mean baseline where the 1850-1900 percentile thresholds were adjusted according to the forced mean trends in the variables (panels d-f). The forced mean trend was identified by a smoothing 'Enting' spline (Enting, 1987) with a 80 yr cut off period. Hatched areas indicate model disagreement, i.e., where more than one model shows a different sign of change than the other models relative to the period 1850-1900 (36.5d yr^{-1}). Contribution models are CESM2, EC-Earth-CC, CNRM-ESM2-1, NorESM2-LM, AWICM-CM1-RECOM (each with SSP5-8.5 forcing for the period 2015-2020), and GFDL ESM2M (RCP8.5 forcing from 2006-2020).

respect to frequency, duration, spatial extent, and intensity) (Collins et al., 2019) as confirmed by CMIP6 results (Fox-Kemper et al., 2021). Marine heatwaves result from various factors within the coupled ocean-atmosphere system, notably from anomalies in (a) air-sea heat fluxes (Oliver et al., 2021; Vogt et al., 2022), (b) upwelling (e.g., increasing surface warming under reduced ocean upwelling), (c) and horizontal water transport. Therefore, better representations of these processes in future models are crucial for improved projections (Pontoppidan et al., 2023). Extreme temperature events in the ocean are not limited to heatwaves since cold spells can also occur (Schlegel et al., 2017; Schlegel et al., 2021), and these may also have

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significant impacts on ecosystems (Schlegel et al., 2021; Tak et al., 2022). Finally, we remark that marine heatwaves may affect not only the ocean surface but also the deeper layers (e.g., Ryan et al., 2021; Hu et al., 2021; Amaya et al., 2023).

5.2 Regional extremes in ocean acidification

Carbonate system variables such as $[H^+]$ (or $pH=-\log_{10}[H^+]$), pCO_2, and calcium carbonate saturation state can change abruptly during extreme events. Variations in these variables and associated extremes are substantial (Torres et al., 2021; Hofmann et al., 2011; Feely et al., 2008; Leinweber and Gruber, 2013; Desmet et al., 2022), particularly in the coastal ocean, where they can exceed the changes occurring over decades due to ocean acidification (Torres et al., 2021). However, extremes also occur in the open ocean, with considerably higher rates of changes on diurnal to interannual timescales than decadal-scale ocean acidification (Torres et al., 2021; Burger et al., 2020). For example, critical thresholds, such as calcium carbonate saturation horizons and hypercapnia thresholds, can be exceeded on seasonal timescales and during extremes well before mean conditions cross the thresholds under ocean acidification (McNeil and Matear, 2008; McNeil and Sasse, 2016; Negrete-García et al., 2019).

Extremes in $[H^+]$ and pCO_2 most often occur together since variations in these two variables are highly correlated (Burger et al., 2022; Orr et al., 2022). However, extremes in calcium carbonate saturation state may not occur at the same time if temperature is the main driver of $[H^+]$ and pCO_2 (Gruber et al., 2021; Xue et al., 2021; Burger and Frölicher, 2023). This is in contrast to ocean acidification on decadal timescales, where increasing dissolved inorganic carbon concentrations synchronously alter all three variables. Our understanding of the evolution and characteristics of ocean acidification extremes is limited by the availability of data at high-enough temporal and spatial resolution. Recent work for the northeast Pacific and California current system used a hindcast simulation with a regional high-resolution ocean model to analyse the evolution of ocean acidification extremes with co-occurring low saturation state and pH in this region since the mid-1980s (Desmet et al., 2022). They identified different event types that strongly vary in their typical duration (from several days to multiple months) and volume covered (from one to more than one hundred cubic kilometres). Aragonite saturation state and pH typically fell below the event thresholds by 0.026 (pH) and 0.075 (saturation state), but with much larger intensities for particularly strong events. In addition, recent advances in data-derived carbonate system products can be used to assess variations in ocean acidification, but only on monthly timescales and relatively coarse spatial resolution (Burger et al., 2022; Fay et al., 2021; Gregor et al., 2021). Abrupt shifts do not only occur during individual extreme events, but shifts also occur in the statistics of extreme events under climate forcing. $[H^+]$, pCO_2, and calcium carbonate saturation state evolve under ocean acidification as a direct consequence of rising atmospheric CO_2 levels. Their changes on decadal timescales are large compared to the natural

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variability in the open ocean, resulting in a considerably larger signal-to-noise ratio than that of variables that are mainly affected by warming, such as ocean temperature. As a result, open ocean extremes in $[H^+]$, pCO_2, and saturation state increase sharply in frequency, intensity, duration, and extent when defined relative to a fixed baseline period (Burger et al., 2020; Burger et al., 2022). $[H^+]$, pCO_2, and saturation state may even transition into a permanent extreme event state (**Figure 15b**; Burger et al., 2020). In addition, variability changes due to the non-linearity of the carbonate system (Kwiatkowski and Orr, 2018), resulting in an increase in frequency and intensity of extremes for pCO_2 (Landschützer et al., 2018) and [H+] (Burger et al., 2020; Kwiatkowski and Orr, 2018): Relative to a shifting-mean baseline, where changes in extremes are driven by changes in variability, Earth system models robustly simulate increases in [H+] extreme event frequency almost over the entire surface ocean (**Figure 15e**). However, these increases in extremes are generally smaller than those under a fixed baseline due to the ocean acidification trends (**Figure 15b**). Additionally, the seasonal phasing of extremes may change with seasonal maxima in pCO_2 and $[H^+]$ in the Arctic Ocean being projected to shift from winter to summer under mid-to-high CO_2 emission scenarios for the future (Orr et al., 2022).

5.3 Regional extremes in oxygen concentration

Besides the mean deoxygenation trends, regional low-O_2 extremes have the potential to exacerbate the impacts of O_2 decline. Such low-O_2 events can be more detrimental to marine species than warming or acidification (Sampaio et al., 2021). Moreover, low-O_2 extremes can cause species to reach their critical O_2 limits decades earlier than expected from the deoxygenation trends as for example shown for the Scotian Shelf and the Gulf of St. Lawrence region (Brennan et al., 2016) and on the shelf in the northern California Current system (Chan et al., 2008). Open-ocean O_2 extremes are likely driven by anomalous water mass distributions and mainly occur on the boundary between low-O_2 tropical waters (OMZs) and high-O_2 subtropical gyres due to lateral movement between these two water masses (Gruber et al., 2021). Studies with models at eddy-permitting resolution show that low-O_2 extremes are commonly driven by open-ocean eddies occurring at the boundaries between Eastern Boundary Upwelling Systems and the low-O_2 tropical OMZs (Atkins et al., 2022; Frenger et al., 2018). Low-O_2 event frequency has increased about fivefold until today, as well as O_2 extreme intensity and duration (Gruber et al., 2021). As a caveat however, the model studies by Gruber et al. (2021) and Atkins et al. (2022) define O_2 extremes whenever O_2 is below the 1st percentile of natural O_2 variability, thereby not considering any species-specific O_2 thresholds (Vaquer-Sunyer and Duarte, 2008). A generalized but species-relevant threshold is applied in the study by Köhn et al. (2022), who consider the volume of hypoxic waters ($[O_2] < 60$ mmol m^{-3}), which generally do not support marine life. Köhn et al. (2022) show vertical compression of oxic habitat by up to 50-70% in extreme shoaling events of hypoxic waters in the Eastern Pacific (Köhn et al., 2022). Of particular importance for potential impact of O_2 extremes to ecosystems seems to be the characteristics of the

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respective extreme event such as its abruptness, magnitude, intensity, duration, heterogeneity, and recurrence (Gruber et al., 2021) together with the species-dependent critical O_2 thresholds in the affected ecosystem (Vaquer-Sunyer and Duarte, 2008).

5.4 Compound extreme events

A special case of extreme events are synchronous extremes in two or more climatic state variables such as temperature/pH, temperature/[O_2], temperature/NPP, or temperature/pH/[O_2] (Gruber et al., 2021; Burger et al., 2022; Tassone et al., 2022; Le Grix et al., 2022). In such cases, ecosystem impacts from the co-occurring extremes can be additive or even synergistic, causing larger ecosystem impacts than individually occurring extremes (Steckbauer et al., 2020; Boyd and Brown, 2015). Based on observation-based data and regional and global models, the North Pacific heatwave "the Blob" (Bond et al., 2015; with devastating effects on marine ecosystems, e.g., Piatt et al. (2020)) could be linked to co-occurring low [O_2] and low pH extremes (Gruber et al., 2021; Mogen et al., 2022). Also, according to evidence from remotely sensed ocean colour derived chlorophyll values, comprehensive compound events of high SST and low chlorophyll concentration (corresponding to low biological productivity) can be identified (Le Grix et al., 2021).

