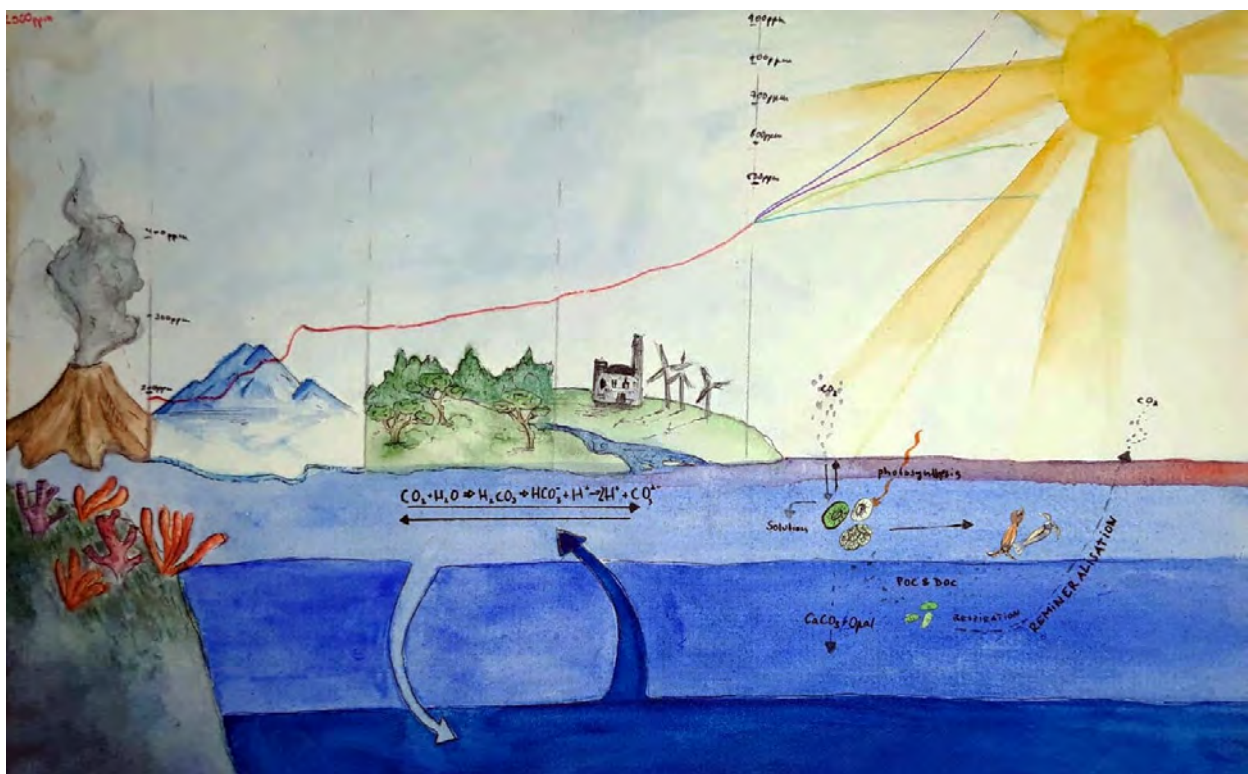


The Changing Ocean Carbon Sink in the Earth System



Tatiana Ilyina

Hamburg 2022

Hinweis

Die Berichte zur Erdsystemforschung werden vom Max-Planck-Institut für Meteorologie in Hamburg in unregelmäßiger Abfolge herausgegeben.

Sie enthalten wissenschaftliche und technische Beiträge, inklusive Dissertationen.

Die Beiträge geben nicht notwendigerweise die Auffassung des Instituts wieder.

Die "Berichte zur Erdsystemforschung" führen die vorherigen Reihen "Reports" und "Examensarbeiten" weiter.

Anschrift / Address

Max-Planck-Institut für Meteorologie
Bundesstrasse 53
20146 Hamburg
Deutschland

Tel./Phone: +49 (0)40 4 11 73 - 0
Fax: +49 (0)40 4 11 73 - 298

name.surname@mpimet.mpg.de
www.mpimet.mpg.de

Notice

The Reports on Earth System Science are published by the Max Planck Institute for Meteorology in Hamburg. They appear in irregular intervals.

They contain scientific and technical contributions, including PhD theses.

The Reports do not necessarily reflect the opinion of the Institute.

The "Reports on Earth System Science" continue the former "Reports" and "Examensarbeiten" of the Max Planck Institute.

