Response to the Editor concerning minor revisions (Heinze et al., esd-2014-76):

We would like to thank the editor for his constructive comments. We have amended the manuscript accordingly. New lines as mentioned below refer to the version with accepted changes.

1) Reviewer #1 suggested to replace ppm by ppmv throughout the text and the authors did this - however, this is not correct. ppm as used in the carbon cycle community denotes "mole fraction" in dry air (actually mumol CO2/mol dry air). This is not equivalent to ppmv because CO2 is a non-ideal gas. Indeed WMO-GAW specifically recommends to use ppm units. We also adhered to this practice in chapter 2 and chapter 6 in IPCC AR5; and also the cited SIO CO2 website consistently uses ppm.

Our response: We changed ppmv back to ppm and added the IPCC AR5 Glossary as a reference; see new lines 82-85, p. 2, and throughout the manuscript.

2) In the greenhouse effect description the authors state that in the absence of the greenhouse effect, the Earth's temperature would be -19C. This is only true if the albedo of the Earth would remain the same, i.e. assuming the same cloud cover. E.g. just removing the atmosphere would not lower the temperature to -19C. The sentence could be made more precise by stating this in order to avoid misunderstandings.

Our response: Change was made; see new lines 96-99, p. 2.

3) The authors refuse to take on the suggestion by referee #2 to also mention the 13C method (revised manuscript: page 20, line 974, original manuscript: page 1631, line 23) in identifying the relative roles of land vs ocean variability and trends. If the O2/N2 method is mentioned here, clearly also the 13C method merits be mentioned.

Our response: We inserted a respective text passage at new lines 893-905, p.18-19. The new references were added to the reference list.

The acknowledgements were updated in addition.

The manuscript with tracked changes is listed below.

The ocean carbon sink – impacts, vulnerabilities, and challenges

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Abstract

Carbon dioxide (CO_2) is, next to water vapour, considered to be the most important natural greenhouse gas on Earth. Rapidly rising atmospheric CO_2 concentrations caused by human actions such as fossil-fuel burning, land-use change or cement production over the past 250 years have given cause for concern that changes in Earth's climate system may progress at a much faster pace and larger extent than during the past 20,000 years. Investigating global carbon cycle pathways and finding suitable adaptation and mitigation strategies has, therefore, become of major concern in many research fields. The oceans have a key role in regulating atmospheric CO_2 concentrations and currently take up about 25% of annual anthropogenic carbon emissions to the atmosphere. Questions that yet need to be answered are what the carbon uptake kinetics of the oceans will be in the future and how the increase in oceanic carbon inventory will affect its ecosystems and their services. This requires comprehensive investigations, including high-quality ocean carbon measurements on different spatial and temporal scales, the management of data in sophisticated data bases, the application of Earth system models to provide future projections for given emission scenarios as well as a global synthesis and outreach to policy makers. In this paper, the current understanding of the ocean as an important carbon sink is reviewed with respect to these topics. Emphasis is placed on the complex interplay of different physical, chemical, and biological processes that yield both positive and negative air-sea flux values for natural and anthropogenic CO_2 as well as on increased CO_2 (uptake) as the regulating force of the radiative warming of the atmosphere and the gradual acidification of the oceans. Major future ocean carbon challenges in the fields of ocean observations, modelling, and process research as well as the relevance of other biogeochemical cycles and greenhouse gases are discussed.

Contents

1 – Historic background

In the atmosphere, carbon dioxide (CO_2) occurs only in a very small fraction (currently around 400 ppm~~v~~; ~~ppmv = parts per million of volume~~; http://scrippsco2.ucsd.edu/graphics_gallery/mauna_loa_record.html; ppm = parts per million, ratio of the number of moles CO_2 in a given volume of dry air to the total number of moles of all constituents in this volume, see IPCC, 2013). Nevertheless, due to its high abundance as compared to other greenhouse gases, it is considered to be the overall most important greenhouse gas next to water vapour. Its importance in regulating the global heat budget has already been documented in the 19th century by Arrhenius (1886). Ultimately, the greenhouse effect of CO_2 can be linked to its molecule structure: Vibrational and rotational motions of the gaseous CO_2 molecules resonate with the thermal radiation leaving Earth's surface at bands centred at different discrete wavelengths, thereby heating up the lower atmosphere (e.g. Barrett, 2005; Tomizuka, 2010). The main absorption band (combined vibrational and rotational resonance mode) of CO_2 is centred at 15 µm wave length (Wang et al., 1976; Liou, 1980). The incoming solar radiation is of short wavelength (mainly between 0.5-1 µm). The thermal radiation outgoing from the Earth is of longer wave length (typically between 5 and 20 µm). Without the natural greenhouse effect and under the assumption that solar absorption and albedo are kept fixed at the present-day values, ~~,~~an average temperature of -19°C would

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dominate Earth's surface instead of the actual average value of around 15°C (Ramanathan et al., 1987).

The pre-industrial level of atmospheric CO_2 expressed as a volume mixing ratio had been around 278 ppmv with minor fluctuations around this level (Siegenthaler et al., 2005) due to the natural variability of carbon reservoirs on land and in the ocean as well as volcanic activities and a small remaining trend going back to the last deglaciation (Menviel and Joos, 2012). The onset of the industrialisation and the Anthropocene as the era of fundamental human impact on the Earth system (Crutzen, 2002) can be dated around 1776 when the improved design of the steam engine by James Watt enabled its operational use. The 300 ppmv boundary was crossed in the early 20th century according to ice core measurements from Law Dome (Etheridge et al., 2001; samples from Law Dome core D08 show values of 296.9 ppmv and 300.7 ppmv for mean air ages given in calendar years of 1910 and 1912 respectively, with an overall accuracy due to analytical errors and age determination errors of ±1.2 ppmv). At the beginning of the instrumental record of atmospheric CO_2 in 1958, its concentration was around 315 ppmv (Keeling et al., 2001). Ten years ago (2003), we had arrived at 375 ppmv. And now, we are crossing the 400 ppmv level (400.01 ppmv as of 25 May 2013; Fig. 1; Keeling et al., 2013). The largest contributor to this human-induced CO_2 release is firstly the burning of fossil fuel reserves, which normally would have been isolated from the atmosphere (Boden et al., 2011). Secondly, land-use change is a significant contributor followed by cement production (Houghton, 1999; Boden et al., 2011). The warming effect due to the combustion of fossil fuel by human beings was first suggested and analysed by Callendar (1938). Since then, scientists have made attempts to quantify the fate of fossil fuels in conjunction with the natural carbon cycle. Bolin and Eriksson (1959) came up with a first estimate of the ultimate uptake capacity of the ocean for fossil fuel CO_2 from the atmosphere: About 11/12 of CO_2 emissions would ultimately accumulate in the ocean water column after repeated oceanic mixing cycles and interaction with the calcareous sediment, a process requiring several 10,000 years (see also Archer, 2005).

When it comes to the importance of human-produced greenhouse gases for changing the atmospheric heat budget and, hence, the climate system, CO_2 is by far the most important one. Other radiatively active trace gases like methane (CH_4), halocarbons, and nitrous oxide (N_2O) have a higher greenhouse potential per molecule than CO_2, but are less abundant in the atmosphere than CO_2, so that CO_2 is the most important anthropogenic driving agent of climate change (Myhre et al., 2013). The focus of this review is, thus, on CO_2 and the oceanic ('carbon') sink. Future CO_2 emission scenarios to drive climate models have been produced on empirical evidence concerning human behaviour and economics. In view of the on-going high energy use in wealthy nations and the accelerating energy production in emerging economies (especially China and India; see Raupach et al., 2007), current and recent annual CO_2 emission rates are at the levels of the most pessimistic emission scenario as produced a few years ago for the climate projections of the 5th assessment report of the IPCC (RCP scenarios; van Vuuren et al., 2011a; van Vuuren et al., 2011b; Peters et al., 2013). Considering the key role of the oceans in the global carbon budget it is therefore fundamental to broaden our knowledge on their past, present, and future quantitative impact in regulating atmospheric CO_2 concentrations.

2 – General concepts of ocean carbon cycling

The oceans regulate atmospheric CO_2 mainly by two mechanisms: The first consists of the abiotic inorganic cycling of carbon that involves CO_2 air-sea gas exchange (Liss and Merlivat, 1986; Wanninnkhof, 1992; Nightingale et al., 2000), CO_2 dissolution (Weiss, 1974) and hydration to carbonic acid, dissociation of carbonic acid (Dickson et al., 2007) as well as transport and mixing of total dissolved CO_2 in seawater. The second mechanism describes the cycling of carbon due to biological activity.

2.1 – Inorganic carbon cycle processes

Seawater is saline and contains practically all elements of the chemical periodic table. Due to its slightly alkaline behaviour, it can keep the ionic compounds of weak acids in solution. Carbon dioxide, or carbonic acid (H_2CO_3) when combined with water (H_2O), dissociates in seawater mostly into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), while only a small amount of the CO_2 is kept in its dissolved state (as an order of magnitude estimate the partitioning of HCO_3^-: CO_3^{2-}:CO_2 is 100:10:1 but significant deviations from this can occur especially with respect to CO_2). The sum of HCO_3^-, CO_3^{2-}, and CO_2 is called 'total dissolved inorganic carbon' (DIC). A huge reservoir of DIC has been built up in the oceans over geologic time through the interaction of seawater with sediments, weathering from land, gas exchange with the atmosphere, and outgassing from the Earth's interior. At pre-industrial times, this DIC pool is 65 times as large as the atmospheric pre-industrial CO_2 reservoir and approximately 20 times as large as the carbon on land bound to living and dead biomass including soils (Degens et al., 1984; Falkowski et al., 2000).

DIC is distributed in the oceans as passive tracer (like dye) by currents and turbulent mixing. In a simplistic model, transportation of carbon in the oceans mainly follows the large scale ocean circulation: In the northern North Atlantic, surface waters are moved to the deep sea in a process of deep-water formation. The solubility of CO_2 gas in seawater increases with decreasing temperature. As newly formed deep water is cold, the downward transport of the carbon fraction dissolved in seawater due to high CO_2 solubility is also called solubility pump (Volk and Hoffert, 1985). However, the dissociation of CO_2 into bicarbonate and carbonate ions is antagonistic to the solubility and decreases with decreasing temperature and compensates to a certain degree for this. In a theoretical ocean with only the solubility pump acting the overall surface to deep gradient of DIC would be slightly positive downwards. On its way through the ocean part of the deep water then upwells in the Southern Ocean around Antarctica, where it is blended with water masses from all oceans before it is re-cooled again to form deep and intermediate waters that spread into the Atlantic, Pacific, and Indian Ocean. The circle is closed through the transport of upper water masses from the upwelling regions back to the deep-water production areas in the North Atlantic and the Southern Ocean (Broecker and Peng, 1982), which occurs via the Indian Ocean ('warm water path') or via the Drake Passage ('cold water path' between South America and Antarctica; Rintoul, 1991). The water that has spent the longest time away from contact with the atmosphere is found in the northern Pacific Ocean below depths of about 2000 m and is approximately 1500 years old. Comparably, the human perturbation of the carbon cycle has occurred only over the last 250 years, and diluting high anthropogenic carbon loads from the upper ocean with large deep-water reservoirs by mixing processes will take at least 6 times as long. Also, the slower oceanic circulation and mixing become with on-going climate change, the smaller the uptake rate of surface waters for human-produced carbon will be and the less efficient the ocean carbon sink will become for absorbing further CO_2 additions to the atmosphere as carbonic acid dissociates less well into bicarbonate and carbonate in water of high pCO_2.