6 Reversibility

We define reversibility here as the ability of the ocean system to reverse anthropogenic-induced changes and return to a state that is equivalent to the initial state prior to external perturbation (e.g., a preindustrial condition) on a certain timescale. The question on whether abrupt Earth system changes are (ir)reversible is important for potential mitigation and adaptation measures. The time frame for potential reversible recovery of the system is essential: often the term “irreversible on human timescales” is used, indicating that after an abrupt change the system in question does not recover at least within the life span of one or two human generations. Marine phenomena for which (ir)reversibility has been assessed by the IPCC (Intergovernmental Panel on Climate Change) include AMOC, Southern MOC (Meridional Overturning Circulation), subpolar gyre cooling, marine heatwave increase, Arctic sea ice retreat, ocean deoxygenation and hypoxic events, ocean acidification, global ocean heat content, and global sea-level rise (Table 6.1 in IPCC SROCC Collins et al. (2019); Table 4.10 in IPCC AR6 WG1 Lee et al. (2021)). While climate state variables and fluxes at and near the ocean surface generally show reversibility (Boucher et al., 2012; Jeltsch-Thommes et al., 2020), this may not be the case for human-induced changes of the sub-surface and deep ocean due its multi-centennial overturning timescale (e.g., Jeltsch-Thommes et al., 2020; Li et al., 2020; Bertini and Tjiputra, 2022).

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Carbon dioxide removal (CDR) is a potential mitigation method to reverse and thus reduce atmospheric pCO_2 concentrations Minx et al., 2018). Different scenarios for CDR from the Earth system and reduction of greenhouse gas emissions to zero have been the subject of Earth system model intercomparison projects whose evaluation phase is still ongoing (CDRMIP – Carbon Dioxide Removal Model Intercomparison Project, Keller et al. (2018); ZECMIP – Zero Emissions Commitment Model Intercomparison Project, Jones et al. (2019)). For linear systems, a change of the system's state variables due to the forcing applied can be directly reversed by reversing the forcing and the forcing is always associated with the same system change regardless of whether the forcing is applied positively or negatively. For non-linear systems, two different systems states can be associated with the same degree of forcing due to hysteresis, the dependence of the state of the system on its history (e.g., Stocker, 2000; Scheffer et al., 2001): in the case of negative hysteresis the system recovers more slowly for a negative forcing and in the case of positive hysteresis the system recovers more quickly than the original system change has happened (e.g., Jeltsch-Thommes et al., 2020). A special case would be that the system cannot recover at all or only partially regardless of any hysteresis behaviour. The latter case applies to the carbon cycle perturbation of the Earth system if not all anthropogenic CO_2 is re-captured (e.g., Archer, 2005).

This section covers (ir)reversibility and hysteresis of physical factors (warming, AMOC, sea ice loss), as well as biogeochemical (ir)reversibility and hysteresis of ocean acidification and deoxygenation. Addressing each of these factors, **Figure 16** quantifies (ir)reversibility and hysteresis of Ocean Heat Content, AMOC, sea ice, aragonite saturation $\boldsymbol{\Omega_{arag}}$ and thermocline (200-600 m) O_2. Here, the Bern3D v2.0s Earth system model of intermediate complexity coupled to the LPX v1.4 dynamic global vegetation model is applied in idealized 5000-year CO_2 overshoot simulations, while also quantifying the impact of different equilibrium climate sensitivities (ECS) in the model. A typical ramp-up (1% CO_2 yr^{-1} increase) scenario was applied to 2, 3, 4, and 5 times pre-industrial CO_2 concentrations, followed by a ramp-down (1% CO_2 yr^{-1} decrease) to constant pre-industrial concentrations which were continued to the end of the simulation. This approach was repeated for three different model versions with ECS of 2, 3, and 5 °C. In general, hysteresis increases non-linearly with increasing ECS.

6.1 Reversibility of warming and other physical factors

6.1.1 Reversibility of ocean warming

Hysteresis behaviour has been studied using a range of idealised as well as realistic overshoot forcing scenarios in fully-coupled Earth System Models, in which the atmospheric CO_2 levels firstly increase and then decrease (e.g., Boucher et al., 2012; Jeltsch-Thömmes et al., 2020; Mathesius et al., 2015; Wu et al., 2015; this manuscript). The reversibility of ocean warming (**Figure 16a**) depends on ocean ventilation timescales, which vary considerably in space. In the ocean surface,

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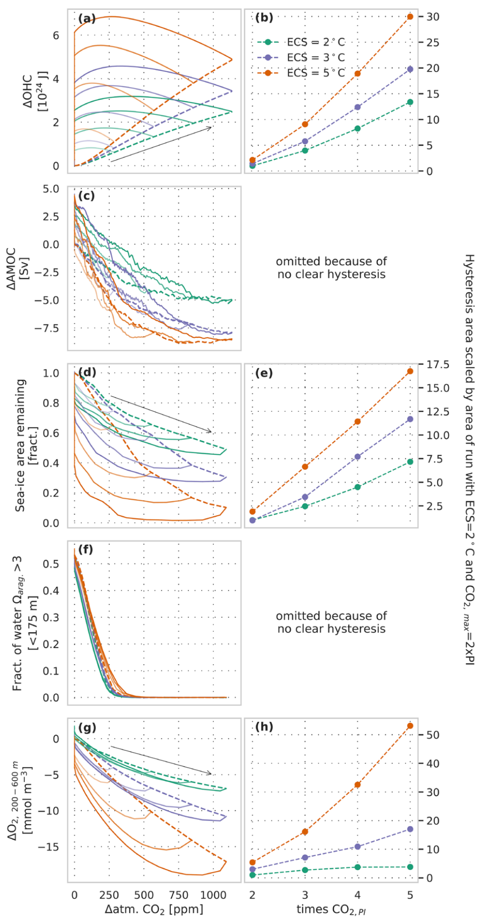

Figure 16: Global changes in (a) total Ocean Heat Content, (c) AMOC, (d) remaining global sea ice fraction, (f) fraction of water with aragonite saturation Ω_{arag} >3 in the top 175m of the water column, and (g) mean O_2 in the thermocline (200-600 m) as well as corresponding scaled global hysteresis area in (b), (e) and (h) for equilibrium climate sensitivities of 2, 3, and 5 °C (colours) and maximum atmospheric CO_2 concentrations of 2-5 times pre-industrial (darkness of the colour). Hysteresis is calculated as the area enclosed by the curve when plotting changes in thermocline O_2 against changes in CO_2. Thick dotted lines show changes during increasing CO_2, thick solid lines during decreasing CO_2, and thin vertical lines at atmospheric ΔCO_2=0 in (a), (c), (d), (f), and (g) show changes after CO_2 has returned to pre-industrial concentrations (i.e., the (ir)reversibility). Scaling of (b), (e) and (h) is done to facilitate comparison between the different variables.

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temperature displays hysteresis after an overshoot because of the inertia of the ocean to absorb heat from the atmosphere (Wu et al., 2015) that can last several decades-to-centuries after the CO_2 level returns back to its pre-industrial level (Li et al., 2020). Such near-surface warming is reversible, but the time lag is larger for larger peak CO_2 concentrations in such overshoot scenarios (Boucher et al., 2012). In the interior ocean, this time lag is considerably longer due to the delayed propagation of the warming/cooling signal from the surface to the deep ocean, which primarily follows the large-scale overturning circulation pattern. In the interior Atlantic, the delay in peak warming varies from decades in the well ventilated subpolar region to multi-centuries in the less-well ventilated tropical region (Bertini and Tjiputra, 2022). Warming in the interior North Atlantic is projected to be reversible at millennia or longer timescales. The recovery of the upper ocean from excess ocean heat content will be strongly delayed after CDR and this delay increases for higher climate sensitivities (Jeltsch-Thömmes et al., 2020) .

6.1.2 Reversibility of reductions in the Atlantic Meridional Overturning Circulation (AMOC)

While a potential collapse of the AMOC is deemed unlikely (Collins et al., 2019), the question remains as to what degree warming-induced AMOC reductions can recover again once greenhouse gas emissions have come to an end. The preliminary answer at this stage is that at least a partial recovery of the AMOC seems possible. The Bern3D model of intermediate complexity shows reversibility of the AMOC (**Figure 16c**) (without clear influence of ECS on hysteresis). In the IPCC SROCC it was stated that it is "unknown" whether an AMOC collapse would be reversible or not (Collins et al., 2019). This has been updated to "reversible within centuries (*high confidence*)" in the IPCC AR6 (Lee et al., 2021) although on the timescale of up to the end of the present century, the AMOC does not come back to the 2040s level in the overshoot concentration-driven and emission-driven scenarios; moreover, the AMOC hysteresis in the esm-SSP534 overshoot projections varies for different latitudes (**Figure 17**). This reduced AMOC recovery on the shorter timescales but a possible AMOC reversibility on the longer ones are in line with recent Earth system model multi-centennial simulations exploring the effect of negative CO_2 emissions (carbon dioxide removal) on the ocean overturning where a partial recovery of the AMOC was predicted following lowered levels of CO_2 in the atmosphere and a respective cooling (Schwinger et al., 2022b). However, the timing in relation to emissions, warming levels, and carbon dioxide removal can cause unwanted negative side effects such as a transient strong cooling of high latitudes when a cooling climate coincides with a still weak AMOC (Schwinger et al., 2022a). Similarly, a cooling hiatus (transient warming) during the ramp down of CO_2 emissions to zero (i.e. without negative emissions) can occur (An et al., 2021). There is an ongoing discussion about the potential persistence of poleward heat transport through the ocean even in case of an AMOC collapse (Roquet and Wunsch, 2022) and a partial decoupling of poleward heat transport trends from AMOC trends (Smedsrud et al., 2022).