Layout

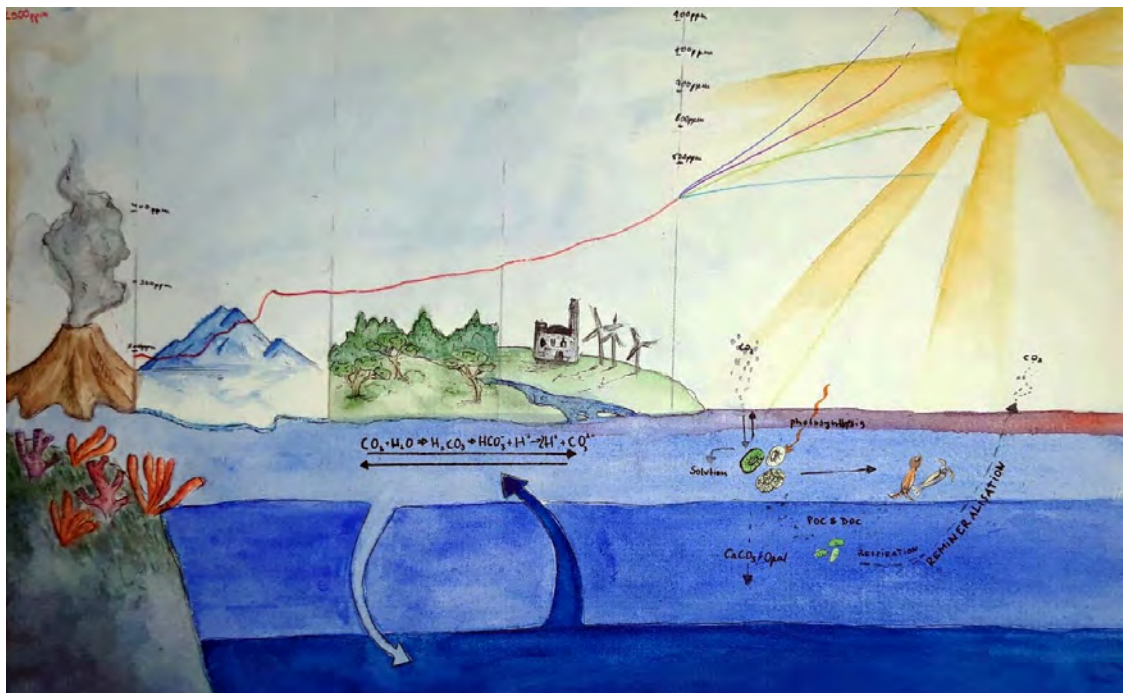
*Bettina Diallo and Norbert P. Noreiks
Communication*

Copyright

*Photos below: ©MPI-M
Photos on the back from left to right:
Christian Klepp, Jochem Marotzke,
Christian Klepp, Clotilde Dubois,
Christian Klepp, Katsumasa Tanaka*



The Changing Ocean Carbon Sink in the Earth System



Tatiana Ilyina

Hamburg 2022

Tatiana Ilyina

Max-Planck-Institut für Meteorologie
Bundesstrasse 53
20146 Hamburg

Als Habilitationsschrift angenommen vom Fachbereich
Erdsystemwissenschaften der Universität Hamburg.

Tag der Habilitation: 30. Juni 2022

To my children Alexej, Sophia, Nikolai without whom this work would have been completed some years earlier, albeit without fun and motivation and to my husband Mikhail who always believed that I'll make it.

Drawing on title page is by Hester Wittke.

Contents

1	Introduction	5
2	Evolution of the ocean carbon sink in response to climate change events	11
2.1	Enhancing the realism of modeled processes	11
2.2	Implications of ongoing and future climate change	18
2.2.1	Impacts of ocean biogeochemistry outside its realm	20
2.2.2	Total alkalinity as a tracer for shifts in the carbon cycle	22
2.3	Ocean carbon cycle during ancient warming	24
2.4	Biogeochemistry of the glacial ocean	27
3	Variability and predictability of the ocean carbon sink	31
3.1	Decadal variability of the ocean carbon sink	31
3.2	Predictability of the ocean carbon sink	34
3.3	Towards predictability of the atmospheric CO ₂ growth rate	35
4	The potential of ocean alkalinity enhancement to mitigate climate change and ocean acidification	39
4.1	Effects on ocean biogeochemistry and the Earth system	39
4.2	Challenges for verification in the presence of climate variability	42
5	Summary and Outlook	45
5.1	Summary of main research achievements	45
5.2	Avenues for future work	49
	Bibliography	52
	Acronyms	67

Chapter 1

Introduction

Eunice Foote, who was the first to measure the solar heating of CO₂ in her early experiments already in the 1850s noted: “*An atmosphere of that gas would give to our Earth a high temperature*“ (Foote, 1856). Indeed, our planet is warming unprecedentedly fast due to rising anthropogenic CO₂ emissions (Masson-Delmotte et al., 2021). Next to catastrophic floodings, wildfires and droughts on land, with tragic consequences for people, the ocean silently suffers from the ongoing heating, acidification, and deoxygenation with tragic impacts for marine systems.

The ocean plays an essential role in regulating Earth’s climate; it is also essential for regulating the Earth’s carbon cycle. The ocean contains around 38,000 Gt of carbon. This is 16 times more than the terrestrial biosphere (plant and the underlying soils), and about 60 times more than the pre-industrial atmosphere (Canadell et al., 2021). Therefore, even a small perturbation to the ocean carbon content by changing its capacity to store carbon would impact atmospheric CO₂ concentrations (Fig.1.1), making the ocean carbon sink a major regulator of the Earth’s climate on a time scale of hundreds to thousands of years. As the ocean currently continuously absorbs anthropogenic carbon from the atmosphere, it thereby has a key role in moderating ongoing climate change.

Based on the Global Carbon Budget (GCB) estimates (Friedlingstein et al., 2020), the global ocean has already taken up about one third of the cumulative anthropogenic CO₂ emissions (Fig.1.2). The strength of the ocean carbon sink is determined by chemical reactions in seawater (carbonate system), biological processes (photosynthesis, export flux, and remineralization by aerobic and anaerobic respiration), and physical processes (including ocean circulation and vertical mixing). But even though these key mechanisms are identified (Landschützer et al., 2021), there are considerable uncertainties regarding their interannual and decadal variations, as well as their susceptibility to ongoing climate change. Here, a major uncertainty arises from the lack of knowledge regarding the contribution of the natural variability of the climate system (Ilyina, 2016).