2.2 – Biological carbon pumps

While purely inorganic carbon cycling leads to a slight increase of DIC with depth, biological carbon cycling - via the two biological carbon pumps (Volk and Hoffert, 1985) - is responsible for most of the gradients existing in the real ocean DIC distribution. These gradients are mainly fuelled by uptake of DIC by biota in the surface ocean to produce particulate matter, the vertical flux of these particles, and degradation of these particles on their downward way through the water column. Biological carbon binding occurs mainly in the ocean surface layer, where phytoplankton through the process of photosynthesis produces biomass that can be utilized by other organisms on higher trophic levels (classical food chain). Next to dissolved CO_2, phytoplankton requires light and nutrients for their growth, the latter two being critical limiting factors. About 25% of the particulate organic carbon (POC), which is produced in the ocean surface layer, eventually sinks through the water column (Schlitzer, 2000) with most of it being remineralised and returned to the dissolved phase already within the upper 1500 m. Normally, less than 1% of POC reaches the open-ocean seafloor by sedimentation (Lee et al., 2004). In addition to POC, marine biota also produce dissolved organic carbon (DOC), which is discriminated from POC based on particle size (Turnewitsch et al., 2007). As increasingly small particles do not sink anymore through the water column but become suspended due to the increasing importance of friction for small particles, DOC is transported through the oceans like DIC as a passive tracer. While a large fraction of DOC may persist and accumulate in the water column before being remineralised to inorganic substances, biologically labile DOC is converted quickly (within minutes to days) in the upper ocean, predominantly by microbial activity (Carlson, 2002). By utilising DOC, bacteria can build up exploitable biomass and part of the dissolved organic carbon may re-enter the classical food chain through the 'microbial loop'. However, as the microbial loop itself includes several trophic levels, a large part of the recycled DOC is converted back to inorganically dissolved carbon along the process (Azam et al., 1983; Fenchel, 2008). In addition to microbial degradation, sorption onto larger particles, and UV radiation may constitute further important processes in the removal of dissolved organic matter (Carlson, 2002). The oceanic DOC pool is overall about one order of magnitude smaller than the marine DIC inventory but larger than the POC pool. Nevertheless, the highly reactive POC dominates the effect on variations in the oceanic DIC distribution. Most of the DOC is quite refractory which is consistent with its high radiocarbon age (4000 - 6000 years, Druffel et al., 1992). Thus, most of the marine DOC does not contribute much to the dynamics of carbon cycling in the ocean within the flushing time scale of the world ocean of about 1500 years. Next to POC and DOC cycling, the formation of calcium carbonate ($CaCO_3$) by shell- and skeleton-building marine organisms is of great importance in the ocean's carbon cycle as it causes shifts in the overall DIC pool. HCO_3^- is converted to CO_3^{2-} to produce $CaCO_3$. During this process, CO_2 is released to the surrounding water (Fig. 2, formula 3; Frankignoulle et al., 1994). Thus, the $CaCO_3$ pump is counteracting the organic carbon pump. As more carbon is bound to POC and DOC during biological production than to $CaCO_3$ (this rain ratio of CaCO3:POC amounts globally averaged to about 15% when counted in carbon atoms bound to particulate matter; Berelson et al., 2007), the $CaCO_3$ counter pump does nowhere fully compensate for the organic carbon pump. Within the oceans, $CaCO_3$ occurs either as aragonite or as calcite, with aragonite being more soluble at given conditions. The solubility of both compounds increases slightly at lower temperature and strongly with increasing depth (pressure) (Mucci, 1983; Zeebe and Wolf-Gladrow, 2001). Shell material sinking together

with POC through the water column is usually degraded at larger depths than the organic material. Nevertheless, it is likely that also partial re-dissolution of calcitic and aragonitic plankton hard parts occurs in shallower depths than the respective $CaCO_3$ saturation horizon. Potential contributors to this are, e.g., zooplankton metabolisms (dissolution of shell material in copepod guts; Jansen and Wolf-Gladrow, 2001), local undersaturation hot spots due to lateral admixture of water or in micro-environments on biogenic particles due to remineralisation of organic matter (Barrett et al., 2014), and admixture of larger amounts of Mg in the $CaCO_3$ material (high-Mg calcites; Feely et al., 2004).

The composition of the sinking material determines also its sinking velocity. Phytoplankton (plant plankton) and zooplankton (animal plankton) grazing on plant plankton or eating other zooplankton can modify the vertical particle flux by producing a variety of carbonaceous or siliceous shell material.

Shallow seas including the continental margins are marked with high accumulation rates of organic carbon (Jahnke, 1996). In contrast, deep-sea sediments are mainly composed of the hard parts of calcareous and siliceous shell material (Leinen et al., 1986; Archer, 1996). In regions of vivid upward motion of water, such as at the Equator, in front of west coasts, in the Southern Ocean, and during vertical mixing in the North Atlantic, the biological productivity can be substantial as new nutrients are supplied from below. This happens especially during plankton blooms, when light availability and stable surface water stratification enables temporarily strong photosynthesis leading first to strong production of phytoplankton and subsequent increase in zooplankton which grazes on the phytoplankton. Particle transport via the biological carbon pump, remineralisation, and ocean circulation are superimposed and are responsible for most of the gradients of dissolved carbon and nutrients in the water column: 1. Regarding the vertical gradient, low concentrations result at the surface due to biological uptake, while values increase with depth due to remineralisation. 2. In deeper layers, concentrations increase horizontally with age of the water along the trajectory of water flow when the respective water volume receives more and more remineralised products from the particles under degradation. The loop for the cycling of biological carbon through the ocean is closed, when the deeper waters well up and eventually return back to the surface mixed layer. These old deep waters are highly enriched in remineralised biogenic carbon, which then outgasses into the atmosphere. Thus, the upwelling regions are sources of carbon to the atmosphere both regarding the biological and the solubility pumps. This source effect dominates over the strong biological carbon uptake in upwelling regions, indicating that they are typically oversaturated in carbon and release CO_2 to the atmosphere (Fig. 3).

Production of $CaCO_3$ shell material and its dissolution work in opposite direction for the dissolved CO_2 in the ocean. Taking out or releasing CO_3^{2-} changes the ability of seawater to dissociate carbonic acid significantly. Stopping the global biological $CaCO_3$ production would lower the atmospheric CO_2 concentration by about 75 ppmv (Broecker and Peng, 1986). This number, though, depends on the size of the global $CaCO_3$ production, which is not yet very well established. The global production rate depends also on the availability of silicic acid: When enough dissolved silicate is available, organisms that produce siliceous shell material ('opal', BSi) dominate due to energetic reasons. Therefore, many BSi-producers are found in upwelling areas, while $CaCO_3$ producers are more abundant in other oceanic domains (Dymond and Lyle, 1985). The sedimentary climate record shows that modifications of biological carbon cycling have significantly contributed to the glacial drawdown of atmospheric CO_2 during the repeated ice age cycles over the past million years (Balsam, 1983; Farrell and Prell, 1989; Oliver et al., 2010).

The organically bound and living biomass carbon reservoirs in the ocean are significantly smaller than the inorganic reservoir (approximate ratio of 1:50; Druffel et al., 1992; Ciais et al., 2013). Nevertheless, continuous growth of plankton at the ocean surface keeps the ocean surface layer CO_2 concentration on the average lower than it would be without them. In a world with a lifeless ocean, the atmospheric CO_2 concentration would have been about twice as high as the pre-industrial one. A sudden hypothetical stop of marine life would increase the atmospheric CO_2 concentration by 200-300 ppmv.

2.3 – Natural variability, timescales, and feedbacks

The variability of the ocean carbon cycle in relation to the atmospheric CO_2 concentration covers a broad range of timescales (from seasonal to interannual, decadal, century-scale, and glacial-interglacial). Seasonal changes in sea surface pCO_2 and, hence, air-sea CO_2 flux are caused mainly by variations in sea surface temperature and biological activity, where often both effects tend to counteract each other. Typical seasonal seawater pCO_2 amplitudes amount to few tens up to ±50 ppmv of pCO_2 (Santana-Casiano et al., 2007; Landschützer et al., 2014). Because of the long equilibration time of the ocean mixed layer and the atmosphere (see Sarmiento and Gruber, 2006), ocean variability has a much smaller influence on the seasonal atmospheric CO_2 variability than the terrestrial carbon cycle. Interannual to decadal variations in air-sea CO_2 fluxes are linked to changes in deep-water formation and coupled to the internal variability modes of the climate system, which complicates the detection of changes in long-term trends in ocean carbon uptake (for climate modes see section 3.3). Long-term observations at ocean time series stations allowed the monitoring of decadal trends in rising sea surface pCO_2 (typical values are +1 to +3 ppmv/yr) and decreasing pH (typical values are here -0.001 to -0.003 pH units per year) at specific sites over the past decades (Bates et al., 2014). Pre-industrial atmospheric CO_2 mixing ratios have been quite stable over the past 10,000 years with a slight increase from ca. 260 ppmv to ca. 280 ppmv which can at least partly be attributed to long-lasting compensation effects from the last deglaciation (Joos et al., 2004). In contrast, the last glacial-interglacial cycles were marked by an amplitude of about 110 ppmv in atmospheric pCO_2 with values around 290 ppmv at interglacials and 180 ppmv at glacial maxima (Siegenthaler et al., 2005). A combination of oceanic processes is likely to have been responsible for these variations (Heinze et al., 1991; Heinze and Hasselmann, 1993; Brovkin et al., 2007), but the concrete details of the relevant processes are so far not well established. In a cold and dry glacial climate, the land biosphere was presumably less well developed as during warm and more humid periods, and therefore, the terrestrial carbon cycle may have provided a CO_2 source to the atmosphere rather than a sink (Crowley, 1995).

A number of feedback processes work between climate and the marine carbon cycle. These processes involve the inorganic as well as the organic carbon cycle in the ocean. Key primary driving factors behind these feedback processes are changes in temperature (physical forcing), changes in circulation as well as sea-ice cover, and changes in atmospheric CO_2 (chemical forcing). For the natural glacial-interglacial carbon cycle variations an overall positive feedback between carbon cycle and climate resulted. Candidate processes contributing to this feedback are lower seawater temperatures during glacial maxima, potentially somewhat altered sea surface salinities, and changes in ocean circulation primarily involving the alterations of the Southern Ocean circulation (Broecker and Peng, 1986; Broecker and Peng, 1989; Sigman and Boyle, 2000) in conjunction with changes in the biological carbon cycling. Respective hypotheses include changes in the production of $CaCO_3$, changes in nutrient utilisation efficiency of organisms, changes in nutrient availability, and varying interactions

between shelf seas and the open ocean under glacial-interglacial sea-level changes (Broecker, 1982; Broecker and Peng, 1989; Archer et al., 2000). The processes governing the oceanic uptake of anthropogenic carbon from the atmosphere may differ from those which had been been responsible for the glacial-interglacial atmospheric CO_2 variability. For the anthropogenic uptake problem, the time scales involved are shorter. Further, while during glacial-interglacial cycles carbon was mainly re-distributed between the different Earth system reservoirs, for the anthropogenic carbon uptake newly added carbon to the Earth system must beredistributed between those reservoirs.

3 – Evolution of the ocean sink for anthropogenic carbon

The cycling of carbon in the oceans is a complex interplay of different physical, chemical and biological processes, yielding both positive and negative air-sea flux values for natural and anthropogenic CO_2 depending on the oceanic region and the seasonal cycle. Due to the rapid increase of atmospheric CO_2 concentrations in the past 250 years and the resulting implications for the global heat budget, it is of great importance to understand the driving forces of carbon sequestration in the oceans as well as their variability, i.e. to understand the role of the oceans as a sink for anthropogenic CO_2.