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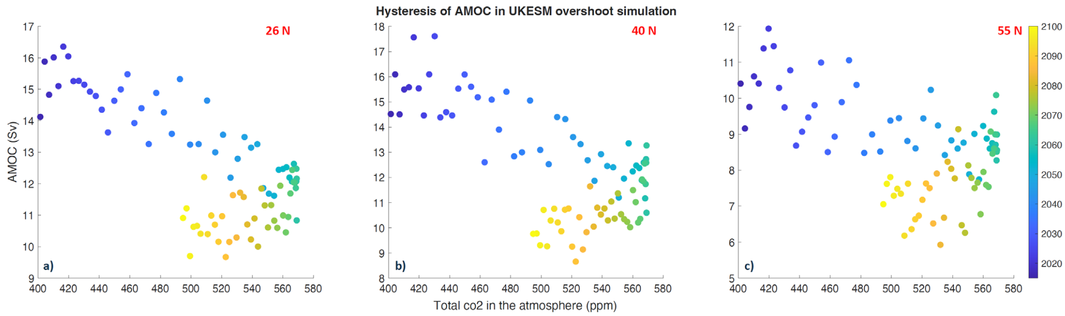

Figure 17. Hysteresis of the annual Atlantic Meridional Overturning Circulation (AMOC) strength (Sv) up to year 2100 in the CDR-MIP esm-SSP534 concentration-driven overshoot scenario integrations with the UKESM model at 26°N – corresponding to the "RAPID" observational array (a), at 40°N (b), and at 55°N (c). Only one ensemble member is shown; the colour bars indicate the time sequence, also note the different vertical axes. See **Figure 18** for the projected atmospheric CO_2 concentration in this scenario.

6.1.3 Reversibility of sea ice loss

Reversibility of the loss of polar sea ice cover in both the Arctic and Antarctic depends on changes in both the ocean circulation and ocean heat content. Arctic sea ice loss extending from the Barents Sea is caused by the northward intrusion of Atlantic Water. Similarly, the intrusion of Pacific Water causes sea ice melt in the Chukchi Sea (Polyakov et al. 2020). "Atlantification" makes the loss of annual-mean Arctic sea-ice irreversible during this century following the realistic esm-SSP5-3.4 overshoot scenario once the atmospheric CO_2 concentration is above 520 ppm (**Figure 18**). On the other hand, the cause of Antarctic sea-ice loss irreversibility is an intrusion of warm waters into the Bellingshausen-Amundsen Sea leading to the melting of the sea-ice, which is projected to occur around 560-580 ppm atmospheric CO_2 concentration. In contrast, in the idealised CDR model experiments, the loss of both summer and winter Arctic sea ice cover were found to be reversible on a timescale of years to decades with high confidence, although the reversibility of Antarctic sea ice changes has not yet been conclusively assessed (Lee et al., 2021). Finally, results from an EMIC (Earth System Model of Intermediate Complexity) show that global sea-ice loss is generally reversible (**Figure 16d**) on centennial timescales, but these timescales increase with increased ECS and lower CDR rates (Jeltsch-Thommes et al., 2020).

6.1.4 Irreversible increase of Arctic marine productivity due to sea -ice loss

Irreversibility of the Arctic sea-ice cover decline in the realistic overshoot scenarios above can trigger the cascading of abrupt changes in the state of Arctic biogeochemistry and ecosystems which do not recover by the end of the 21st century. The esm-

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SSP534 overshoot scenario integrations with the UKESM model ensemble members show an approximately two-fold increase in the pan–Arctic Net Primary Production (NPP) between the 1950s and the 2100s (**Figure 18**). The abrupt change in the state of the Arctic NPP occurs between the 2000s and 2040s and is characterized by changes in both the NPP mean and decadal variability. The hysteresis (with respect to the CO_2 concentrations) evident in the sea ice area in this overshoot scenario is not present in the NPP, suggesting that sea ice decline in summer tips the Arctic marine ecosystem into a different state through removal of the light limitation constraints (Yool et al., 2013).

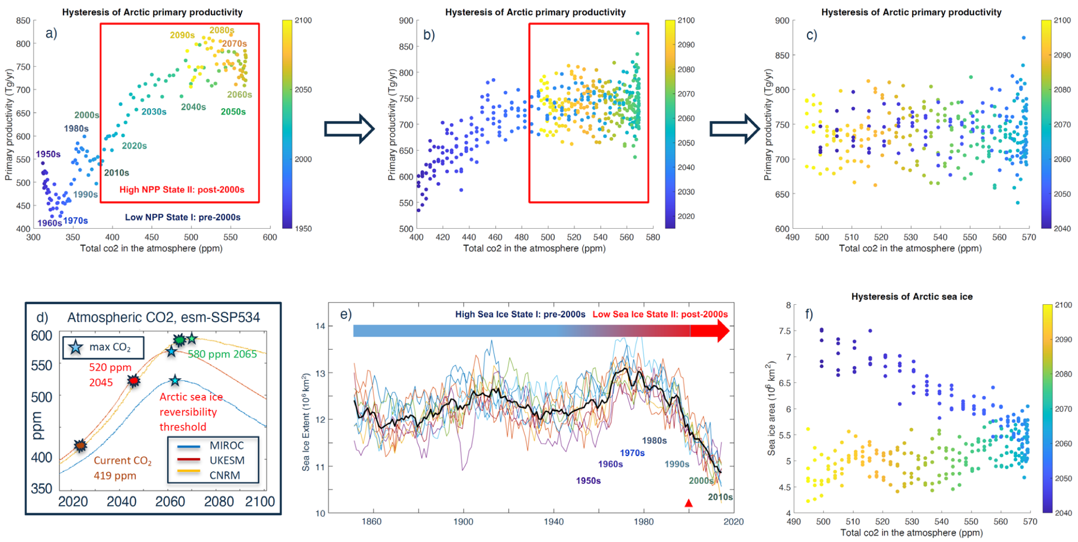

Figure 18: Hysteresis of the annual mean Arctic Net Primary Production (NPP) and sea-ice in CDR-MIP esm-SSP534 overshoot concentration-driven scenario integrations with the UKESM model. (a) hysteresis of the NPP in the UKESM one ensemble member from the combined historical-esm534 continuous model integrations for the period 1950-2100, the low and the high NPP states are marked; (b) and (c) zoom in to the scenario periods 2015-2100 and 2040-2100 respectively to show the spread of the UKESM model ensemble marked with circles; (d) projected atmospheric CO_2 concentrations in esm-SSP534 overshoot scenarios in the only three participating models (CNRM, MIROC, and UK ESM), coloured "blob" symbols mark the current 2022 CO_2 concentration, along with the thresholds in 6.1.3 for the irreversible Arctic and Antarctic sea ice loss, "star" symbols show the maximum achieved CO_2 concentration in the individual model ensembles; € Arctic sea ice extent in the historical UKESM integrations, coloured lines are 9 ensemble members, and the black line is the ensemble mean; (f) hysteresis of the Arctic sea ice extent in the esm-SSP534 overshoot scenario for 2040-2100 with 5 ensemble members of the UKESM model (ensemble members are marked with circles). The colour bars indicate the time sequence, also note the different vertical axes.

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6.2 Reversibility of ocean acidification and carbon fluxes

Under an idealized peak-and-decline scenario, the evolution of surface pH in the North Atlantic corresponds strongly to the atmospheric CO_2 concentration trajectory, such that when the CO_2 concentration is returned to the preindustrial level, the ocean gradually turns from a carbon sink to a carbon source and the surface pH level returns to its initial state (Bertini and Tjiputra, 2022). pH change in the interior is more sophisticated, however, as low-pH water masses are transported to depth by the overturning circulation at a much slower rate than the atmospheric CO_2 evolution. Although the propagation of acidification signals into the interior predominantly follows the anthropogenic carbon pathways (Tjiputra et al., 2010), such as ventilation processes, vertical mixing, diffusion, subduction, and meridional overturning circulations, changes in other environmental parameters such as temperature, alkalinity, and O_2 consumption during aerobic respiration also influences interior acidification rates (Canadell et al., 2021; Fransner et al., 2022). As with temperature, the reversibility timescales of interior acidification varies spatially depending on the water mass ventilation characteristics. Well ventilated and deep-water formation regions, such as the North Atlantic and the Southern Ocean, will experience stronger acidification rates and are projected to recover faster than less ventilated regions such as the tropical regions (Bertini and Tjiputra, 2022). In the equatorial Pacific, ENSO strongly affects air-sea CO_2 fluxes by modulating the upwelling rate of DIC-rich deep-water such that anomalously strong outgassing is observed during La Niña and vice versa during El Niño. Under a high CO_2 future scenario, where the upper ocean steadily takes up excess carbon from the atmosphere, the strong vertical DIC gradient observed today is projected to weaken. In some models, this reduced vertical gradient leads to a reversal in the ENSO-CO_2 flux relationships, which could have an impact on the climate carbon cycle feedback (Vaittinada Ayar et al., 2022). Such a shift is reversible in principle once the atmospheric CO_2 level is brought back to preindustrial levels and the surface ocean begins to outgas its excess carbon restoring the initial vertical DIC gradient. For upper ocean acidification, the recovery with respect to aragonite saturation state is quite efficient under CDR (**Figure 16f**) but deeper layers recover only with considerable delay (Jeltsch-Thömmes et al., 2020).