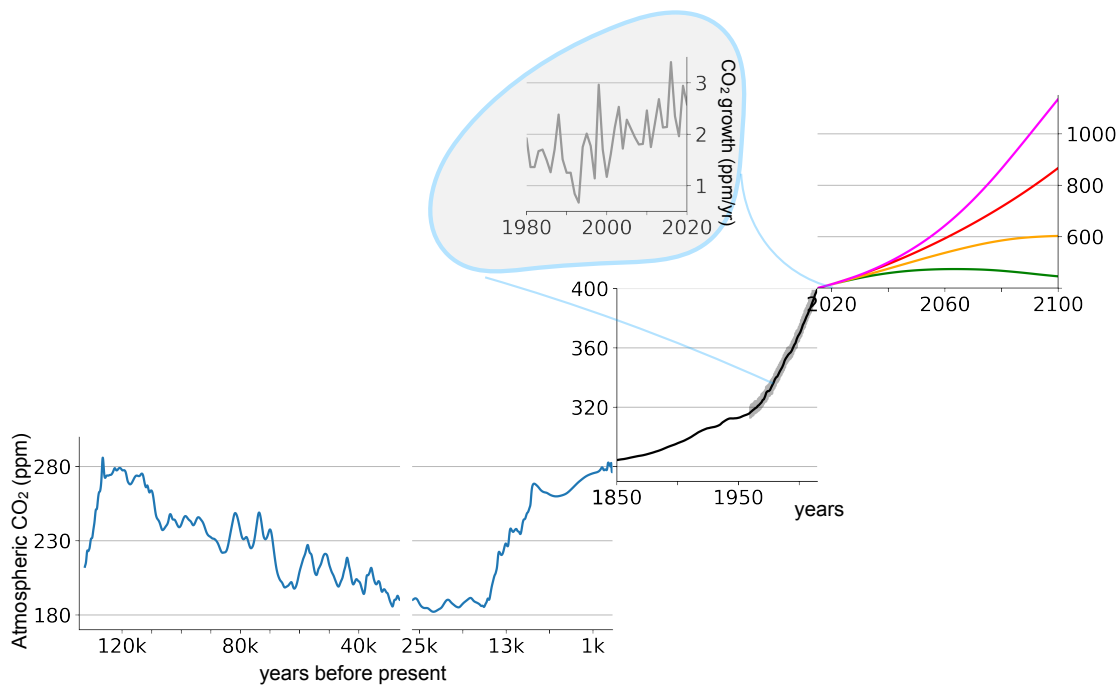


Figure 1.1: Evolution of Earth’s atmospheric CO₂ concentration (ppm) spanning (left panel) the last glacial cycle based on data from Köhler et al. (2017), (middle panel) in CMIP6 scenarios (O’Neill et al., 2016) historical (overlaid with Mauna Loa measurements for 1958-2015) and (right panel) future climate change projections SSP585 (magenta), SSP370 (red), SSP245 (orange) and SSP12.6 (green) used to force concentration-driven MPI-ESM simulations. Highlighted zoomed panel shows the growth rate of atmospheric CO₂ (ppm/yr) over the years 1980-2020, inferred from Mauna Loa measurements. Note the different ranges on the x- and y-axes on individual panels.

There is a consensus among model-based and observational studies about the overall temporal evolution of the ocean carbon sink, both confirming its increase over the past decades. Yet, there are gaps in understanding the role and feedbacks of natural biogeochemical and physical processes and how these processes will operate under a changing climate. As a result, near-term and longer-term future changes in the ocean carbon uptake and storage are unconstrained (Ilyina and Friedlingstein, 2016).

The focus of my research over the past years was to address these major gaps in the understanding of ocean biogeochemical cycles, and my philosophy has been to tackle these cycles as an interactive component of the Earth system. I investigated the evolution of the ocean carbon sink, with a focus on the processes that act as main drivers for carbon uptake and storage in the ocean, as well as their susceptibility to rapid past and future climate change events. Furthermore, I stud-