3.1 - The key process for anthropogenic carbon uptake

The equilibrium concentration of gaseous CO_2 in seawater depends both on the concentration of DIC and the concentration of hydrogen ions. Since the beginning of the Industrial Revolution, atmospheric CO_2 concentrations have been rapidly rising. The addition of CO_2 to the oceans through gas exchange with the atmosphere leads to a shift in the partitioning of HCO_3^-, CO_3^{2-}, CO_2, and the concentration of hydrogen ions (Fig. 2, formulas 1 & 2). The more CO_2 gets absorbed by the ocean the lower the amount of CO_3^{2-} becomes. In parallel, the concentration of hydrogen ions increases, causing a decrease in open ocean pH that is referred to as ocean acidification. Projections of future ocean pH suggest a potential total reduction by 0.4-0.5 units by the end of the 21st century as compared to pre-industrial levels, resulting in a pH of 7.7-7.8 (Haugan and Drange, 1996; Brewer, 1997; Caldeira and Wickett, 2003; Bopp et al., 2013). Furthermore, a shifting ratio of HCO_3^-:CO_3^{2-}:CO_2 results in a decrease in CO_2 buffering: the larger the concentration of DIC in the ocean becomes, conversely the smaller the fraction of increased carbon added to the atmosphere that can be taken up by the ocean will be. Or in other words, the higher the cumulative CO_2 emissions to the atmosphere become, the less effective seawater will be in dissociating a part of this CO_2 into HCO_3^- and CO_3^{2-}.

The biological carbon pump does not sequester anthropogenic carbon added to the ocean itself on decadal to centennial time scales (as the process for new crude oil works on geologic time scales). However, alterations of the biological pump caused by changes in ocean circulation and rising carbon concentrations in the surface layer could modulate the marine uptake of human-produced CO_2 to some degree. Among these biological changes are a potential decrease in biological $CaCO_3$ production (Heinze, 2004; Gehlen et al., 2007; Ridgwell et al., 2007) and a potential change in carbon to nitrogen ratios in oceanic organic matter under high CO_2 (Riebesell et al., 2007).

The main three-dimensional distribution of DIC, oxygen (O_2), and nutrients in the ocean is determined by the action of biota and their degradation together with the three-dimensional ocean circulation. To demonstrate that ocean carbon cycle models work properly, the inclusion of the organic carbon cycling in these models, therefore, is an important necessary condition. On the other hand, uptake of anthropogenic excess CO_2 from the atmosphere is mainly determined by the physico-chemical buffering mechanism and transport of water with high anthropogenic carbon concentrations into the ocean interior. Nevertheless, simulations of biologically mediated tracers such as O_2, PO_4^{3-} etc. help to constrain the oceanic velocity field of the respective model, especially because respective measurements are abundant. Further, the biologically mediated CO_3^{2-} ion distribution is a powerful constraint on whether the inorganic carbon cycle is correctly described by the models. The simulation of anthropogenic marine carbon uptake in purely inorganic carbon cycle models (i.e. those which do not include ecosystem representations, no nutrient tracers, and no oxygen cycle) can to some degree be validated by age tracers which are employed also for evaluation of ocean model velocity fields in general. Radiocarbon ^{14}C, which enters the ocean mainly from the atmosphere, is still the most used age tracers for validating oceanic transport rates as well as patterns in ocean circulation models. With its half-life of 5730 years (sometimes also the slightly smaller Libby half-life is used; see Stuiver and Polach, 1977), radiocarbon of DIC results in substantial surface to deep gradients. The natural radiocarbon distribution is contaminated by bomb ^{14}C, which entered the ocean in large amounts due to atmospheric tests of nuclear weapons until the atmospheric test ban treaty in the mid-1960s was implemented. To some degree, bomb ^{14}C can also be used as tracer for water mass exchange in itself, but the lack of knowledge about the pristine ^{14}C distribution on already contaminated areas remains a problem in spite of attempts to reconstruct natural pre-bomb ^{14}C values in the ocean interior (Broecker et al., 1995). Nevertheless, for the large scale ocean, ^{14}C remains one of our best tracers for assessing turnover rates of water masses in the ocean (cf. Schlitzer, 2007). Another, in principle powerful, age oceanic tracer is the noble gas isotope ^{39}Ar. Its shorter half-life of 269 years (Stoenner et al., 1965) would even be more suitable to resolve upper ocean gradients for validation of ocean ventilation time scales in models (Müller et al., 2006). New measurement techniques allowing for small sample size may enable building a larger ^{39}Ar data base for the ocean (Collon et al., 2004).

As supporting evidence for pathways of anthropogenic carbon from the atmosphere over the surface layer and into the ocean interior, also ^{13}C and chlorofluorocarbons are used. Fossil fuel CO_2 in the atmosphere has a low ^{13}C signature (plant material that had been the basis for crude oil formation has a deficit in the stable carbon isotope ^{13}C relative to ^{12}C, also known as the Suess effect; see Keeling, 1979). Waters with a deficit of ^{13}C in DIC relative to natural background conditions, therefore contain carbon from anthropogenic sources (Racapé et al., 2013). Unfortunately, the reconstruction of the pristine ^{13}C distribution in the ocean is not straightforward (Olsen and Ninnemann, 2010), and further the ^{13}C distribution in the ocean is strongly influenced by formation as well as degradation of biogenic matter (Kroopnick, 1985). Chlorofluorocarbons or 'CFCs' (such as $CFCl_3$ or 'F-11' and CF_2Cl_2 or 'F-12') are purely human-produced substances (also known for their negative effect on the stratospheric ozone layer) which entered the oceans from the atmosphere in small amounts following their atmospheric concentration and their respective solubilities in seawater. Though their atmospheric concentration time series and their uptake mechanisms in the ocean are different than for CO_2, they nevertheless give a constraint on where large amounts of anthropogenic carbon have entered deeper layers and what time scales are involved with this uptake (Smethie, 1993; Schlitzer, 2007; Steinfeldt et al., 2007).

3.2 – Long-term ocean carbon uptake kinetics

The classical view about the marine uptake of anthropogenic CO_2 from the atmosphere is that the ocean sink averaged over the entire globe is operating continuously and reliably and is less variable than the exchange between the atmosphere and the land biosphere including soil and plants (though the classical view also includes that the ocean atmosphere transport of CO_2 co-varies with short-term climate variability). This view was supported by the basic inorganic carbon buffering mechanism and by the fact that the equilibration timescale between the ocean surface layer and the atmosphere is approximately 6-12 months. The variability of air-sea CO_2 gas exchange is dampened, because not only the CO_2 molecules are taking part in the equilibration process, but the entire surface layer volume needs to achieve chemical equilibria for the compounds HCO_3^-, CO_3^{2-}, and dissolved CO_2. Therefore, seasonal variations in DIC due to biological production and remineralisation occur quicker than for respective air-sea gas exchange fluxes to compensate for them. Thus, also, the seasonal cycle in the instrumental atmospheric CO_2 record is dominated by the seasonal variation of the land biosphere, especially for the northern hemisphere (Keeling et al., 2001). However, with significantly improved observing systems in the past two decades, it has become obvious that on a regional scale air-sea carbon fluxes may considerably differ between years (Le Quéré et al., 2007; Schuster and Watson, 2007). There are indications that these regional and temporal variations have been smoothed out on decadal time scales over the past 20 years (McKinley et al., 2011), but nevertheless observations and models suggest that the ocean sink is vulnerable to a decrease in efficiency during further climate change and further rising ambient CO_2 levels (Friedlingstein et al., 2006; Le Quéré et al., 2007; Watson et al., 2009; Arora et al., 2013).

In general, one has to discriminate between the ultimate uptake capacity of the ocean for anthropogenic CO_2 from the atmosphere and the marine uptake kinetics for this CO_2. Both are societally relevant and need to be taken into account for emission reduction strategies and development of improved renewable energy systems.

The ultimate uptake capacity denotes the amount of anthropogenic carbon emitted to the atmosphere that in total eventually ends up in the ocean, long after the human-caused greenhouse gas emission perturbation has happened and when the ocean carbon cycle has achieved quasi-equilibrium. This time scale is of the order of several 10,000 years, because the ocean water column has to fully equilibrate with the $CaCO_3$ sediment on the seafloor, where a considerable portion of the $CaCO_3$ will become dissolved after repeated cycling of deep water (Broecker and Takahashi, 1977; Archer, 2005). The respective CO_3^{2-} ions made available in seawater can, thus, be employed for neutralising anthropogenic carbon in the ocean. On very long time scales, this redissolution of $CaCO_3$ from the sediment, thus, provides an important negative feedback process to climate change. In addition, high atmospheric CO_2 levels enhance the weathering rate of carbonates on land. This process also works effectively only on long time scales with potentially quicker changing hot spots (Archer, 2005; Beaulieu et al., 2012). The ultimate storage capacity of the ocean critically depends on the total amount of carbon emitted. Burning of 5000 GtC (GtC = gigaton of carbon) of potentially available fossil fuel reserves would lead to a higher long-term CO_2 level in the atmosphere and a reduced fractional ocean uptake capacity in comparison to, e.g., burning only 1000 GtC (Archer, 2005). The impact on societies and life even after 100,000 years depends, thus, on our behaviour concerning usage of fossil fuel reserves today. This fact as well has to be taken into account for greenhouse gas emission reduction strategies.

The oceanic CO_2 uptake kinetics denote the speed with which human-produced CO_2 emissions to the atmosphere can be buffered by the oceans. Due to the limiting effect of gas exchange, CO_2 dissociation, turbulent mixing and ocean large-scale circulation, only a certain percentage of the excess CO_2 in the atmosphere can be taken up at a given unit of time by the ocean (Maier-Reimer and Hasselmann, 1987; Joos et al., 2013). Regionally, this also depends on the seasonal variations in circulation, biological productivity, as well as light, temperature, sea-ice cover, wind speed, and precipitation. It is expected that climate change will lead to a more stable density stratification in the ocean and a general slowing down of large-scale mixing and circulation (Meehl et al., 2007). The consequence will be a reduced uptake of anthropogenic carbon from the atmosphere at the ocean surface and also a lower downward mixing of anthropogenic CO_2 into deeper waters. In addition, high CO_2 in the atmosphere implies high CO_2 in surface waters and a reduction in the ocean's capability to dissociate the CO_2 into the other compounds of DIC, i.e. a decreasing buffering ability with rising ambient CO_2 levels. We have, thus, a physical and a chemical driving force acting on the carbon balance simultaneously and slowing down the transfer of anthropogenic carbon from the atmosphere into the ocean. The net effect is a reduction in carbon uptake efficiency with warming climate and rising atmospheric CO_2, i.e. a positive feedback to climate change. In a situation with reduced ocean ventilation, also the biological pump will be affected and should be considered in the assessment on how the ocean carbon cycle is impacted. The oceanic CO_2 uptake kinetics depend on the rate of CO_2 emissions to the atmosphere: The faster the emissions are increasing, the stronger is the climatic effect on slowing down the uptake and the stronger the chemical effect on decreasing the CO_2 buffering. These effects are caused by water with high anthropogenic carbon load that cannot be mixed into the interior of the ocean with the original efficiency and because the buffering ability of seawater decreases with increasing CO_2 partial pressure in the water. The oceanic bottleneck effect is obvious in several decade-long future scenarios with ocean models (Maier-Reimer and Hasselmann, 1987; Sarmiento and Le Quéré, 1996), fully coupled Earth system models (Friedlingstein et al., 2006; Roy et al., 2011; Arora et al., 2013), as well as EMICs (Earth system models of intermediate complexity; these have a lower resolution than usual Earth system models, but demand much less computational resources; Steinacher et al., 2013; Zickfeld et al., 2013). Earth system models are complex computer programmes, which include dynamical representations of the various Earth system reservoirs (atmosphere, ocean, land surface, ice) and the simultaneous interaction between these reservoirs (Bretherton, 1985; Mitchell et al., 2012). Earth system models are driven by solar insolation and greenhouse gas emissions and deliver expected time- and space-dependent distributions of important climatic variables. These variables can be of physical nature, such as temperature, precipitation, salinity, wind fields, ocean currents, sea-ice cover, or of biogeochemical nature, such as CO_2 concentration in ocean and atmosphere, pH value in the ocean, nutrient and dissolved oxygen concentrations, soil organic carbon, or biological productivity. The temporary build-up of high CO_2 concentrations in the atmosphere increases directly with the human-produced CO_2 emissions. At pessimistic scenarios with high annual emissions, the annual fraction of emissions buffered by the oceans is reduced, while pathways with reduced emissions enable a more efficient oceanic uptake rate. Inclusion of carbon dynamics in ocean and land models increases the sensitivity of climate models with respect to radiative warming. This means that models with carbon cycle representations and respective carbon-cycle-climate-feedbacks lead to an overall stronger warming than with conventional climate models that do not include an interactive carbon cycle. The range of this feedback is still large due to inherent model uncertainties and a partial lack of process understanding in all relevant disciplines.