When considering millennial and multi-millennial timescales, it is important to take into account the general limitations of the ocean buffer system and the loss of $CaCO_3$ sediment due to fossil fuel CO_2 uptake and respective acidification of the water column. Without any carbon dioxide removal, the atmosphere and ocean will approach an equilibrium where approximately 10% of the total budget of carbon added through human-caused emission will reside in the atmosphere and 90% in the ocean, with a state of 0% percent anthropogenic carbon in the atmosphere never being regained (Bolin and Eriksson, 1959; Egleston et al., 2010; Revelle and Suess, 1957). A portion of the fossil fuel CO_2 neutralisation in the ocean will occur on multi-

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millennial timescales, with the redissolution of ocean floor $CaCO_3$ (Bolin and Eriksson, 1959; Broecker and Takahashi, 1977) from the sediment mixed layer occurring until it gets sealed off by quasi-inert clay material, see (Broecker and Takahashi, 1977). Additionally, carbonate weathering on land (Archer, 2005; Archer et al., 1998; Archer et al., 1997) can contribute to the neutralisation process. Direct observations of the $CaCO_3$ saturation (Ólafsson et al., 2009) and biogeochemical ocean modelling (Gehlen et al., 2008) support this view. The slow $CaCO_3$ neutralisation of CO_2 highlights the very long legacy of the human-induced climate perturbation over several tens of thousands of years.

6.3 Reversibility of deoxygenation

Since O_2 in the sea surface depends on temperature (e.g., Helm et al., 2011), sea surface O_2 changes generally follow the sea surface temperature evolution, which experience a small hysteresis that recovers along with halting CO_2 levels. At intermediate depths (200-600m), our simulations with ECS=2 °C show very little hysteresis for O_2 for all CO_2 overshoot scenarios and seem to level off for higher maximum CO_2 concentrations (**Figure 16h**). For ECS=3 °C, hysteresis at intermediate depths increases about linearly with maximum CO_2 concentrations whereas for ECS=5 °C, hysteresis seems to increase exponentially with higher maximum CO_2 over the covered range (**Figure 16h**). Deep ocean O_2 levels are affected up to thousands of years after a peak in anthropogenic CO_2 emissions thanks to the millennial timescales of ocean overturning (Frölicher et al., 2020; Oschlies, 2021; Battaglia and Joos, 2018). Applying an ESM forced by idealized rapid climate change followed by a rapid mitigation scenario (Keller et al., 2018; Bertini and Tjiputra, 2022) indeed shows that much of the projected O_2 anomalies in the deep North Atlantic experienced during the ramp-up (1% CO_2 yr^{-1} increase) and ramp-down (1% CO_2 yr^{-1} decrease) periods are not reversible for at least 400 years. Bertini and Tjiputra (2022) further showed that interior O_2 changes in less ventilated low latitude regions are mostly driven by enhanced biological consumption during aerobic respiration and restructuring of the water masses because of a slowing down of the overturning circulation. Therefore, even if the circulation pattern recovers, the respiration induced O_2 deficit will remain until newly ventilated water masses are brought in. Consequently, the ventilation timescale of the interior ocean is the determining factor for reversibility of O_2 changes there, i.e., well ventilated regions such as the subpolar North Atlantic will be reversible faster than less ventilated low latitude regions. Noteworthy, sub-surface O_2 may present regional positive or negative hysteresis, i.e., higher or lower O_2 concentrations than before the overshoot, depending on the interplay between changes in the ventilation of the water masses and organic matter export (see Frölicher et al., 2020; Jeltsch-Thömmes et al., 2020). Following from the long-term irreversibility of interior ocean deoxygenation, negative impacts of interior deoxygenation on deep-dwelling marine organisms would be irreversible on centennial timescales (e.g., Oschlies, 2021). In the Bern3D model, positive deoxygenation hysteresis (higher thermocline O_2 concentrations during recovery) is found mainly in the North Atlantic (in agreement with

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Bertini and Tjiputra (2022)), Indian, North Pacific, and the Atlantic sector of the Southern Ocean while negative hysteresis is found in the South Atlantic, Pacific, Arctic, and Indian and Pacific sector of the Southern Ocean (**Figure 19**). This pattern is comparable for ECSs of 3 °C and 5 °C and maximum CO_2 concentrations of 2 and 3 times pre-industrial and results from a combination of changes in circulation, particulate organic matter export production and subsequent remineralization, as well as temperature effects on O_2 solubility (see e.g., Jeltsch-Thommes et al., 2020).

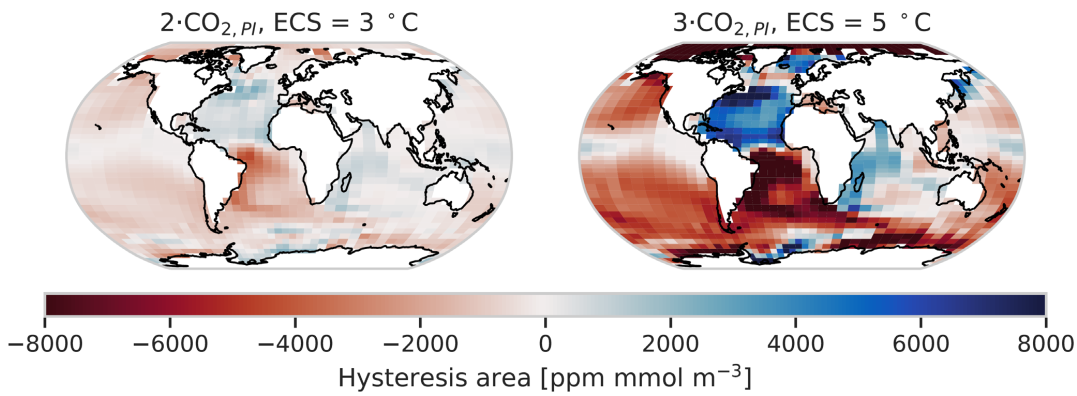

Figure 19: Spatial pattern of O_2 hysteresis for 2 scenarios, 2 times CO_2 with ECS=3°C and 3 times CO_2 with ECS=5°C (ppm · mmol m^{-3}). Negative values indicate lower thermocline O_2 during CO_2 recovery and vice versa for positive values. Hysteresis is calculated as the area enclosed by the curve when plotting changes in thermocline O_2 against changes in CO_2 (see **Figure 16a,c,d,f,g**).

7 Potential consequences of gradual and abrupt changes for ecosystems

The above-described gradual and abrupt climate-induced changes and shifts can have severe consequences for marine species and ecosystems. The magnitude of these impacts and the likelihood of regime shifts depend not only on the rate of change and the duration of exceeding a threshold in the system, but also on the buffer capacity of species, i.e., their adaptability (e.g., genetic diversity, dispersal capacity, see for example the review by Pinsky et al. (2020) and the overall resilience of the ecosystem (Scheffer et al., 2015). In the following, several ecological examples will be presented.

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7.1 Phytoplankton

Phytoplankton, which forms the base of the marine food web and the biological carbon pump, is strongly affected by warming and acidification. In addition, phytoplankton responds to changed nutrient and light availability caused by stronger stratification due to warming in the upper ocean (Sallée et al., 2021). Warming together with higher light availability stimulate phytoplankton growth, whereas lower nutrient availability reduces phytoplankton growth (Seifert et al., 2020). The effect of rising pCO_2 is two-fold: an increase in pCO_2 generally has a positive effect on phytoplankton growth until an optimum is reached and above that optimum a negative effect on phytoplankton growth can found (Seifert et al., 2022; Bach et al., 2013). Dissolved inorganic carbon is a substrate for photosynthesis ('carbonation'), but high H^+-concentrations have detrimental effects on the growth (Bach et al., 2013; Kottmeier et al., 2016). The optimum is phytoplankton group-specific, as the growth responses to increasing CO_2 were positive for all groups except for coccolithophores within the tested pCO_2 range (Seifert et al., 2020). Usually, ESMs do not account for the effects of ocean carbonation and acidification on phytoplankton growth as they are considered second-order effects relative to nutrient availability and light conditions (e.g., Tagliabue et al., 2021). Implementing an explicit representation of CO_2-sensitivity of phytoplankton growth revealed large differences in regional projections of future primary production (Seifert et al., 2022). Depending on the initial perturbation of phytoplankton growth rate by the CO_2-sensitivity, the composition of the phytoplankton community depends on amplified or dampened nutrient and light availability, as well as grazing pressure by zooplankton. This example illustrates how the gradual warming and acidification and their complex cascading effects on phytoplankton structure can be studied in models.