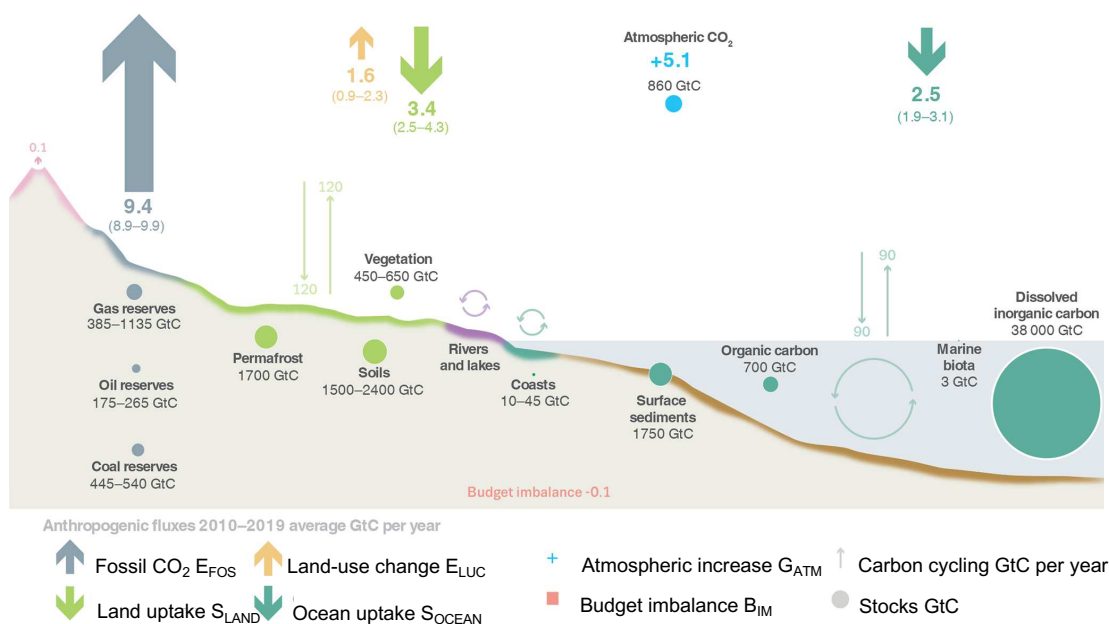


Figure 1.2: Schematic representation of the overall perturbation of the global carbon cycle caused by anthropogenic activities, averaged globally for the decade 2010–2019 from GCB 2020; modified after Friedlingstein et al. (2020). The small uncertainty in the atmospheric CO₂ growth rate (± 0.02 GtC yr⁻¹) is neglected for the figure. The anthropogenic perturbation occurs on top of an active carbon cycle, with fluxes and stocks represented in the background and taken from Ciais et al. (2013) for all numbers, with the ocean gross fluxes updated to 90 GtCyr⁻¹ to account for the increase in atmospheric CO₂ since publication, and except for the carbon stocks in coasts, which are from a literature review of coastal marine sediments (Price and Warren, 2016). Cement carbonation sink of 0.2 GtCyr⁻¹ is included in E_{FOS}.

ied the effects of decadal variability on the processes regulating the ocean carbon sink and carbon-climate feedbacks. This brought me to questioning whether by knowing natural climate variability, the near-term variations in the carbon cycle can be predicted. This is an emerging topic requiring fast advances as it relates to the United Nations Framework Convention on Climate Change (UNFCCC) global stocktakes. Finally, I quantified the potential of the ocean-based Carbon Dioxide Removal (CDR) strategy of enhancing ocean alkalinity to mitigate climate change and ocean acidification. These are vibrant scientific topics of increasing political and societal relevance, where I could contribute by basic research directly into international processes as reflected in my leadership of the World Climate Research Program (WCRP) Grand Challenge on Carbon Feedbacks in the Climate System (GC-Carbon) (Ilyina and Friedlingstein, 2016).

Changes in ocean biogeochemical cycles always occur in concert and are affected

by changes in Earth's climate and ocean physics. Therefore, I investigated these research topics in concert with the variability and changes in Earth's climate and ocean physics in past, present, and future climates in the framework of the Earth System Model (ESM).

In this essay, I present my research contributions based on my papers explicitly mentioned in the text. My research was guided by the following questions:

1. How do ocean biogeochemical cycles accommodate perturbations brought about by anthropogenic activities or natural forcings?
2. What are the predictability horizons of variations in the ocean carbon sink?
3. What is the potential of the ocean carbon sink, artificially enhanced by ocean alkalinity additions, to mitigate climate change?

This essay is accordingly organized around these three research questions. As ESMs have always been the main tool in my research, in Chapter 2, I address how ESMs represent the ocean carbon sink during rapid climate change events. This topic requires simulations on time scales ranging from centuries to millennia. For me this work inevitably starts by questioning how well models are suited to address the susceptibility of ocean biogeochemistry to changes in ocean physics and climate? Hence, I devoted substantial attention (and personal fondness) to the development of the Hamburg Ocean Carbon Cycle model (HAMOCC) as a component of Max Planck Institute's Earth System Model (MPI-ESM), with the purpose of enhancing its realism, needed for performing cutting-edge research. Using HAMOCC, I studied future ocean acidification, including its effects outside the biogeochemical realm, i.e. (i) via the feedbacks due to indirect aerosol effects of the marine emissions of dimethylsulfide (DMS) and (ii) the effects of changing seawater pH on ocean acoustics. I investigated the susceptibility of marine carbonate chemistry to climate change, as it largely determines the capacity of the ocean carbon sink to absorb and store anthropogenic carbon. My more recent focus has been on understanding perturbations in ocean biogeochemistry in response to ancient warming of the Paleocene-Eocene Thermal Maximum (PETM) and Permian-Triassic Boundary (PTB). Furthermore, a major topic that currently tickles my scientific curiosity is the glacial cooling of the Last Glacial Maximum (LGM) with subsequent deglaciation. One common feature among all these different climate change events is the intimate connection between ocean biogeochemistry, ocean circulation and the physical climate.

The presence of Internal Climate Variability (ICV) driven by the chaotic nature of the Earth system opens another exciting avenue for research in the ocean carbon cycle, which I focused on. The ocean provides decadal memory for climate variations, which in turn determine the near-term evolutions of the carbon cycle

that deviate from the pace of anthropogenic CO₂ emissions. My interest in the potential of ICV to shape the variations of the ocean carbon sink led to another research focus, presented in Chapter 3. An obvious question for me in this context was whether variations of the ocean carbon sink driven by ICV are predictable in the framework of ESM-based decadal prediction systems. This chapter further gives estimates of predictability horizons for the ocean carbon cycle and presents some very recent work from my group on the predictability of atmospheric CO₂ growth.