3.3 – Detection of ongoing ocean carbon sink strength variability

In the past two decades, the number of ocean carbon observations has considerably increased (Sabine et al., 2010). Data collection ranges from the surface to the deep ocean, encompasses different oceanic regions and includes various time series to capture both spatial and temporal variations. Satellite measurements have been extremely useful to identify the geographical distribution of biological primary productivity at the sea surface over seasonal as well as interannual cycles and to derive wind fields of high value for quantification of gas transfer velocities across the air-water interface. Targeted research cruises as well as the use of commercial ships (voluntary observing ships, VOS) equipped with automated systems are the backbone of surface ocean CO_2 concentration measurements, the data being synthesised in the SOCAT project (Fig. 3) (Pfeil et al., 2013; Sabine et al., 2013; Bakker et al., 2014). Selected buoys and floats are used to capture the spatio-temporal variability of ocean carbon. The most prominent network of floats was established in the framework of ARGO (Array for Real-time Geostrophic Oceanography) that delivers valuable temperature, salinity, and current data for a better understanding of mixed layer and subsurface dynamics. However nowadays, ocean floats are also successfully exploited as platforms for measuring e.g. pCO_2, O_2, optical variables, or nitrate (Boss et al., 2008; Johnson et al., 2010; Fiedler et al., 2013), overall increasing the possibilities for detailed, autonomous ocean monitoring with high vertical resolution and data recovery in remote areas (Fiedler et al., 2013). For the deep ocean, data synthesis products cover at least parts of the major oceans (GLODAP, CARINA, PACIFICA; Key et al., 2004; Key et al., 2010; Suzuki et al., 2013), but only episodically include seasonal cycles and do not enable the study of year to year variations in three-dimensional measurement fields (of DIC, nutrients, and dissolved oxygen). A small number of time series stations allow a quasi-continuous view at selected ocean sites (HOTS, BATS, ESTOC, PIRATA moorings, CVOO, PAP, PAPA, DYFAMED, Station M, IS-ts and further; see http://www.oceansites.org/ and Olafsson et al., 2009). These time series stations have often been established in areas of fairly low short-term variability in order to allow a reliable establishment of long-term trends in the observations.

Though the observational basis for assessing changes in the oceanic carbon cycle is limited, a number of major findings have been achieved. Sabine et al. (2004) compiled a global map of the ocean water column storage of anthropogenic carbon for the year 1994. In this map, the North Atlantic and the Southern Ocean with adjacent regions are recognized as hot spot areas for anthropogenic carbon storage. By combining observations with statistical and process-based model approaches, it could be shown that in these regions the annual uptake of CO_2 from the atmosphere has temporarily decreased, though the total inventory of the anthropogenic water column burden has monotonously increased.

Both the North Atlantic and the Southern Ocean are deep-water production areas that would be very vulnerable regions with respect to climate-change induced slowing of oceanic carbon uptake. Internal variability modes of the climate system can be linked to variability in marine uptake of anthropogenic carbon. These internal variability modes have been identified through analysis of oceanic and atmospheric physical state variables (such as temperature, pressure, precipitation, and salinity). The variability modes cause atmospheric and oceanic anomalies with specific spatial patterns and time scales associated. The most important ones are ENSO (El Niño Southern Oscillation; Philander, 1990), NAO (North Atlantic Oscillation; Hurrell, 1995), SAM (Southern Annular Mode; Limpasuvan and Hartmann, 1999), and the PDO (Pacific Decadal Oscillation; Mantua and Hare, 2002). For the North Atlantic, a 50% change of the oceanic CO_2 sink could be deduced from the VOS line measurement network during the years 2002-2007 (Watson et al., 2009). Also other studies support the temporary

644 decrease of North Atlantic CO_2 uptake during several years of the past decade (Corbière et al.,
645 2007; Schuster et al., 2009). These variations are at least partially attributed to oceanic
646 variability in the North Atlantic associated with a surface pressure pattern change known as
647 North Atlantic Oscillation (Wetzel et al., 2005; Thomas et al., 2008; Tjiputra et al., 2012). In a
648 model study with six coupled Earth system models, Keller et al. (2012) identified a see-saw
649 pattern of variations in sea surface pCO_2 between the North Atlantic subtropical gyre and the
650 subpolar Northern Atlantic with an amplitude of ±8 ppmv. Such variations make
651 identification of long-term trends in oceanic carbon uptake more difficult. With the help of
652 deep repeat hydrography measurements, Pérez et al. (2013) could show that variations in
653 North Atlantic CO_2 uptake are coupled to changes in meridional overturning large-scale
654 circulation (linked to varying deep-water production rates). For the Southern Ocean, the
655 observational ocean carbon data base is comparatively small, mostly due to the lack of regular
656 shipping routes except for supply ships to Antarctic weather and research stations.
657 Nevertheless, it could be shown, that the oceanic CO_2 uptake from the atmosphere did not
658 keep up with the rising atmospheric CO_2 for some time. This result could be achieved using
659 models driven with realistic atmospheric forcing in combination with observations primarily
660 from the Indian Ocean sector of the Southern Ocean (Le Quéré et al., 2007; Metzl, 2009).
661 Partly, this change can be attributed to climatic oscillations (Southern Annular Mode, SAM)
662 in the southern hemisphere and their modifications due to changes in wind forcing associated
663 with the decrease in stratospheric ozone (Lovenduski et al., 2007; Lenton et al., 2009). The
664 SAM is a mode of atmospheric variability that is marked in its positive phase by a southward
665 shift of the westerlies, which would enhance upwelling of old water with high concentrations
666 of DIC. Due to the fairly short observational time series for the Southern Ocean, a weakening
667 of the Southern Ocean anthropogenic carbon uptake has been controversally discussed. While
668 atmospheric inversion approaches give results consistent with Le Quéré et al. (2007), the bulk
669 of forward biogeochemical ocean models do not predict a decrease in Southern Ocean CO_2
670 uptake strength (Lovenduski et al., 2008; Lenton et al., 2013). Also the tropical Pacific Ocean
671 with the strongest known short-term climate variation of Earth called ENSO (during El Niño
672 phases upwelling in the eastern equatorial Pacific is reduced due to accumulation of
673 anomalously warm surface waters) induces large temporary interannual variability (amplitude
674 of ca. ±0.3 GtC/yr; Valsala et al., 2014) in ocean carbon uptake. The increased sea-surface
675 warming during ENSO events and reduced upwelling of carbon-rich waters result in a
676 temporarily reduced outgassing and an enhanced oceanic carbon uptake, respectively (Feely
677 et al., 1999; Ishii et al., 2009). ENSO variations also have implications for air-sea fluxes in the
678 tropical Atlantic as documented by Lefèvre et al. (2013). Decadal pCO_2 variations in the
679 Pacific can be attributed to the Pacific Decadal Oscillation (PDO) leading to long-term
680 anomalies of tropical sea surface pCO_2 on the order of ±10 ppmv (Valsala et al., 2014). PDO
681 is also made responsible for pCO_2 variations in the North Pacific (McKinley et al., 2006; Ishii
682 et al., 2014) though details of the mechanism are difficult to identify and associated CO_2 flux
683 variations seem to be quite small (McKinley et al., 2006).
684
685 Not only internal variability modes affect the air-sea CO_2 flux, but also external factors such
686 as aerosol forcing from volcanic eruptions. Such volcanic forcing tends to temporarily cool
687 the troposphere and the sea surface with respective implications for carbon cycling. Brovkin
688 et al. (2010) could identify a temporary small decline of atmospheric pCO_2 by about 2 ppmv a
689 few years after major eruptions over the last millennium, where decreasing respiration on land
690 is a potential leading candidate with the ocean having only a small effect. This is corroborated
691 by Frölicher et al. (2011) for a model study on the effect of Mt. Pinatubo type eruptions on the
692 carbon cycle, where again the terrestrial carbon cycle dominates the atmospheric pCO_2 signal.
693 Nevertheless, transient changes in ocean uptake of about 2 GtC are in a realistic realm as

consequences to large volcanic eruptions (Frölicher et al., 2011). Further, it cannot be excluded that also the biological carbon binding is stimulated under deposition of volcanic dust to the ocean surface (Hamme et al., 2010).

In view of the internal and external factors on ocean carbon cycle variability, it is intriguing to ask, when long-term climate change signals become identifiable against the background noise. This problem is of specific concern for large impacts of ocean acidification (see detailed discussion below). Ilyina et al. (2009) identified the equatorial Pacific Ocean to be the oceanic domain where a change in marine biogenic $CaCO_3$ production due to ocean acidification may become at first visible through large-scale changes in ocean surface alkalinity. This can be explained by large background values of pelagic $CaCO_3$ production in the tropical Pacific, though the impact per unit of $CaCO_3$ produced would be highest in the high-latitude surface waters where decreasing $CaCO_3$ saturation proceeds fastest. Generally, the time of emergence of a climate change signal is an important variable: When can we see changes in oceanic state variables which clearly can be attributed to human-induced climate change, i.e. when do trends in key ocean variables emerge as robust on the background of analytical uncertainty and interannual variability? Keller et al. (2014, 2015) provided new insight into this issue. Earth system modelling suggested that sea surface pCO_2 and sea surface pH trends could rise beyond the detection threshold already after 12 years from now. DIC trends would become clear after 10-30 years and trends in the sea surface temperature after 45-90 years (Keller et al., 2014). Accordingly, an earlier detection threshold for changes in mean ENSO-induced carbon cycle variability (pCO_2, pH, biological productivity) than for ocean temperature changes during the 21st century was predicted by Keller et al. (2015). Therefore, ocean carbon cycle observations play a key role as early warning indicators when monitoring climate change. For the time interval 1960-2005, Séférian et al. (2014), however, state that the evolution of the global carbon sink can mainly be explained through rising CO_2 in the atmosphere and oceanic carbon uptake without invoking a climatic feedback. Nevertheless, at regional scale, trends in climate change become also visible in shaping the regional sink strength pattern.

Regarding future scenarios for the evolution of ocean carbon sinks, Earth system models driven by solar insolation and greenhouse gas concentrations indicate the strongest areas for sequestration of anthropogenic carbon are in the Southern Ocean as well as the tropical ocean (Tjiputra et al., 2010; Roy et al., 2011). The Southern Ocean seems to be the ocean fly wheel for changes in atmospheric CO_2, not only for anthropogenic carbon uptake, but also for natural variations in atmospheric CO_2 (Sigman and Boyle, 2000; Heinze, 2002; Watson and Naveira Garabato, 2006). Long-term observational capacity for the Southern Ocean is critical to monitor the ocean sink strength for anthropogenic carbon.