7.2 Detection of ecosystem changes

The detection of abrupt shifts or tipping points in phytoplankton abundance or community structure is hampered by the limited length of most observed time series, in particular for characteristics of plankton diversity. Most suitably long-time series are restricted to coastal or shelf regions, due to logistical constraints of regular sampling, although satellite-derived chlorophyll concentrations are able to provide a measure of phytoplankton abundance on the global and decadal scale. Evidence of tipping points in plankton time series is relatively sparse, with only one study (to our knowledge) finding evidence of an abrupt shift in satellite-derived chlorophyll concentration, i.e., Gulf of California (Hakspiel-Segura et al., 2022) or using long-term monitoring (> 50 years), i.e., North Sea (Beaugrand et al., 2014). Of the five plankton groups studied in Beaugrand et al. (2014) (diatoms, dinoflagellates, copepods, holozooplankton and meroplankton), the shifts impacted ~40% of the present taxa, with the timing of the shift varying with group. The 1980s regime shift in the North Sea was later found to be quasi-synchronous with other zooplankton assemblages in long time series from the shelf regions of the North Pacific, North Atlantic

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and Mediterranean Sea (Beaugrand et al., 2015). Given the relative paucity of suitably long plankton time-series, alternative routes to investigating potential tipping points have been explored. Microcosm experiments, for example, have demonstrated that warming can result in abrupt declines in phytoplankton production and biodiversity loss (Bestion et al., 2020). Machine learning methods have been applied to tease tipping point-like phenomena out of large and noisy datasets, suggesting that temperature and pCO_2 are important drivers of change in phytoplankton productivity (Ban et al., 2022). Some biogeochemical models may also be able to simulate regime shifts (e.g., Beaulieu et al., 2016), although only relatively complex ecosystem models have the potential to simulate changes in plankton community structure. Under future climate change, it can be expected that abrupt shifts will become more widespread in plankton, particularly for heterotrophic and larger organisms (Cael et al., 2022). Also, phytoplankton with specific resource requirements, such as diatoms, were found to be more prone to abrupt shifts using a plankton complex ecosystem model (Cael et al., 2021). Abrupt shifts in biomass, productivity and community structure were all identified, particularly in the subtropics (**Figure 20**, after Cael et al., 2021), although standard early warning indicators did not precede the shifts. The abrupt shifts in community structure were generally not preceded by abrupt shifts in potential drivers, such as temperature or nutrient concentration, but were instead occurring in response to gradual environmental changes. It is important to note, that overall no or very few shifts have been projected for the Northern Pacific and Atlantic as compared to other oceanic regions (**Figure 20**).

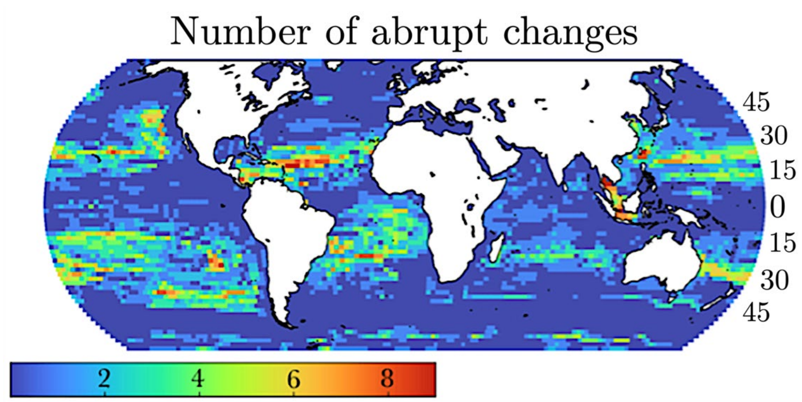

Figure 20: Number of predicted abrupt shifts in plankton abundance, ecosystem structure, and function in the 21st century at different locations (after Cael et al., 2021; Creative Commons Attribution License 4.0 (CC BY)). Colour corresponds to number of ecosystem metrics in which abrupt shifts are detected at each location.

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7.3 Warm-water corals

Besides plankton, warm-water coral reefs have been a particular focus in climate impact and regime shift studies (e.g., Ranith and Kripa, 2019; Ranith et al., 2016; Graham et al., 2015)). In the Indian Ocean, for example, coral bleaching events have been associated with marine heat waves (MHW) (Hobday et al., 2016), as thermal stress is the primary cause for large-scale coral bleaching events and associated mortality, especially during summer. In addition to MHWs, Degree Heating Week (DHW) is a proxy for physiological temperature stress, calculated as cumulative heat stress over 12 weeks. Over the past 35 years, a strong east-west warming gradient in the Indian Ocean has been observed, with more occurrences of DHWs in the

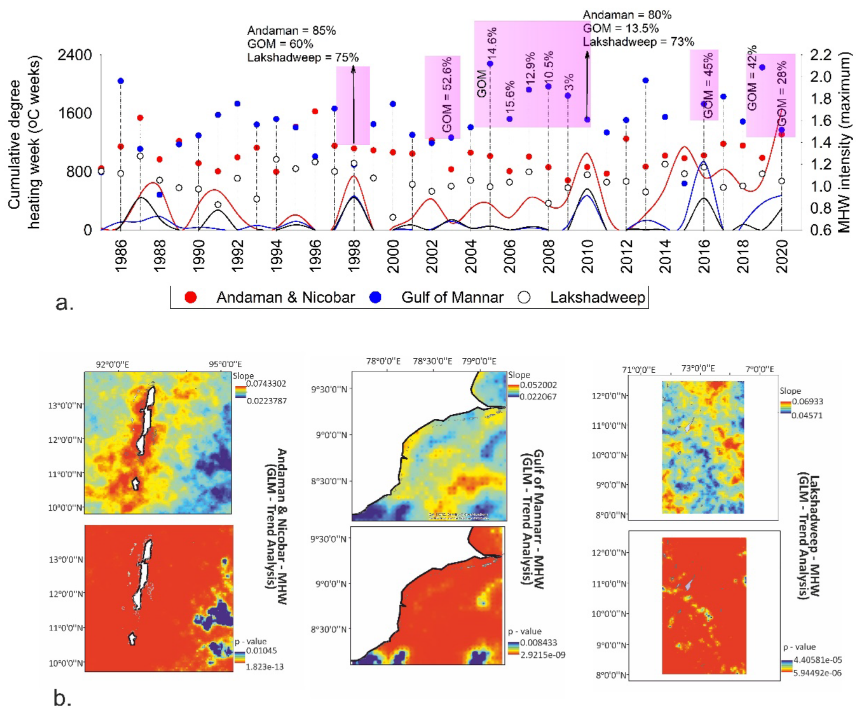

Figure 21: (a) Cumulative degree heating weeks (line plot) and MHW maximum intensity (lollipop plots) along the three coral reef systems in Indian waters. Periods recorded with coral bleaching events are represented in pink shade along with the percentage of bleaching (b) Trend analysis of the MHW events over the study period.

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northeast Indian Ocean, i.e., more than 40 DHWs close to the Andaman and Nicobar Islands, than in the centre, i.e., 12 DHWs in the Gulf of Mannar and in the northwest, i.e., less than 10 DHWs in Lakshadweep (**Figure 21a**). Over the same period, MHWs occurred more frequently at all three locations (**Figure 21b**). Such extensive warming history possibly acclimatized the corals to continuous warming in summer as documented for other coral reefs systems (Donner et al., 2005; Middlebrook et al., 2008; Ulstrup et al., 2006). While DHWs greater than 4°C per week (Liu et al., 2013; Liu et al., 2017) are considered to result in significant coral bleaching, not all coral bleaching events observed in the Gulf of Mannar could be associated with an exceedance of the DHW threshold, indicating the limitation of DHW in identifying bleaching events from acute warming over only a few days (e.g., Decarlo et al., 2017). Instead, the coral bleaching events coincided with the occurrence of MHWs that clearly capture short time extreme ocean temperatures. Using both indicators, DHW and MHWs are needed to improve the prediction capability of coral bleaching at various intensities and regional scales. In general, the more frequent occurrence of extreme events such as marine heat waves is of concern, as the likelihood for shock-induced regime shifts in marine ecosystems is very likely to increase (e.g., Wernberg et al., 2016; Ciappa, 2022).

7.4 Cold-water corals

Cold-water corals are also impacted by human-induced climatic forcing. At millennial timescales as the Atlantic Meridional Overturning Circulation (AMOC) favours the spreading of deep-sea cold-water corals (CWC) in the Atlantic, but their near future is threatened by the deep transport of acidified seawater, exposing corals to corrosive waters. Deep convection in subarctic regions transports acidified surface water to deep layer where CWC are living –here, the anthropogenic CO_2 is increasing at rates of from 0.6 to 0.8 mmol m^3 yr^{-1} (García-Ibáñez et al., 2016) in the whole water column (3000 m). The deep layers in the subpolar region showed similar acidification rates to those observed at the surface, but their lower pH levels are closer to the aragonite saturation horizons (García-Ibáñez et al., 2021). Pérez et al. (2018) showed that the present rate of supply of acidified waters to the deep Atlantic could cause the aragonite saturation horizon to shoal by 1,000–1,700 metres in the subpolar North Atlantic within the next three decades. A decrease in the concentration of carbonate ions in the Irminger Sea caused the aragonite saturation horizon to shoal by about 10–15 meters per year between 1991 to 2016 with the reduction of the volume of aragonite saturated (Pérez et al 2018).