Chapter 4 presents my work on the potential of a CDR method of Artificial Ocean Alkalinization (AOA) to mitigate climate change and ocean acidification. AOA assumes enhancement of ocean alkalinity, and while being discussed as a means to enhance the ocean carbon sink and mitigate atmospheric CO₂ levels, the effects on ocean biogeochemistry and marine ecosystems are not understood. Likewise, carbon climate feedbacks invoked by this form of climate engineering can only be computed in the scope of an ESM allowing for the interactive carbon cycle with prognostic atmospheric CO₂. With these tools being available to me, I addressed scenarios of AOA in MPI-ESM. I furthermore also studied another aspect related to any CDR strategy – the detectability and attribution of its effects in the Earth system – necessary for monitoring its success.

Finally, the outline of the novelty of the research outcomes, their implications, and avenues for future work are summarized in Chapter 5.

Chapter 2

Evolution of the ocean carbon sink in response to climate change events

2.1 Enhancing the realism of modeled processes

Since the beginning of my work as Group Lead of the Ocean Biogeochemistry Group, model development of HAMOCC (Fig.2.1), the main working tool of the group (Ilyina et al., 2013a), has been a continuous effort. Advancing HAMOCC as the ocean biogeochemical component of the ESMs developed at the Max Planck Institute for Meteorology (MPI-M) became the backbone of my research. As a result, my research was scoped to enable continuous progress in ocean biogeochemical modeling maintained by incorporating new and updating the existing processes based on empirical and theoretical advances, as well as continuously confronting old and new uncertainties in biogeochemical models.

Already in my PhD project, I developed a new Fate and Transport Ocean Model (FANTOM) for persistent organic pollutants (Ilyina, 2007). A major focus was to assess and implement the main physical, chemical, and biogeochemical processes that shape the distributions and temporal evolutions of some selected organic pollutants that were abundant in the North Sea, despite policy measure to reduce their loads. An evaluation against observational data turned out to be satisfactory (Ilyina et al., 2006). This enabled a novel quantification, based on FANTOM, of the sink and source behavior of the North Sea, regarding these pollutants, for the outer world (Ilyina et al., 2008). These comprehensive results drove further model implementation for another organic pollutant of industrial origin, with somewhat different environmental properties and usage history (Ilyina and Hunziker, 2010). Later on, I co-supervised a follow-up detailed analysis of

the loadings and trends of the organic pollutants in the North Sea with FANTOM (O’Driscoll et al., 2013).

In my group at the MPI-M, we develop the model HAMOCC as a tool to test our ideas. Thereby, we need to enhance the realism of ocean biogeochemical processes. The model has undergone major re-design, including the incorporation of new processes, refining the existing parameterizations, transferring HAMOCC into the Icosahedral Nonhydrostatic model (ICON), and an extensive evaluation of model performance. Simulations with HAMOCC are performed within MPI-ESM in the Coupled Model Intercomparison Project (CMIP) simulations within Phase 5 (Ilyina et al., 2013a; Giorgetta et al., 2013) and Phase 6 (Mauritsen et al., 2019; Müller et al., 2018), as well as in coupled simulations with ICON (Jungclaus et al., 2022). The most important model developments include:

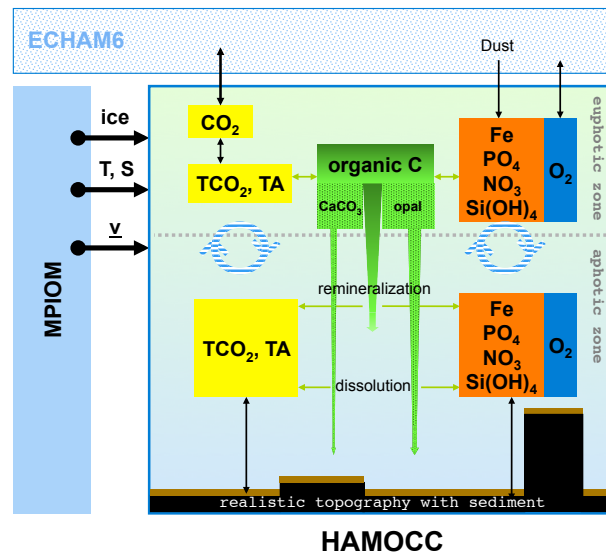


Figure 2.1: A schematic overview of the global ocean biogeochemistry model HAMOCC (Ilyina et al., 2013a)

- Hanna Paulsen within her PhD project supervised by me (Paulsen, 2018), incorporated an explicit representation of cyanobacteria as an additional tracer in HAMOCC (Fig.2.2). The standard model before this new work had unrealistically high N_2 fixation rates in cold waters in high latitudes and a strong coupling to NO_3 -depleted zones. In the new scheme, growth dynamics of N_2 fixers are parameterized explicitly based on the physiological properties of the wide spread cyanobacterium *Trichodesmium*. The chosen temperature dependency of diazotrophic growth confines N_2 fixation to the tropical and subtropical ocean, i.e. within roughly $40^\circ S$ and $40^\circ N$. As a result, N_2

fixation in HAMOCC evolves in response to the environmental conditions shaping cyanobacteria’s ecological niche.