4 – The impact of human-produced carbon on warming and marine ecosystems

The ocean carbon sink provides a major service to human societies in removing anthropogenic CO_2 from the atmosphere and, thus, reducing the additional radiative forcing of the Earth system. On the other hand, dissociation of anthropogenic CO_2 in seawater increases ocean acidification, whose potential impacts on the diversity and functioning of marine ecosystems are not yet fully understood. Understanding the role of the oceanic carbon sink in controlling Earth's heat budget and influencing marine life is of great importance to project future effects of climate change. Scenarios with Earth system models (advanced climate

models, for a more detailed explanation see chapter 3.2) reveal that the fraction of fossil fuel emissions absorbed by the ocean over the 21st century is projected to be lower for high emission scenarios (business as usual scenarios) than stringent emission mitigation scenarios (Jones et al., 2013).

4.1 – Impact of the ocean carbon uptake on Earth's heat budget

The net carbon uptake rates of land and ocean determine the future time evolution of radiative forcing of the atmosphere and, hence, climate change for a given emission scenario (for a detailed definition of radiative forcing see Myhre et al., 2013). Joos et al. (2013) used different Earth system models to compute an average integrated global warming potential for a pulse emission of 100 GtC) into the atmosphere. In the study it is also stressed that quantifying the global warming effect for certain retentions of CO_2 emissions to the atmosphere depends critically on the time horizon considered. For the 100 Gt-C pulse to the atmosphere, e.g., 25±9% of the pulse emission would remain in the atmosphere after 1000 years, during which the ocean and land would have absorbed 59±12% and 16±4%, respectively. This emphasizes the long time horizon for the anthropogenic perturbation, which has to be taken into account even for a world with strongly reduced CO_2 emissions (Plattner et al., 2008). For higher total emission pulses, the overall retention in the atmosphere would be higher and likewise the global warming potential per kg CO_2 brought into the atmosphere (Maier-Reimer and Hasselmann, 1987; Archer, 2005) due to the weakening buffering capacity of the ocean at high ambient CO_2 partial pressure.

A future global warming limit of 2°C above the average preindustrial surface temperature has been suggested as a not yet very ambitious, and thus, potentially achievable political target for greenhouse gas emission strategies (Tol, 2007; Meinshausen et al., 2009; Schellnhuber, 2010; United Nations, 2010). Recent experiments with a coarse resolution Earth system model taking into account multiple climate targets, i.e. limits for maximum amplitudes of specific variables such as surface air temperature increase, sea-level rise, aragonite saturation, and biomass production on land, reveal that CO_2 emissions need to be substantially reduced for achieving several mitigation goals simultaneously, rather than for meeting a temperature target alone (Steinacher et al., 2013). Accounting for the carbon cycle climate feedback as well as other physical and biogeochemical feedbacks in climate models is of great importance for estimating the allowable emissions for a certain time line of atmospheric CO_2 concentration and global warming. Complex Earth system models are needed for this. Simplified climate models as, e.g., employed in Integrated Assessment Models (for simulations of economical developments under climatic change and for construction of typical future scenarios) are insufficient for this purpose as they do not account for internal feedbacks in the Earth system in a dynamical way (Jones et al., 2013).

4.2 – Ocean acidification and its impact on marine ecosystems

The term 'ocean acidification' refers to the decrease of oceanic pH by 0.1 units over the past 250 years and the predicted lowering of pH by another 0.3-0.4 units until the year 2100 (Caldeira and Wickett, 2003; Raven et al., 2005). Its main cause is the uptake and dissociation of excess CO_2 from the atmosphere that leads to an increase in the oceanic hydrogen ion concentration. Thorough monitoring of ocean acidification is of great importance, and by

collecting values in observational carbon data bases (e.g. like SOCAT and fixed time series stations) as well as by conducting long-term carbon time-series measurements (e.g. as reported in Vázquez-Rodríguez et al., 2012) our understanding of this process and its spreading throughout Earth's oceans can be significantly advanced (Fig. 3; Fig. 4). In addition, investigating the potential effects of 'high CO_2-low pH' conditions on the diversity and functioning of marine biota and ecosystems is currently the focus of many scientific studies. The interpretation of the observed responses in a species- and ecosystem-relevant context thereby suggests that the two ocean acidification stressors high CO_2 concentration and decreased pH are very often only one part of a complex equation. Other environmental stressors like temperature, light availability, oxygen concentration, nutrient concentration, $CaCO_3$ saturation state or trace metal speciation (to name only a few) as well as time and physiological characteristics of the investigated organisms themselves have to be taken into account when elaborating on ocean acidification impacts (Raven et al., 2005; Pörtner, 2008; Ries et al., 2009; Dupont et al., 2010).

The most immediate response to an increase in CO_2 concentration and a decrease in seawater pH is expected for marine calcifying organisms, including corals, molluscs, crustaceans, echinoderms, coccolithophores, foraminifera as well as coralline and calcareous algae. Maintenance and production of shells and skeletons may cost more energy in an environment with reduced pH, and altered organism physiology may increase the vulnerability of certain species and compromise their ecosystem functions (Bibby et al., 2007; McClintock et al., 2009; Tunnicliffe et al., 2009). Calcification rates are likely to decline with a reduced saturation value for aragonite and calcite, the two most common forms of $CaCO_3$ in seawater (Feely et al., 2004; Guinotte and Fabry, 2008), caused by a decrease in CO_3^{2-} concentration when CO_3^{2-}, excess atmospheric CO_2, and H_2O react to HCO_3^- and hydrogen ions. Projections indicate the potential undersaturation for both aragonite and calcite within the current century for all polar regions (see Fig. 5) and parts of the subpolar Pacific Ocean as well as the deep North Atlantic Ocean (Orr et al., 2005; Fabry et al., 2008; Steinacher et al., 2009; Orr, 2011). Because aragonite dissolves at higher CO_3^{2-} concentrations than calcite, corals and other aragonite-producing organisms are expected to experience corrosion of their hard shell materials due to ocean acidification first. At natural CO_2 seeps in Papua New Guinea, a decline in coral diversity was documented in areas of reduced pH as structurally complex corals were replaced by massive *Porites* corals (Fabricius et al., 2011). The consequences arising from this diversity shift could be similar to those anticipated for a general reduction in coral cover and include a loss in biodiversity, habitat availability and quality as well as reef resilience (Fabricius et al., 2011). The decrease in $CaCO_3$ saturation as a result of ocean acidification combined with other environmental impact factors such as an increase in temperature can be critical (Kleypas et al., 1999; Hoegh-Guldberg et al., 2007; Veron et al., 2009; Fabricius et al., 2011). Recent scenario computations with Earth system models document that a drastic reduction of CO_2 emissions is required to preserve major coral reefs during the Anthropocene (Ricke et al., 2013). However, aspects such as potential adaptation processes and migration need yet to be included in regional studies (Yara et al., 2012).

The effects of ocean acidification on different groups of marine biota can be rather diverse and complex. For example, specimens of the economically and ecologically important blue mussel *Mytilus edulis* recovered from the North Sea showed drastically reduced calcification rates, while specimens recovered from a coastal area of the Baltic Sea did not show any sensitivity to increased pCO_2 values (Gazeau et al., 2007; Thomsen et al., 2010; Schiermeier, 2011). Mussels from the Baltic seemed to be adapted to thriving in waters that generally experience strong seasonal pCO_2 fluctuations, and food availability may have potentially

outweighed the effects of ocean acidification (Thomsen et al., 2010; Thomsen et al., 2013). In a study comparing different types of benthic marine calcifiers it could be shown that certain species experienced dissolution, while others were able to exploit the higher pCO_2 content in seawater and increased their net calcification. Physiological characteristics like the organism's ability to regulate pH, shell-protection with organic layers, biomineral solubility, and photosynthesis utilization seemed to play a role (Ries et al., 2009). Species-specific reactions as well as an organism's life cycle stage are further factors that may have to be taken into account as it has been shown e.g. for echinoderms (Dupont et al., 2010; Dupont et al., 2013; Dupont and Pörtner, 2013). Results obtained for phytoplankton communities additionally stress the importance of community composition and/or shifts when assessing ocean acidification impacts, but still a lot has to be explored about the response of marine microbes to ocean acidification (Raven et al., 2005; Liu et al., 2010a; Joint et al., 2011; Brussaard et al., 2013; Oliver et al., 2014).

Ocean acidification does not only affect calcifying biota. Sensitivity towards ocean acidification has been detected for fish and other invertebrates, with increased risks of acidification of body fluids and tissues as well as hindered respiratory gas exchange (Raven et al., 2005). Beneficial effects were observed e.g. for seagrass (Palacios and Zimmerman, 2007; Hall-Spencer et al., 2008; Fabricius et al., 2011) and various algal species (Hall-Spencer et al., 2008; Connell et al., 2013).

Projecting the precise impact of ocean acidification on the diversity and functioning of marine organisms and ecosystems is challenging. A meta-analysis of 228 published studies by Kroeker et al. (2013) revealed a decrease in calcification, growth, survival, development, and abundance across a wide range of taxa, but also showed a certain degree of variability among groups suggesting different scales of sensitivity. It is not well established to which degree organisms can adapt to quasi-permanent changes in ocean pH due to rapid anthropogenic carbon input. It is also not known, if and in what way consequences like the physiological impairment of vulnerable species and the reduction and/or shifts in biodiversity may be mastered provided that ecosystem functionality shall be preserved. With regard to the sustainable development of marine resources, future research will need to focus on multiple stressor studies over various time scales to reveal the functional impact of ocean acidification (and climate change in general) on marine ecosystem services and provide both comprehensive monitoring and solution-oriented results.

4.3 – Future impact research

For future modelling approaches, not only the effects of atmospheric and oceanic warming as well as ocean acidification have to be considered, but also the influence of multiple stressors. These include physical and chemical drivers as well as circulation and stratification changes, freshening, changes in ice cover, deoxygenation, anthropogenic nitrogen input, changes in dust supply, marine pollution by offshore activities (e.g. Deepwater Horizon disaster; Mearns et al., 2011), and plastic waste (also on the micro-scale; Gross, 2013) or overfishing and bottom trawling. Earth system models that represent the marine carbon cycle and related biogeochemical cycles have been successfully used to establish the regional combination of some major stressors and the future evolution of these combinations (Bopp et al., 2013). Yet, robustness in regional projection is strongly dependent on the considered stressors and regions, and identifying the onset of emission induced change is still a challenging task that is especially sensitive to the considered emission-scenario (see Fig. 5). The combined action of stressors has to be accounted for in the next generation of Earth system model climate

projections (Steinacher et al., 2013). A critical variable within this context is the sustained generation of exploitable biomass in the ocean for human food production, where overall biological carbon fixation rates will presumably decrease with a more stagnant ocean circulation (Steinacher et al., 2010).

5 – The ocean carbon sink in relation to the land carbon sink

The atmospheric CO_2 concentration is determined by the CO_2 emissions and the CO_2 exchanges between the land biosphere and atmosphere as well as between the atmosphere and ocean. Quantification of the regional as well as global land carbon sink is associated with high uncertainties due to the direct coupling of CO_2 consumption and release on the land surface with the atmosphere in combination with the heterogeneity of the land biosphere, its constant change and different forms of land use including forestry changes. Complex soil processes like the degradation of organic material and permafrost melting processes (Schuur et al., 2009), episodic events such as fires (wild fires, peat fires; Schultz et al., 2008; van der Werf et al., 2008), and the multitude of possible reactions of land plants to different drivers (Kattge et al., 2011) make the determination of the land carbon sink difficult. Recent studies indicate that it may have been overestimated as the limiting effect of nitrogen (N) on plant growth has not yet been accounted for in most models, potentially giving too much value to the CO_2 fertilisation effect, while on the other hand human-caused additions of nitrogen to the Earth system regionally enhance plant growth (Zaehle and Dalmonech, 2011). Only two Earth system modelling frameworks employed for the projections as summarised in the 5th assessment report of IPCC (Collins et al., 2013) included N limitation on land, and related processes and feedbacks are under discussion.