7.5 Upwelling

It has been suggested that global warming will lead to a general strengthening of coastal upwelling (Bakun, 1990; Bakun et al., 2015), with important ecological and fisheries implications. However, in the case of the NW Iberian Peninsula upwelling, long-term climatological analysis reveals a weakening of the upwelling that correlates with an increase in SST and NAO

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(North Atlantic Oscillation) (Cabrero et al., 2018). This weakening of upwelling has led to noticeable changes in the ecosystem. Over the last 40 years, on the outer shelf, a decrease in new production has been detected, which has been related to a reduction in sardine catch. On the inner shelf of the Galician Rías, the weakening of the upwelling has slowed the non-tidal circulation that fertilises the euphotic layer by increasing the stratification of the water column, although it has promoted the local regeneration of nutrients by increasing the remineralization of organic matter. The phytoplankton community has also been modified with an increase in the percentage of dinoflagellates and a reduction of diatoms, favouring the proliferation of harmful algal blooms which reduces the aquaculture harvesting period of mussels (Pérez et al., 2010). Padin et al. (2020) compiled a data product of 17 653 discrete samples that aggregate measurements of pH, alkalinity, and other biogeochemical variables in this region from 1976 to 2018. Respective long-term trends in surface water pH show acidification ranging from -0.0012 in the open ocean to -0.0039 per year in the inner coastal zone that is associated with a reduction in dissolved oxygen. This result is also associated with an increase in alkalinity driven by changes in surface salinity and surface water fertilisation. The doubling of acidification rates due to the coupling of reduced upwelling with increased CO_2 in the atmosphere forces a change in aragonite saturation and chemical speciation in marine areas, which endangers the important and extensive aquaculture crops present in the region.

7.6 Fishes

The analysis of tipping points in the dynamics of higher trophic levels within marine ecosystems and associated fisheries reveals varying outcomes, depending on non-linear relationships between a specific ecosystem condition and the magnitude of a driving mechanism. On the one hand, a systematic study of the sensitivity of stock characteristics such as abundance, biomass, and average length to temperature changes, based on data from more than 40 exploited marine fish stocks in the North Atlantic used for parameterizing bioenergetically driven nonlinear age-, size-, and stage-specific life-history dynamics with density-dependent recruitment, shows that fishery productivity drops more sharply for negative warming impacts on fish life histories than it rises for positive warming impacts, suggesting an overall detrimental net effect (Shchiptsova et al., 2023 in prep.). This analysis also helps identify multiple fish stocks – including sole in the Bay of Biscay, herring in the Gulf of Riga, sandeel in the south-eastern North Sea, Iberian sardine, and whiting in the waters west of Scotland – that are particularly vulnerable to ocean warming. On the other hand, an investigation of Northeast Arctic cod, the world's largest cod stock, shows, based on a detailed bio-socio-economic model, that yield, profit, and employment in this fishery stand to benefit from ocean warming (Joshi et al., 2023, in preparation). Moreover, the risk of this stock collapsing, i.e., tipping over, due to overexploitation is mitigated by ocean warming. Together, results from these studies underscore the importance of stock-

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specific quantitative studies based on sufficiently realistic process-based models suitable for extrapolating the dynamics of stock and fisheries to unprecedented temperature conditions.

7.7 Ecoregions and biogeographical provinces

Besides analysing the changes in specific species or trophic groups (like plankton, corals or fish), changing habitat conditions can be described within ecoregions or biogeographic provinces defined by their physical and biological characteristics (Reygondeau et al., 2020). For example, in the Arctic Ocean, surface pelagic ecoregions can be clustered based on a set of physical forcing and geophysical environment parameters corresponding to those by Fendereski et al. (2014). As nutrient fields and the representation of primary producers is prone to uncertainty across different ESMs, using only abiotic parameters to define ecoregions avoids bias associated with modelled primary production within past, present and future projections. The evolution in time and space for 10 different ecoregions in the Arctic Ocean since 1950 agree well with Pabi et al. (2008); while the projections until 2100 in a high emission scenario reveal strong shifts in the composition of the regions (**Figure 22**). The ecoregions that dominated more than 50% of the Arctic Ocean over the historic period, will be replaced over the course of the 21st century, while some will be lost completely. The as such defined Arctic Ocean pelagic habitat will shift to a "New

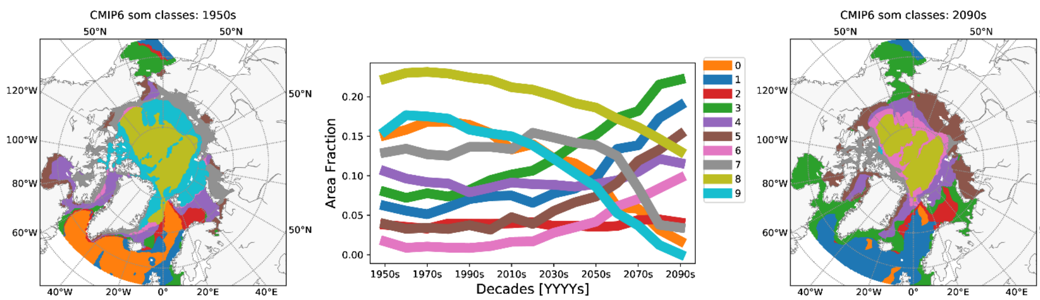

Figure 22: Ocean dynamic ecoregions [0-9] in 1950s (left panel) and 2090s (right panel) identified by self-organizing maps (SOM) classification and decadal temporal changes of their area fraction (middle panel) in the Arctic Ocean. Based on monthly mean data of the historical model run (1950 to 2015) and future projection SSP5-8.5 (2016 to 2100) obtained from CMIP6 NorESM2-MM model output (Bentsen et al., 2019). Abiotic parameters used for the ecoregion classification: annual mean and seasonal variation of mixed layer depth, sea surface temperature, sea surface salinity, shortwave radiation, and ocean bathymetry.

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Arctic" after a transitional period between 2030 and 2060, suggesting a potential tipping point in the Arctic Ocean marine habitat after 2070. Noticeably this occurs after the rapid loss of projected summer sea ice until 2030, i.e., the composition of ecoregions remains relatively stable until the 2040s, suggesting that a safe operating space is sustained for another decade after significant summer sea ice loss. Moving beyond the Arctic Ocean, novel and disappearing ecosystem provinces in the global ocean are of critical concern. Overall, species will be affected by the absolute changes and the rates of changes in physiological, behavioural, evolutionary adaptation and dispersal characteristics, their absolute and relative abundances in addition to changes in their interactions (Pinsky et al., 2020; Blois et al., 2013; Lurgi et al., 2012; Blakeman et al., 2003). Niche theory suggests that species will react individualistically to multiple environmental changes and the appearance of novel provinces by sometimes unexpected changes in species distribution, disruption of existing communities, and formation of novel species associations, as experienced, for example, on land in the last deglaciation (Jackson and Overpeck, 2000; Williams and Jackson, 2007). One important aspect that determines the responses of species and communities is the availability of future habitats. It is therefore important to focus not only on novel conditions but also on the disappearance of conditions which, under our current knowledge, make it difficult that certain species can survive in the future (Blenckner et al., 2021; Lotterhos et al., 2021). This might be especially true for top predators, such as fish, who are disproportionately affected by climate change under future high emissions with severe consequences for the structure of marine ecosystems, affecting energy transfer, ecosystem stability and ecosystem functioning (Boyce et al., 2022).

Besides absolute changes in novel and disappearing conditions, their rate is also highly important (see e.g., Ammar et al., 2021) as the novelty rate determines if species can adapt fast enough through adaptation strategies (Pinsky et al., 2020) under new biogeochemical conditions. Warming and deoxygenation, as previously discussed, will alter aerobic habitats which can be tailored to species-specific thermal and hypoxia sensitivity traits (Deutsch et al., 2015; Deutsch et al., 2020). Gradually changing environmental conditions may result in abrupt shifts for marine organisms to conditions where aerobic respiration is no longer supported. Consistent for a wide range of aerobic limits, changepoints in the timeseries of metabolic indices that indicate such abrupt shifts are projected to occur more frequently until 2100 (Fröb et al., 2023), especially in response to large-scale reorganization of sea-surface temperature patterns (Di Cecco and Gouhier, 2018). This pattern is generally more pronounced at depth than in the upper water column, and the most vulnerable areas for abrupt habitat loss are detected close to the aerobic limits of marine species (Fröb et al., 2023). In order to overcome the potential habitat loss, species might be able to a) migrate into regions that allow maintaining a viable population, both horizontally (Poloczanska et al., 2016), but also to different depth levels (Santana-Falcon and Séférian, 2022), or b) acclimate and adapt, e.g., by exploiting physiological

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plasticity in the aerobic energy metabolism (Oellermann et al., 2022). However, species that are only adapted to low fluctuations in the available aerobic habitat are particularly vulnerable (Mora et al., 2013), i.e. the adaptive capacity is particularly low especially in presence of abruptly changing habitats.