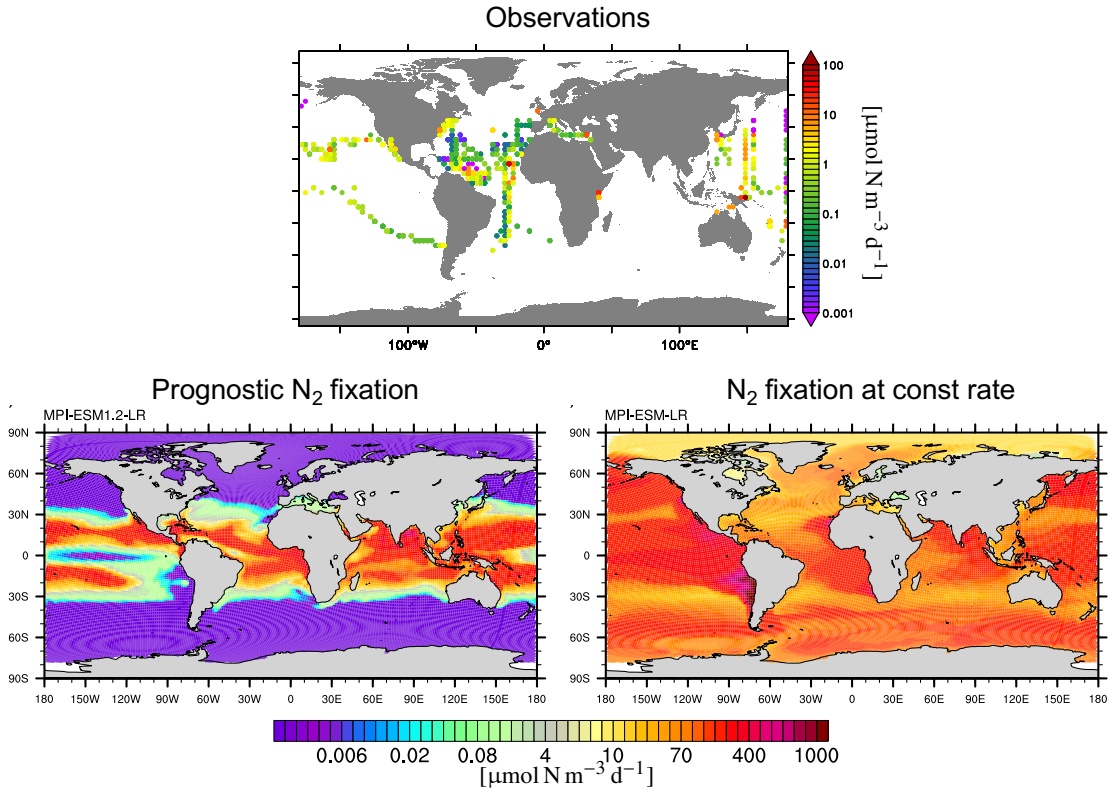


Figure 2.2: Surface N_2 fixation rates in observations (upper panel) and in the model (lower panel) at a constant rate in the older model version and with prognostic cyanobacteria; adapted after Paulsen et al. (2017) and Mauritsen et al. (2019). Note the different colorbars.

The new scheme improved N_2 fixation representation in comparison to observations (Paulsen et al., 2017). Moreover, HAMOCC is now better equipped for future simulations, as the warmer and more stratified future ocean might favor N_2 fixing cyanobacteria by increasing their ecological niche, as opposed to other phytoplankton species, leading to a shift in community composition. Finally, we showed that this newly added feedback mechanism (via light absorption) has a regulative role for tropical ocean sea surface temperature and its variability (Paulsen et al., 2018), determined by the abundance of and changes in N_2 fixing cyanobacteria.

- With the aim of improving the representation of the coastal carbon stock, within the PhD project of Fabrice Lacroix (Lacroix, 2020), which I super-

vised, we extended HAMOCC to include nutrient, carbon and alkalinity inputs from rivers. While rivers deliver vast amounts of terrestrially derived biogeochemical compounds to the ocean, they are not considered in the standard MPI-ESM simulations. Also most other ESMs either omit or have a very simplistic representation of biogeochemical river inputs. As shown in an earlier study with my contribution (Regnier et al., 2013), the implications of biogeochemical river inputs for the coastal and the global ocean carbon sinks remain largely unconstrained, representing a major gap in constraining the Global Carbon Budget.

In the new scheme in HAMOCC, preindustrial riverine inputs are integrated based on a hierarchy of state-of-the-art weathering and organic matter land-ocean export models as a function of surface runoff and temperature (Lacroix et al., 2020). These additional inputs from rivers induced changes in marine biological production and in the air-sea CO₂ flux, both at the global and regional scales in a pi-control simulation (Lacroix et al., 2021a).

These new simulations, furthermore, allowed us to draw two important and novel conclusions on the state of the preindustrial coastal ocean. First, they show that due to a relatively short residence time of terrestrial organic carbon, the global shelf ocean acted as a weak carbon sink already in the preindustrial age. Second, due to the enhancement of net primary production by riverine fluxes, the preindustrial coastal ocean was autotrophic, i.e. characterized by conditions at which gross primary production (limited by temperature, as well as light and nutrient availability) prevails over net ecosystem respiration (determined by the composition and chemical reactivity of terrigenous and autochthonous organic matter, as well as by the availability of oxidants). This implies that organic carbon cycling on the shelf drives a sink for dissolved inorganic carbon. These findings provide a basis for addressing the role of the changing carbon cycle in the global coastal ocean under ongoing anthropogenic perturbation and in past climates.