In comparison to the land carbon sink, the large-scale oceanic sink is considered to be less variable on an interannual time scale (though considerable perturbations of the ocean carbon cycle are linked with, e.g., the ENSO cycles; Feely et al., 2006) and, even though a 3-dimensional approach is required due to water motion, somewhat easier to quantify. This traditional view is exploited to estimate the year-to-year land sink for anthropogenic carbon from the atmospheric observations and ocean models (evaluated through observations). The terrestrial carbon sink is then the residual of CO_2 emissions, atmospheric CO_2 concentrations, and ocean-atmosphere CO_2 fluxes (Canadell et al., 2007; Le Quéré et al., 2013). Until precise quantifications of the land carbon sink become available through direct observations and modelling, estimating it through the ocean carbon sink is a valid option. However, with increasing detail in oceanic carbon sink determinations, oceanographers are starting to run into similar heterogeneity problems in the oceans as geo-ecologists on land, especially when the continental margins, the shelf seas, and coastal and estuarine systems are taken into account (Borges, 2005; Liu et al., 2010b; Regnier et al., 2013). These likewise heterogeneous systems are so far not (or at best partially) included in global Earth system model scenarios, because the resolution of these models does not allow for the resolution of the respective topographic features and super-computers are currently insufficient to run respective high-resolution models as yet (Mitchell et al., 2012). Measurements of the O_2/N_2 ratio in the atmosphere and marine oxygen budgets can help to further specify the land carbon sink (Keeling et al., 1996). Alternatively, the stable carbon isotope ratio $^{13}C/^{12}C$~~s~~ (or its deviation $\delta^{13}C$ from a standard ratio~~measure $\delta^{13}C$~~) can be employed to discriminate between the land and ocean carbon uptake taking the low $\delta^{13}C$ in fossil fuel CO_2 emissions to the atmosphere

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(Suess effect; see Keeling, 1979) and the isotopic disequilibria between atmosphere, ocean~~-~~, and terrestrial biosphere into account (Ciais et al., 1995; Battle et al., 2000). The isotopic fractionation for oceanic CO_2 absorption is small so that $^{13}C/^{12}C$ ratio~~n~~s can be used directly for quantifying oceanic CO_2 uptake through budgeting approaches given that a sufficient number of observations in atmosphere and ocean is~~are~~ available (Quay et al., 1992; Tans et al., 1992; Heimann and Maier-Reimer, 1996). In contrast, carbon uptake in terrestrial biomass leads to a substantial fractionation (leading~~-~~ to low $\delta^{13}C$ in plant material). When quantifying the respiratory carbon release~~, whereby also~~ the age of the biomass has to be considered as carbon that was assimilated decades earlier may still contribute to the respiration process ~~when respiratory carbon release is quantified~~ (Ciais et al., 1995; Battle et al., 2000)~~.~~

The interannual variability of land-atmosphere carbon fluxes appears to be higher than the respective variations for ocean-atmosphere fluxes when computing the land carbon sink as the residual between oceanic uptake and atmospheric CO_2 retention (Canadell et al., 2007). On a multi-millennial time scale, peat formation and organic carbon burial in lakes contribute to slow long-term accumulation on land (Einsele et al., 2001; Gorham et al., 2012). Due to the overall smaller carbon inventory of the land biosphere as compared to the inorganic ocean carbon pool (Fig. 6), it is expected that the ocean through inorganic buffering and $CaCO_3$ sediment dissolution would ultimately account for the major part of removal of the human-induced addition of CO_2 to the atmosphere (Archer, 2005).

6 – Major ocean carbon challenges and key knowledge gaps

Some aspects of marine carbon cycling can be regarded as well-established research fields, such as the inorganic carbon buffering system. However, other elements are more difficult to approach, partly due to inherent principle difficulties and partly based on the lack of technological and infrastructural effort. Within this section, some major ocean carbon challenges and key knowledge gaps in ocean carbon research will be addressed.

6.1 – Observational data bases

Based on measurements, our knowledge of inorganic and organic carbon cycling has significantly improved over the past decade. This is especially due to measurements of inorganically dissolved substances including the 3-dimensional data sets GLODAP (Key et al., 2004; GLODAPv2), CARINA (Key et al., 2010), the surface ocean CO_2 data compilations from Takahashi et al. (2009), and SOCAT (Pfeil et al., 2013; Sabine et al., 2013; Bakker et al., 2014). Semi-continuous measurements are necessary due to the variability of the ocean carbon sink, the continuously changing atmospheric CO_2 concentrations as well as the variability of oceanic circulation. The aims are to identify vulnerabilities of carbon sinks, to validate feedback mechanisms and to provide detailed information for other researchers or commercial users regarding the impact of climate change on the marine realm.

Measurements of dissolved oxygen are of key importance for carbon cycle research. Oxygen data are the basis for improving estimates of the land carbon sink (Keeling et al., 1996) and for identifying any emergent fingerprint (Andrews et al., 2013), an extensive O_2 measurement programme is needed. In addition, measurements of at least two carbon variables of the marine inorganic carbon system are necessary. Here, pH and pCO_2 are likely the ones where the techniques first will be available on floats, though this combination is not optimal for deriving the other inorganic carbon variables. Another option would be to measure DIC and alkalinity as the latter easily can be measured in seawater and determines together with DIC

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the marine inorganic carbon system (see Wolf-Gladrow et al., 2007). In combination with O_2 measurements on automated float systems, this altogether would provide a significant advance in ocean carbon observations. Pilot studies conducted in recent years yielded promising results for a world-wide application of such systems (Gruber et al., 2010; Fiedler et al., 2013).

For improved estimates of the biological carbon pump variations, reliable shallow flux estimates as well as state-of-the-art biogenic $CaCO_3$ (aragonite, calcite) and biogenic silica (BSi) production maps would be desirable. Respective maps for $CaCO_3$ export production are at present possibly associated with large errors and give partly incongruous results (Sarmiento and Gruber, 2006; Balch et al., 2007). Highly accurate total alkalinity observations and a reliable $CaCO_3$ surface map could be used as reference points for future developments of biocalcification under high CO_2 (Ilyina et al., 2009). Satellite observations have greatly improved our understanding about primary production in the ocean (Henson et al., 2012), but remote sensing efforts have still to be better exploited and extended in order to fill the gaps of fragmental in-situ observations, especially also for production of hard part shell material.

Anthropogenically induced elevated carbon levels in the ocean (C_{ant}) cannot be observed directly, which is why indirect methods have to be used (Gruber et al., 1996; Hall et al., 2002; Touratier and Goyet, 2004; Friis et al., 2005). Even though year-to-year changes in DIC are measurable in ocean surface waters, it is a challenge to determine them in deeper layers as the anthropogenic perturbation in seawater is relatively small when compared to the natural background. Over the past years, major international networks and projects (EU framework programmes, OCB, PICES, SOLAS, IMBER, IOCCP etc.) have helped to make much scientific progress in ocean carbon research worldwide. However, extensions and new projects are required to continue the work (GEO/GEOSS, GOOS, FOO, ICOS etc.).

In contrast to the atmosphere, oceanic meso-scale circulation features are marked by short spatial scales and large time scales. While an atmospheric pressure system has a typical length scale of 1000 km and a lifetime of days to weeks, comparable oceanic meso-scale eddies have scales of 2-100 km and several months. Therefore, selected oceanic observations can be aliased through meso-scale motion and may not reflect the long-term mean state.

Time series stations in the ocean are still rare and mostly cover low to mid-latitudes (e.g. HOTS, BATS, ESTOC, PAP, PAPA, DYFAMED). These time series have provided a lot of insight into the long-term evolution of carbon cycle tracers, e.g. the local decline of mean sea surface pH has been documented as unequivocal proof of progressing ocean acidification (Santana-Casiano et al., 2007; Bates et al., 2014). An expansion of time series stations at higher latitude areas would be desirable as, e.g., the change in sea surface pCO_2 and pH would be largest over time, although the mean signal there would be somewhat more blurred by interannual variability (Olafsson et al., 2009; Bauerfeind et al., 2014).

Apart from the issues described above, general challenges for determination of oceanic carbon budgets within the Earth system exist, which possibly never can be met adequately: 1. The annual net uptake rate of anthropogenic carbon from the atmosphere is small as compared to the gross upward and downward fluxes occurring over one year in different oceanic regions. That means that we always will have to quantify small net exchange fluxes as difference of large gross fluxes into and out of the ocean. 2. The pristine carbon fluxes between the atmosphere and the ocean as well as the pre-industrial 3-dimensional distributions of DIC have not been measured and need to be reconstructed (Khatiwala et al., 2009; Khatiwala et al.,

2013). It is unlikely that ocean carbon variables can be reconstructed with high accuracy for the pre-industrial from potential proxy record development.

6.2 – Process and impact knowledge

A major obstacle for improvements in future projections of the Earth system for selected future scenarios of driving factors is the lack of sufficient process understanding, process quantification, and process identification. Though some major biogeochemical principles are known, detailed dynamical formulations of processes are scarce and in their infancy. There is a considerable uncertainty about the gas transfer velocity of CO_2 and other gases across the air-water interface (Carpenter et al., 2012; Garbe et al., 2014). While the global ocean carbon sink estimates may not too strongly depend on this choice (otherwise projections with simple two box models for the global ocean would not have worked at all; Oeschger et al., 1975), the projected local CO_2 concentration in ocean surface waters is highly influenced by the chosen gas transfer velocity values, also for appropriate regional validation of ocean models. The co-limitation of biological production by various factors is an established concept, however, crucial details are not uniformly established, such as the potential variation of carbon to nitrogen ratios in biogenic matter under different environmental conditions (Riebesell et al., 2007; Jiang et al., 2013). Marine particle fluxes and their dynamics are still poorly understood and not yet adequately quantified in a dynamic way in response to external drivers (Klaas and Archer, 2002; Gehlen et al., 2006). The ongoing and future impacts of high CO_2 on marine organisms have yet to be clarified (Gattuso and Hansson, 2011). Formulations on how to quantify the production as well as degradation of phyto- and zooplankton particulate matter (organic, inorganic) are not mature enough or not even existing for providing step-change improvements of complex ocean models as well as coupled Earth system models. This includes, in particular, potential adaptation of organisms and ecosystems to conditions not experienced since the geologic past (Langer et al., 2006). Respective modelling approaches remain questionable until more detailed and reliable information about the effect of changing external drivers, like decreasing carbonate saturation, on the functioning of marine organisms and ecosystems becomes available. For a suite of land plants, functional relationships between drivers and physiological reactions have been established in large data compilations for trait-based modelling of the land biosphere (Kattge et al., 2011). Approaches for the simulation of ocean ecosystems with multiple plankton functional types have been initiated (Le Quéré et al., 2005), but trait data bases for marine organisms are not yet available in a suitable format and information from mesocosm and laboratory experiments is scarce and may not be straightforwardly transferable to the real Earth system.

6.3 – Integrative modelling and combination with measurements

For simulations of the ocean carbon sink and its impact, suitable models are needed to explain past and present events as well as to predict potential future pathways. Biogeochemical ocean general circulation models are employed either through observed forcing or within coupled Earth system models (for review see e.g. Heinze and Gehlen, 2013). There is a trade-off between their resolution (space and time) and a technically feasible length of the simulation period. High-resolution models with eddy dynamics (large-scale turbulent mixing) are often too computationally expensive for integrations exceeding a few decades. However, multiple future scenarios calculated over decades, centuries, and millennia are necessary to achieve reliable future projections. In addition, biogeochemical models whose water mass properties shall be fully predicted by the models need very long and costly spin-up periods in order to bring the tracer distributions including the carbon cycle tracers into quasi-equilibrium.