In addition, one of the most vulnerable areas for species and biodiversity loss are coastal areas and estuaries worldwide that are largely affected by climate change in addition to other anthropogenic activities, such as nutrient load from land, fisheries, coastal constructions, maritime transport, and hazardous substances (Blenckner et al., 2015; Breitburg et al., 2018; Halpern et al., 2015). Different combinations of these factors, together with climate-induced changes in the rate, novelty, and disappearance, are likely to affect the species and communities as a whole. Experience on the interplay between climate change and fishing indicates the decrease in ecosystem resilience, which in some cases led to regime shifts. Many regime shift examples exist, e.g., the North Sea (e.g., Sguotti et al., 2022), Baltic Sea (Blenckner et al., 2015; Mollmann et al., 2021; Mollmann et al., 2008) coral reefs (Hughes, 1994; Bellwood et al., 2004; Graham et al., 2015), and kelp forest (Wernberg et al., 2016; Steneck et al., 2002). However, their exact position of tipping points and the often non-stationary interactions of multiple drivers leading to these regime shifts are often context-dependent and cannot be generalised (Spake et al., 2022). Further research is needed to understand better the processes and their operating scales leading to tipping points and regime shifts in ecosystems**.**

8 Concluding remarks

Abrupt ocean biogeochemical changes have been identified for all three basic types (as introduced in section 2 of this paper) and are summarised in **Figure 23** and **Table 1**. A large number of these changes has been identified from modelling studies. The long timescales and small spatial scales of oceanic mesoscale activity (2-100 km in the ocean in contrast to 1000 km in the atmosphere) can often lead to corresponding aliasing of selected hydrographic measurements in the ocean. In conjunction with an overall still sparse observational network (in particular there exist only a few long oceanic time series stations) this leads still to only limited possibilities for the search for and analysis of abrupt marine biogeochemical changes. Thus, the identification of abrupt changes in warming, acidification, and deoxygenation, as well as their cascading impacts on marine ecosystems remains a major research challenge, and we are just at the beginning of understanding causal effects in abrupt changes.

Concerning the identification and monitoring of abrupt ocean state changes a suite of analysis tools exist but still methodological obstacles remain. Dimension-reduction tools and multivariate analysis techniques such as empirical orthogonal functions (EOFs) and principal component analysis (PCA) (e.g., Von Storch and Zwiers, 2010) help to assess temporal patterns in physical and biogeochemical drivers and their ecosystem responses. However, difficulties remain in detecting abrupt changes in marine biodiversity and ecosystem functioning and attributing rapid shifts to causes with statistical confidence. Making progress with the challenge, however, could ultimately provide insight into anthropogenic impacts on marine ecosystems and contributions to abrupt change by natural patterns of ocean variability. So far, changepoint detection methods (e.g., Killick and Eckley, 2014; Killick et al., 2010; Beaulieu and Killick, 2018) have widely and successfully been applied to identify abrupt changes in time series (including the principal component time series from EOF analysis), however, confidently detecting shifts in the entire structure of a complex system still poses a difficulty. Especially in the presence of trends and autocorrelation within the underlying data, the performance of these methods can be limited if time series are short. Further analysis methods such as optimal fingerprinting (e.g., Hasselmann, 1993; Hegerl et al., 1997; Fröb et al., 2020) have been explored, but these methods also rely on consistent time series and decades of sustained measurements. However, observational data is often unevenly spaced in time and space. Further, these data may be subject to sampling bias, i.e., aliased by short-term climate variability. Modelled data on the other hand cover entire regions and longer time intervals but are only an approximative picture of reality with limits in process parameterisation, resolution in space and time, and data mass storage capacity. The combination of both tools, i.e., integrating observed time series with model output, could help to better understand causal effects in abrupt changes by distinguishing the contributions of underlying processes.

As outlined in section 2, the abrupt ocean state changes as described here have to be seen relative to a reference period. The longest timescale considered here is the overall increase in ocean heat uptake and carbon content (in parallel with progressing ocean acidification) due to the human-induced climate forcing. On the other end of the spectrum are the extreme events with timescales of months to a few years, however, with long lasting effects. These effects arise not only to overall trends in the occurrence of extreme events, but can be triggered by individual marine heatwaves or other extreme events. In our analysis, we have included a number of oceanic Earth system tipping elements associated with respective tipping points (thresholds) that are in detail addressed elsewhere (e.g., Lenton et al., 2008; Mckay et al., 2022), where also definitions of climate tipping points and corresponding elements have been presented including quite severe restrictions (including self-enforcing positive feedbacks, irreversibility etc.). We do not stress the term tipping point in our analysis here due to the different meanings and

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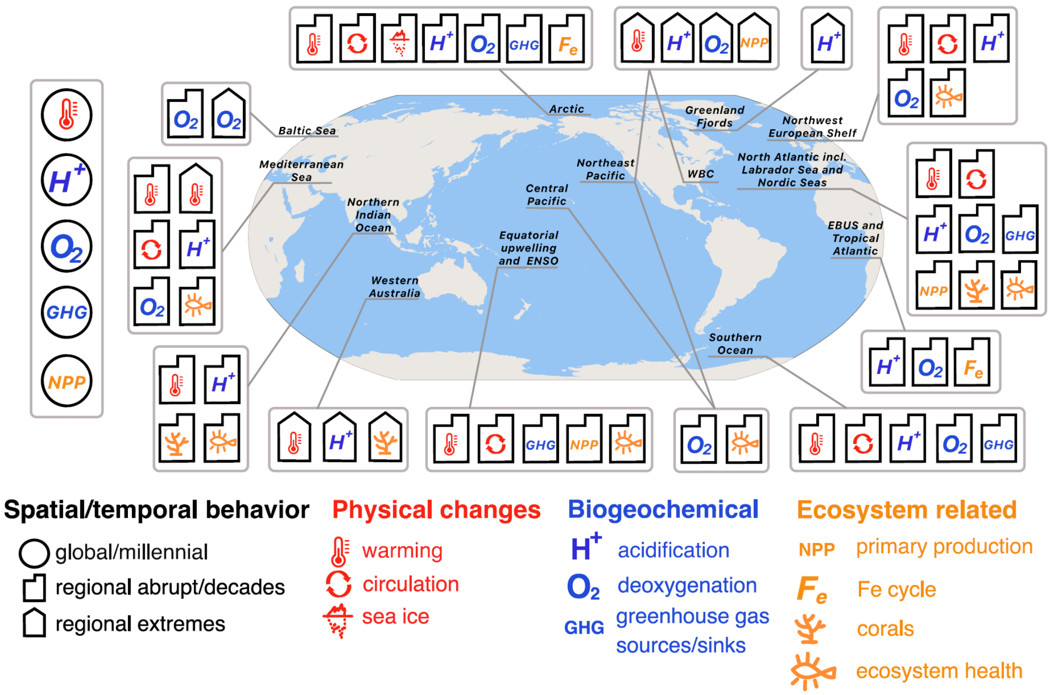

Figure 23: Summary map of key abrupt changes discussed in this paper. The symbols denote the different types of abrupt changes as outlined in section 2 and the various regional expressions of respective ocean state changes as described in sections 3-7. (See also **Table 1**)

sophisticated history and problematic use of this term in climate science (see Russill and Nyssa, 2009). However, we would like to emphasise that regionally occurring abrupt changes within the Earth system can accumulate globally and provide a considerable issue for adaptation to climate change as aggregated impacts (Heinze et al., 2021; Oppenheimer et al., 2014; O'neill et al., 2017).