Interestingly, over the course of the 20th century, some coastal regions switch their role as net carbon sources or sinks. Coastal oceans thereby remain an inefficient sink of anthropogenic CO₂ (Lacroix et al., 2021b). Overall, river inflow of carbon, nutrients, and alkalinity based on an interactive weathering scheme leads to more CO₂ outgassing and an improved representation of the coastal ocean (Fig.2.3).

- Persistent and large uncertainty in the response of the ocean carbon sink to climate change is caused by missing or insufficiently represented processes related to marine biology in global models. In particular, representation of marine aggregates – the primary vehicles of Particulate Organic Carbon

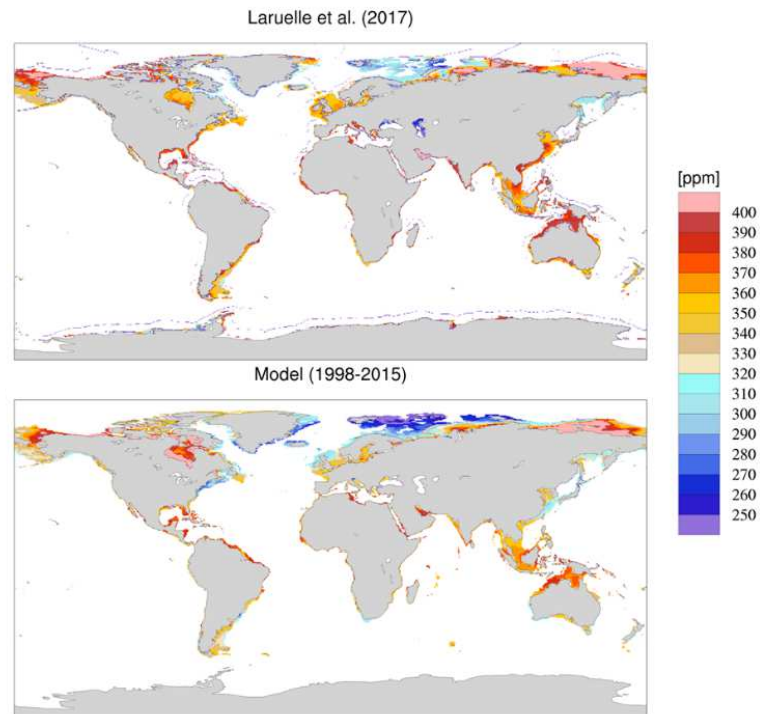


Figure 2.3: Comparison of HAMOCC-simulated global coastal annual mean pCO₂ distribution over the period 1990-2010 (lower panel) against the observation-based pCO₂ climatology (upper panel); modified after Lacroix et al. (2021b)

(POC) transport from the surface into the deep ocean – remains challenging. Yet, their importance in regulating the biological carbon pump, as well as elemental cycling and food-web structures, are a pivotal variable in the oceans’ response to climate change. As part of an institutional collaboration between MPI-M and MPI for Marine Microbiology in the project MARMA, within the work of Jöran März supervised by me, we investigated the biological carbon pump efficiency.

In earlier versions of HAMOCC, fluxes of POC are calculated either following a Martin curve approach with linearly increasing sinking velocity with depth and constant remineralization rates, or even with prescribed constant sinking speeds (Ilyina et al., 2013a). The new particle scheme M4AGO incorporated in HAMOCC explicitly represents marine aggregates and their measurable properties (e.g. size, microstructure, porosity, excess density) and includes temperature-dependent remineralization. As a result, the representation of the global POC transfer efficiency (a fraction of POC exported out of the euphotic zone that reaches a particular depth) in HAMOCC was substan-

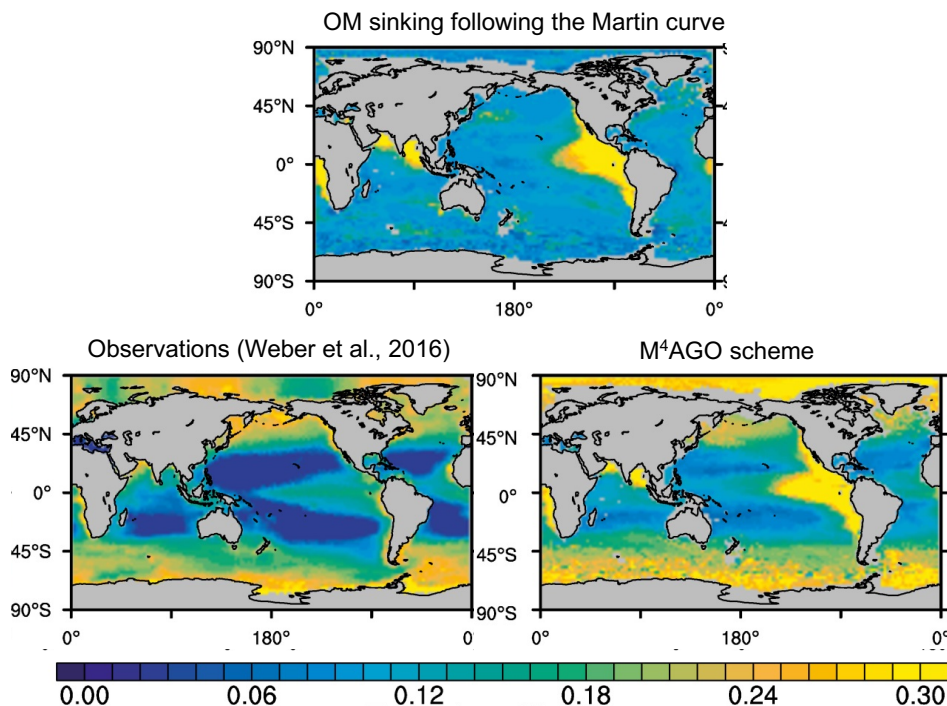


Figure 2.4: Annual mean transfer efficiency for POC at export depth of 100m to about 1000m (960m in the model) in observations (upper panel), in the standard HAMOCC following a Martin curve approach (bottom left), and in the new scheme M4AGO (bottom right); adapted after Maerz et al. (2020)