Integration periods need to be at least as long as one full oceanic circulation cycle of about 1500 years. Even for still fairly coarse resolutions this is currently quite costly in terms of super-computer processing time. Global model simulations of deep-sea carbon distributions as well as other deep-sea properties are therefore often limited to a lower resolution as compared to their distributions in surface or shallow waters (e.g., Ilyina et al., 2013; Séférian et al., 2013; Tjiputra et al., 2013).

Models need systematic improvement by combining them with and comparing them to observational data. By applying data assimilation procedures (Brasseur et al., 2009), existing discrete observations of oceanic variables can be interpolated (gap filling) and free adjustable parameters in models (such as, e.g., the particle sinking velocity) can be calibrated. Data-driven diagnostic models (Usbeck et al., 2003) are important for suggesting first order values of free parameters in dynamical process descriptions and can be implemented in complex forward models, which can be used for predictions as well. Systematic model assessment with observations and model optimisation with data assimilation have made progress in recent years, but for integrated biogeochemical cycle simulations these approaches need to be extended. Skill score metrics, which can be used to rank models according to their ability to reproduce physical and biogeochemical variables simultaneously, may become a valuable tool for future simulations. A simplified short cut method in order to assess the quality of future projections of Earth system models is the emergent constraint approach (Cox et al., 2013; Hoffman et al., 2014; Wenzel et al., 2014). In this approach, an interrelation is sought between a specific Earth system sensitivity as resulting across an ensemble of comparable models and a corresponding observational trend or variability (see also Flato et al., 2013). This method has just started to also be used for addressing ocean biogeochemical problems (Hoffman et al., 2014) and respective constraints have to be identified for this research field. Model scenarios can diverge depending on slight modifications of the starting (initial) and boundary conditions during a model run as well as due to internal variability in the model. Therefore, for a given CO_2 emission scenario the expected evolution of the results can differ. Ensemble simulations are necessary for establishing a range of statistically valid, potential outcomes that are associated with different degrees of probability. Due to the immense costs for multiple integrations of complex Earth system models, scenarios with large ensembles, though, have been attempted in only few ocean carbon uptake studies.

6.4 – Specific regional foci for ocean carbon cycle studies

There are at least 6 major regional domains, which warrant more attention in the coming years of ocean carbon cycle research:

1. The Southern Ocean is quantitatively the most important region for worldwide carbon dynamics (today: Mikaloff Fletcher et al., 2006; glacial/interglacial: Watson and Naveira Garabato, 2006; future: Tjiputra et al., 2010; Roy et al., 2011), but it is also one of the least well year-round observed regions (Takahashi et al., 2009; Swart et al., 2012; Pfeil et al., 2013; Sabine et al., 2013) due to its remoteness and high seasonality. Research priorities include the improvement of data coverage for carbon variables, dissolved oxygen, and related tracers. The water mass formation, mixing and deep convection processes, in particular in the Southern Ocean, are the 'Achilles heel' of global ocean models, and a step-change improvement is needed in order to achieve more physically based deep-water production representations in ocean models as well as Earth system models (Lenton et al., 2013). This includes also the representation of Antarctic shelf regions and respective water-mass formation mechanisms relevant for large-scale simulations.

2. Highly dynamic systems such as shelf areas, coastal zones, estuaries and continental margins will need to be accounted for in global carbon cycle quantifications. This is of key importance for impact studies as shallow seas are major spawning and living grounds for commercially exploited fish and food production. In addition, anthropogenic stressors such as mega cities, pollution from riverine loads and deposition of reactive nitrogen (Duce et al., 2008) have to be considered. Progress has recently been made in providing advanced combined river runoff and river load data for use in biogeochemical models (Mayorga et al., 2010). Ocean biogeochemical models should include both pelagic ocean sediment models (Heinze et al., 2009) and shallow sediment representations to involve high fluxes and regeneration rates of organic sediments as well as respective low oxygen and anoxic reactions and matter transformations like methanogenesis or denitrification (Naqvi et al., 2010; Mogollón et al., 2012). Land-ocean coupling of natural and anthropogenically perturbed systems (Regnier et al., 2013) needs inclusion in global Earth system models, especially with regard to quantifying nation-wide closed carbon budgets.

3. The Arctic Ocean is a hot spot of climatic and environmental changes, and represents the area in which ocean acidification accelerates most rapidly (Steinacher et al., 2009). Like the Southern Ocean, the Arctic is highly undersampled, making it difficult to determine reliable CO_2 sink estimates (Schuster et al., 2013). New process understanding (Wåhlström et al., 2012, 2013) has to be integrated into large-scale ocean models. Shifts in water mass formation processes, including the cold halocline structure at the Arctic Ocean surface domain (Aagaard et al., 1981; Anderson et al., 2013), need to be identified. A strongly reduced Arctic sea-ice cover and changes in annual sea-ice formation will have fundamental consequences for both organic and inorganic carbon cycling as well as ocean circulation and mixing (Loeng et al., 2005). The net effect on ocean carbon sink behaviour for a summer ice-free Arctic Ocean is not yet firmly assessed. Future studies need to include both sea-ice physics and sea-ice biogeochemistry. In addition, the potential climatically and tectonically induced degassing of CH_4 from Arctic Ocean sources needs to be further monitored as a potentially significant greenhouse gas source (Biastoch et al., 2011; Shakhova et al., 2014).

4. The tropical ocean is another key sink area for anthropogenic carbon (Mikaloff Fletcher et al., 2006; Roy et al., 2011). Future research needs to focus on ENSO-related variability in its carbon sink potential as well as on it being a region of high phytoplankton production rates in respective upwelling areas, where large-scale impacts of ocean acidification may be measured already during an early stage (Ilyina et al., 2009). Both the Pacific and Atlantic Ocean equatorial areas can be affected by short-term climatic fluctuations (Cadule et al., 2010; Lefèvre et al., 2013) and the overall long-term effect of shifts in occurrences and patterns of these events needs attention.

5. Oligotrophic regions play a significant role for sustained ocean time series stations as the interannual and seasonal variability is small and long-term trends may be easier to deduce. Current investigations should be complemented with measurements of nitrogen fixing processes as well as with their potential changes under altering dust fluxes and ocean acidification. Additionally, future research should include the identification of changes in the cycling of the greenhouse gas N_2O (Freing et al., 2012; Voss et al., 2013).

6. Coastal upwelling areas have proven to be useful study areas for ocean acidification, deoxygenation, and biological carbon pump studies and will remain a major focus of future monitoring (Feely et al., 2008; Paulmier et al., 2008; Gruber et al., 2011). It will therefore be

crucial to appropriately resolve the physically and biogeochemically highly dynamic regimes along continental margins both in observational campaigns and modelling efforts.

7. Of course, the traditionally comparatively well observed North Atlantic and North Pacific domains (see, e.g., Bakker et al., 2014) should be further kept in the focus of monitoring and modelling programmes. The North Atlantic is a critical area for anthropogenic marine carbon uptake and changes in this may occur due to changes in meridional overturning and deep-water production. It has still to be firmly established whether any long-term (more than two decades) changes in the trend of anthropogenic CO_2 uptake occur in these regions that are marked also by internal variability in coupling to prevailing climate variability modes such as the North Atlantic Oscillation and the Pacific Decadal Oscillation.

6.5 – Using the ocean natural laboratory for case studies on complex couplings

The ocean and Earth system need to be better used as laboratories to understand processes and the resulting effects on a global scale. This can, for example, be achieved by using a biogeographic approach, where ecosystems are analysed along natural gradients in both space and time. Natural, environmental variability needs to be better exploited to obtain results for impact research. Transient large-scale variations of the Earth system and the ocean carbon cycle's role in these patterns need to be explained.

6.6 – Combination with other biogeochemical cycles and greenhouse gases

The ocean carbon cycle needs to be studied and assessed in combination with other biogeochemical cycles in a more focussed way than in the past. The oceanic sources/sinks of CH_4, N_2O, and CO_2, all three being natural and anthropogenic greenhouse gases, are controlled by coupled elemental cycles involving among others carbon compounds, nutrients, and gases. Only integrative approaches can ensure a full understanding of the coupled cycles and a full exploitation of respective observational evidence. The simultaneous quantifications of the oxygen and carbon cycles are vital for closing the global carbon budget including the terrestrial biosphere. Nutrient cycles and their anthropogenic perturbations directly control the biological carbon cycling on land and in the oceans. Their more detailed dynamical implementation in land and ocean models is needed, including a better understanding of nutrient limitations (including effects of micronutrients such as iron) under changing environmental conditions.

7 – Conclusion

The ocean carbon sink has two parallel effects: 1. Parts of the anthropogenic CO_2 emissions are absorbed by the ocean and, thus, the radiative forcing associated with the human-caused excess CO_2 is reduced. 2. The more anthropogenic CO_2 enters the ocean, the stronger ocean acidification will be. Both aspects have to be considered simultaneously for establishing future mitigation strategies on emission reductions as well as for establishing adaptation measures to environmental and climatic change. The two aspects, though, have opposite effects. Increasing the ocean carbon sink may lead to less warming, but at the same time will promote ocean acidification. Critical to both is the speed of progression. Climatic warming and lowered pH values in the oceans will prevail long after the anthropogenic CO_2 emission period to the atmosphere, and it is not possible to associate a specific lifetime to CO_2 in the

atmosphere (Tans, 1997). Determining extent, timing, and impact of the ocean carbon sinks and sources will, thus, remain a key task in the future establishment of sustainable development strategies on Earth, especially with regards to the further rising greenhouse gas emissions to the atmosphere as expected for the coming decades. We have for the first time arrived at an atmospheric CO_2 mixing ratio of 400 ppmv (Mauna Loa observatory, May 2013, http://keelingcurve.ucsd.edu/) since 850,000 years (as measurements from atmospheric CO_2 concentrations in Antarctic ice cores document; Siegenthaler et al., 2005). Human CO_2 emission rates are currently increasing further (Le Quéré et al., 2013; Le Quéré et al., 2014). Strategies on feasible emission reduction procedures need to take the timing of the ocean sink (slow kinetics, large capacity) and the associated impact through ocean acidification into account.

Acronyms

BATS	Bermuda Atlantic Time-series Study
CARINA	CARbon dioxide IN the Atlantic Ocean (data synthesis project)
CVOO	Cape Verde Ocean Observatory
DYFAMED	DYnamics oF Atmospheric fluxes in the MEDiterranean sea (time-series study)
ENES	European Network for Earth System modelling
ESTOC	European Station for Time-series in the Ocean Canary islands
FOO	GOOS Framework for Ocean Observing
GEO/GEOSS	Group on Earth Observations/Global Earth Observation System of Systems
GOOS	Global Ocean Observing System
GLODAP	Global Ocean Data Analysis Project
HOTS	Hawaii Ocean Time-Series
ICOS	Integrated Carbon Observation System
IGBP	International Geosphere-Biosphere Programme

IMBER	Integrated Marine Biogeochemistry and Ecosystem Research
IOCCP	International Ocean Carbon Coordination Project
IPCC	Intergovernmental Panel on Climate Change
OCB	Ocean Carbon and Biogeochemistry
PACIFICA	PACIFic ocean Interior Carbon database
PAP	Porcupine Abyssal Plain observatory
PAPA	Ocean station Papa (North Pacific)
PICES	North Pacific Marine Science Organization
PIRATA	PredIction and Research moored Array in the Tropical Atlantic
RCP	Representative Concentration Pathways
SOCAT	Surface Ocean CO_2 ATlas
SOLAS	Surface Ocean Lower Atmosphere Study

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Figures

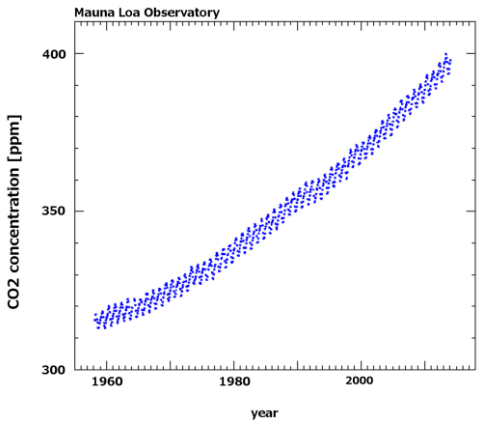
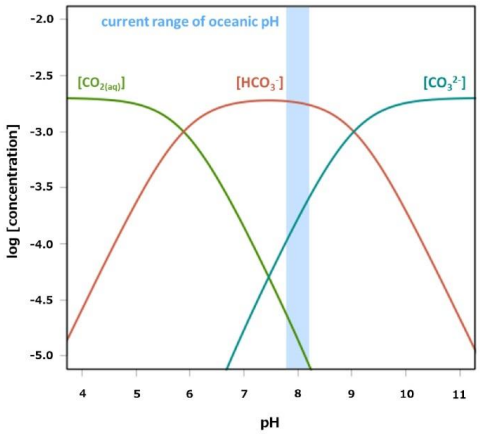


Figure 1: Atmospheric CO_2 concentrations recorded at Mauna Loa Observatory between 1958 and 2014. Due to human-produced emissions, CO_2 levels in Earth's atmosphere have been rapidly rising since the beginning of the Industrial Revolution and nowadays are crossing 400 ppmv (400.01 ppmv on 25 May 2013), equalling a 44% increase when compared to pre-industrial CO_2 concentrations of around 278 ppmv. Source: Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends) and Dr. Ralph Keeling, Scripps Institution of Oceanography (scrippsco2.ucsd.edu/).