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Variable	Region	Reference period [yr]	Typical timescale [yr]	Reversibility on human timescales	Sections in paper	Selected impacts
Θ	World Ocean	10^4	100-1000	no	3.2, 7	Vanishing ecosystem provinces
Ω_{arag}	World Ocean	10^5	100-10^4	no	3.3, 7	$CaCO_3$ shell producers, $CaCO_3$ sediment
$[O_2]$	World Ocean	10^4	100-1000	no	3.4, 7	ODZ spreading, fishes, N_2O release
GHG	World Ocean	10^4	100-1000	no	3.3, 3.4	Acidification, hypercapnia
NPP	World Ocean	10^4	100-1000	no	3.4	Biomass standing stock?
Θ, **v**, SIC, Ω_{arag}, $[O_2]$, GHG	Arctic Ocean	100-500	1- ~50	no	4.1.2, 4.2.1-4, 4.2.9, 4.3.2, 5, 6, 7.6-7	Species composition, habitats, loss of $CaCO_3$ producers, nutrient availability due to coastal erosion, fishes, CH_4 release from hydrates, changes in Fe speciation
v	AMOC	100-500	1-100	partial	4.1.1, 6.1.2	Nutrient redistribution, NPP
Θ, Ω_{arag}, $[O_2]$, GHG	North Atlantic incl. Labrador Sea and Nordic Seas	100-500	1- ~50	no	4.1.1, 4.2.4, 4.3.2, 6, 7.4	NPP, cold water corals, CO_2 uptake
Θ, **v**, Ω_{arag}, $[O_2]$	Northwest European Shelf	100-200	1- ~50	no conclusion	4.1.|1, 4.2.7, 4.3.3	NPP, species composition, fishes
$[O_2]$	Baltic	100-100	1- ~25	no conclusion	4.2.7, 4.3.3, 7.7	ODZ spreading, fishes
$[O_2]$	North Pacific				4.3.1, 4.3.4	ODZ spreading, fishes, N_2O release
Θ, **v**, Ω_{arag}, $[O_2]$, GHG	Equatorial Pacific and ENSO domain	100-500	1- ~50	no	4.1.3, 4.2.6	NPP supply, CO_2 uptake
Θ, Ω_{arag}	Northern Indian Ocean	100-500	1- ~50	no	7.3	Warm water corals
Θ, **v**, Ω_{arag}, $[O_2]$	EBUS	100-500	1- ~50	no conclusion	4.3.1, 4.2.9, 7.6	NPP changes, $CaCO_3$ producers, fishes, N_2O release, changes in Fe speciation
Θ, **v**, SIC, Ω_{arag}, $[O_2]$, GHG	Southern Ocean	100-500	1- ~50	no	4.1.2, 4.2.3, 4.3.2	CO_2 uptake variability, $CaCO_3$ producers
Ω_{arag}	Arctic Fjords, acidification extremes	5-50	0.5-3	no conclusion	4.2.1, 5.2	$CaCO_3$ producers, habitats
$[O_2]$	Baltic, negative O_2 extremes occurrence	5-50	0.5-3	no conclusion	5.3	NPP changes, fishes
Θ, Ω_{arag}, $[O_2]$	Western Boundary Current, Coastal Upwelling Regions, Northern Pacific	5-50	0.5-3	selected regime shifts & increase in occurrence	3, 4.1.3, 4.2.6, 4.3.1, 6	NPP changes, regime shifts, temporary loss of also higher trophic species incl. sea birds
Θ, Ω_{arag}	Tropical Ocean, Australia	5-50	0.5-3	selected regime shifts & increase in occurrence	5, 6, 7.3	NPP changes, regime shifts, warm water corals

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Table 1: Overview of selected key abrupt ocean state changes. Θ = pot. temp. of seawater, **v** = circulation/mixing, SIC = sea ice cover, Ω_{arag} = $CaCO_3$ saturation state for aragonite equivalent to increase in H^+ concentration or pH decrease), [O_2] = dissolved oxygen concentration, GHG = greenhouse gas sources and sinks, NPP = Net Primary (marine biological) Production. EBUS = Eastern boundary upwelling systems. For human timescales we take 73.6 yr (average life expectancy, World Health Organisation, value for 2019, see: https://www.who.int/data/gho/data/themes/mortality-and-global-health-estimates/ghe-life-expectancy-and-healthy-life-expectancy, last accessed 10.07.2023). See also **Figure 23**.

Abrupt changes in ocean biogeochemistry have important implications: beyond a general stress on marine organisms due to gradually changing environmental conditions, abrupt changes can override the potential (species dependent) ability to acclimate or adapt accordingly. Abrupt marine biogeochemical changes and the associated irreversibility on human timescales need to be taken into account for climate mitigation strategies but have not been adequately taken into consideration here due to the challenges in mapping and monitoring them. A large-scale framework to address and potentially tackle the different threats to the Earth system the framework of planetary boundaries and Earth system boundaries (Nash et al., 2017; Rockström et al., 2009; Steffen et al., 2015; Rockström et al., 2023) has been developed outlining the goal to stay within a safe operating space for humanity. Attention has been raised to the coupling of the various planetary boundaries and the synergistic action of different environmental forcings as well as drivers including noise that require climate mitigation targets to become more stringent (Lade et al., 2020; Steinacher et al., 2013; Willcock et al., 2023). While gradual changes of the Earth system are now in many cases approaching critical values for ecosystem and human health, the occurrence of abrupt changes on top of these gradual developments requires the further lower climate mitigation targets in order to limit the damage to the marine environment and thus to present and future generations.

Appendix A. Acronyms:

AABW: Antarctic Bottom Water
AMOC: Atlantic Meridional Overturing Circulation
AO: Arctic Oscillation
CCD: Calcium carbonate compensation depth
CDR: Carbon dioxide removal
CDRMIP: Carbon Dioxide Removal Model Intercomparison Project
CMIP6: Coupled Model Intercomparison Project (Phase 6)
DHW: degrees heating week
DIC: dissolved inorganic carbon (sum of the concentrations of gaseous CO_2, bicarbonate, and carbonate)

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ECS: Equilibrium climate sensitivity
ENSO: El Niño Southern Oscillation
ESM: Earth system model
ERF: Effective radiative forcing
GHG: Greenhouse Gas
Ka BP: thousand years before present
LSW: Labrador Sea Water
Ma BP: million years before present
MHW: Marine heatwave
N_r: reactive nitrogen
NPP: Net Primary Production
ODZ: oxygen deficient zone
OMZ: oxygen minimum zone
pCO_2: Partial pressure of CO_2
RCP: Representative Concentration Pathway
SAT: Surface air temperature
SSP: Shared Socioeconomic Pathway,
SST: Sea surface temperature
SV: 1 Sverdrup (= 1 million m^3/s)
ZECMIP: Zero Emissions Commitment Intercomparison Project

Appendix B. Glossary:

Abrupt change: A change (in a system) that is substantially faster than the typical rate of the changes during a reference period.

Calcium carbonate saturation state: Usually denoted by Ω , it represents the thermodynamic tendency of a calcium carbonate mineral, e.g., calcium or aragonite, to form (Ω>1) or to dissolve (Ω<1).

Deoxygenation: The loss of oxygen in the ocean due to warming, changes in ocean circulation, or changes in the biological cycling of organic matter.

Effective radiative forcing ERF: The radiative forcing of the climate system once rapid adjustments (fast feedbacks) below the climate timescale are accounted for.

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Equilibrium Climate Sensitivity ECS: The amount of warming after several hundred years in response to a doubling of atmospheric CO_2 concentrations relative to preindustrial conditions.

Eulerian framework: Fixed to a certain point in latitude, longitude, and depth.

Eutrophication: Anomally high biological production caused by excessively high nutrient supply.

Hysteresis: The inability (or the delayed ability) of a system/state variable to return to its initial state when the previously applied forcing (which induced the original change in the system/state variable) is reversed.

Net Primary Production: The amount of organ carbon produced by phytoplankton per unit area and time where the respiratory loss has been subtracted from the total organic carbon produced through photosynthesis.

Ocean acidification: The shift in the marine carbonate system in response to the oceanic uptake of anthropogenic CO_2, resulting in, e.g., a reduction in ocean pH and the saturation states with respect to calcite and aragonite.

Ocean conveyor belt circulation: Conceptual model of the global ocean circulation starting with a descent of waters in the high northern latitudes, deep flow along the western side of the Atlantic, temporary upwelling and recooling in the Southern Ocean, spreading of southern high latitudes source waters at depth into the Indian and Pacific Oceans and an upper ocean return flow back to the northern high latitudes (going back to the works of Broecker and Peng (1982) and Gordon (1986)).

Regime shift: Large, abrupt, persistence change in the function and structure of a system.

Tipping Point: A critical threshold beyond which a system reorganises (from one stable state to another stable state), often abruptly and/or irreversibly.

Code availability: Not applicable (this review paper does not include any new original computations or model codes).

Data availability: : The data used for plotting Figure 3 are available through: Somes, C., UVic-MOBI Anthropogenic Biogeochemistry Simulations, 2023, *https://zenodo.org/record/8214421*.
The data used for plotting Figures 16 and 19 are available through: Jeltsch-Thömmes, Aurich, & Joos, Fortunat. (2023). Bern3D model output data from idealized CO_2 increase-decrease simulations to investigate reversibility in the Earth system (v1.0) [Dataset]. Zenodo. *https://doi.org/10.5281/zenodo.8224373*

Author contributions:

CH provided the overall concept and outline of the paper, wrote the two introductory sections as well as most of the conclusion section and glossary, and compiled the text and figure contributions into one manuscript including the references. TB, PB, FF, ALM, ALN, CN, SR, IS served as lead authors for the various sections on warming/physical changes, carbon

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cycle/acidification, oxygen cycle/deoxygenation, and ecosystem impacts as well as collated the respective text and figure contributions from the relevant contributing authors for their sections. The lead authors also contributed to the other sections. YAK, YAR, TB, FB, JB, BBC, VÇY, MC, CD, UD, AF, TF, GG, MG, AGG, MGD, NG, ÖG, JH, MH, SH, JH, IEH, FJ, AJT, FJ, JJ, SK, NM, PM, LO, SÓ, JP, FFP, RRP, JR, TR, DR, MSC, YSF, JS, RS, MS, AS, BS, CS, RS, DT, JT, AU, CV, TW, and YY served as contributing authors of specific text paragraphs and/or figures. All authors reviewed the manuscript and commented on it for improvements.

Competing interests:
The authors declare that they have no conflict of interest.

Disclaimer:
The contents of this article reflect only the authors' views—the European Commission and their executive agencies are not responsible for any use that may be made of the information it contains.

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