$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (1)$$

$$CO_2 + H_2O + CO_3^{2-} \leftrightarrow 2HCO_3^- \quad (2)$$

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O \quad (3)$$

Figure 2: Bjerrum plot created according to equations reviewed in Sarmiento and Gruber (2006) and Zeebe and Wolf-Gladrow (2001) as well as main reactions of carbon chemistry referred to in this review.

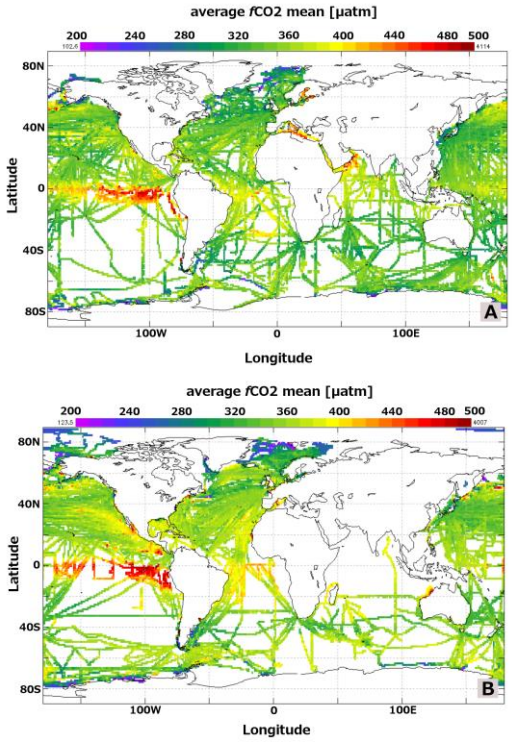


Figure 3: Mean unweighted surface water fCO_2 (µatm) for the years 1970-2002 (A) and 2003-2011 (B) using the SOCATv2 monthly 1x1 degree gridded data set (Bakker et al., 2014). The maps were generated by using the online Live Access Server.

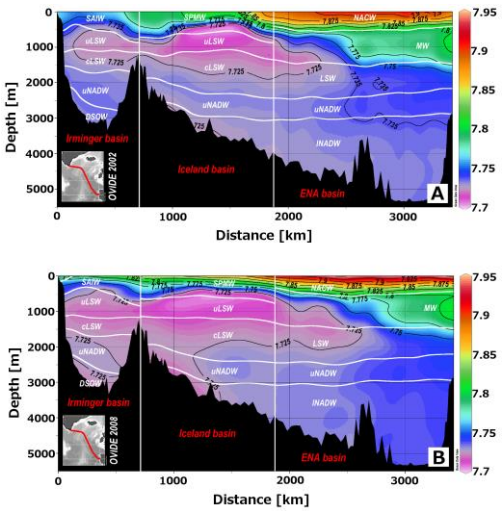


Figure 4: Spatial and temporal change of seawater pH measured across the North Atlantic Subpolar Gyre between Greenland and the Iberian Peninsula. The vertical distribution of pH followed the anticipated natural distribution, with higher pH in surface waters and lower pH in deep waters. A comparison of pH values measured in 2002 (A) and 2008 (B) revealed an overall decrease in seawater pH in intermediate and deep waters. This acidification was most evident in water depths between 1000 and 2000 m, where over the years the water layer with pH values below 7.725 had thickened several-fold (Vázquez-Rodríguez et al., 2012, Biogeosciences, 9, 5217-5230, doi: 10.5194/bg-9-5217-2012, 2012).

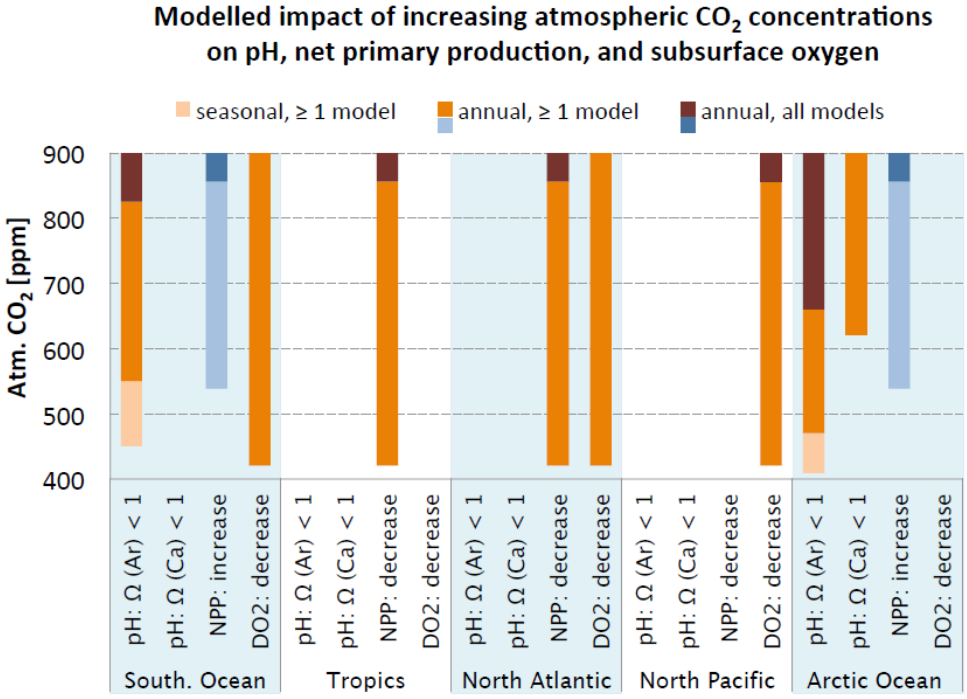


Figure 5: Modelled impact of increasing atmospheric CO_2 concentrations on stressors of ocean ecosystems, that is surface undersaturation of aragonite (pH: Ω(Ar) < 1) and calcite (pH: Ω(Ca)<1), net primary production (NPP), and oxygen at 200–600 m depth (DO2). Bright orange bars denote a seasonal development, while orange and light blue bars denote annual developments projected by one or more models. Red and blue bars indicate that all considered models agree on the depicted development. Orange and red bars denote furthermore a negative impact on marine ecosystems, while blue and light blue bars indicate an increase of the modelled parameter with the ecologic impact of this development not yet fully being determined. Impacts are based on a comprehensive suit of Earth system models and IPCC emission scenarios. The choice of models and scenarios is based on the IPCC AR5 report and references denoted within (Plattner et al., 2001; Orr et al., 2005; McNeil and Matear, 2008; Feely et al., 2009; Steinacher et al., 2009, 2010; Keeling et al., 2010; Bopp et al., 2013; Cocco et al., 2013). Note that DO2 and NPP are only analysed at the final year of the IPCC scenarios (year 2100), and their projected developments start most likely already at lower atmospheric CO_2 concentrations.

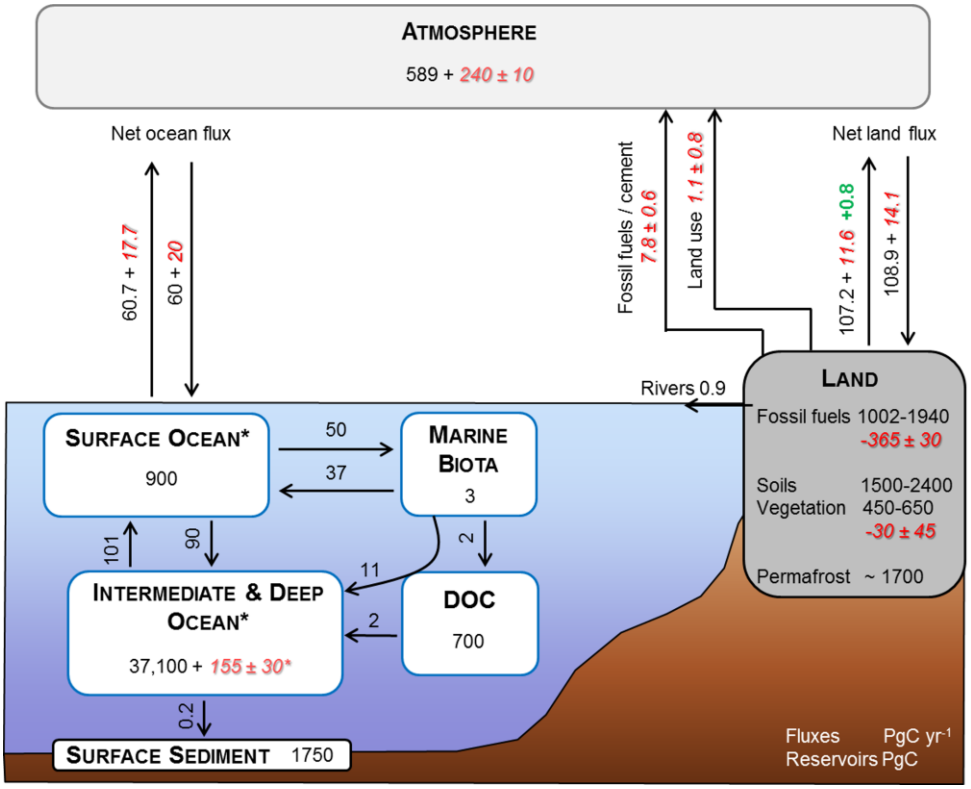


Figure 6: Simplified illustration of the global carbon cycle, adapted from Ciais et al. (2013). Reservoir mass numbers and annual exchange fluxes are given in PgC (10^{15} gC) and PgC yr^{-1}, respectively. Black numbers refer to pre-industrial values (before 1750). Red flux numbers represent annual anthropogenic fluxes averaged over the years 2000-2009 and red reservoir numbers depict cumulative changes of anthropogenic carbon between 1750-2011 (90% confidence interval). A positive cumulative change denotes an increase in (gain of) carbon since the onset of the Industrial Era. Land-atmosphere carbon fluxes caused by rock weathering, volcanism, and freshwater outgassing amount in total to a flux of 0.8 PgC yr^{-1} and are represented by the green number. Purely land-based processes like further rock weathering, burial, and export from soils to rivers are not depicted in the scheme above. The star (*) indicates that the given accumulation number refers to a combined value for Surface Ocean and Intermediate and Deep Ocean.