tially improved (Maerz et al., 2020), and compares well with the latitudinal pattern constrained from observations (Fig.2.4). The integration of this advanced particle sinking scheme improved regional results and made it possible for the first time in HAMOCC to investigate how opal and calcium carbonate (CaCO_3) fluxes co-determine higher transfer efficiencies of POC in high latitudes and lower ones in the subtropical gyres. Temperature was thereby identified as a driving factor for remineralization, with implications for projections of the future biological carbon pump, that are being investigated in an ongoing study.

- We extended HAMOCC with a new stable carbon isotope (^{13}C) module within the work by a PostDoc (Bo Liu) that I supervise (Liu et al., 2021). Now ^{13}C is explicitly resolved for all oceanic carbon pools that are considered in HAMOCC (at a price of adding seven new advective tracers). Additionally, biological fractionation associated with photosynthetic carbon fixation during phytoplankton growth as well as fractionation during air-sea gas exchange is accounted for. Furthermore, as it was not clear which parameteri-

zation of ^{13}C biological fractionation would be more suitable in the context of HAMOCC architecture, we tested the two often-used ones.

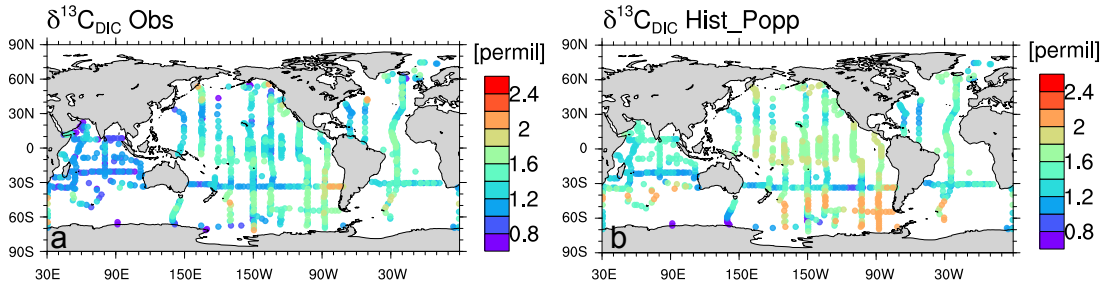


Figure 2.5: Observed surface ^{13}C (Schmittner et al., 2013) (a) and simulated ^{13}C in the simulation in Hist_Popp following a preferred parameterization of ^{13}C sampled at the location, month and year of the observation (b); (Liu et al., 2021)

Comparison to present-day observations (Fig.2.5) shows satisfactory performance of the model. While both parameterizations perform similarly well for dissolved inorganic carbon, the one by Popp et al. (1989) is considerably better for particulate organic carbon. Moreover, the so called ^{13}C Suess effect, characterizing the intrusion of the isotopically light anthropogenic CO_2 into the ocean, is also captured.

This new feature in HAMOCC opens opportunities for direct comparison with isotopic data in paleo and present-day. Moreover, including stable carbon isotopes in MPI-ESM simulations enables unique opportunities to address responses of ocean biogeochemistry to changes in atmospheric CO_2 and climate.

- Furthermore, for the first time, the integration of land to ocean carbon and nutrients transfer via the associated sea level change during deglaciation is interactively computed (Extier et al., 2022) based on the dynamical land-sea mask and hydrological discharge. During flooding, HAMOCC receives carbon from the land carbon pools' wood, woody litter and humus, which have to be transferred to corresponding oceanic pools in the water column and sediment, manifested by 3 new prognostic tracers. In the case of drying of an ocean grid cell, all pore water tracers, i.e. phosphate, nitrate, dissolved inorganic carbon and alkalinity are redistributed to the water column to guarantee mass conservation. The solid parts of the sediment are thereby considered as inactive land pools. Outcomes of this, as of now, rather unique model component, enabling an improved understanding of the ocean carbon cycle during the last deglaciation, are summarized in section 2.4.

With this work my group continues addressing some major gaps in our understanding of the processes regulating ocean biogeochemical feedbacks in the Earth system. This includes further development of HAMOCC in order to keep it at the frontier of ocean biogeochemical research. Our ongoing activities are strongly focused on the evaluation of the new features available in ICON-O on the performance of biogeochemical tracers in HAMOCC. Early outcomes by Fatemeh Chegini and Lennart Ramme, from tuning of HAMOCC in ICON, indicate that different values of the Gent-McWilliams parameterization have a notable impact on ocean biogeochemistry. Furthermore, a novel, seamless approach to integrate the coastal ocean in a global setup of ICON-Coast using a global grid configuration with regional refinement in the coastal ocean (Mathis et al., tted), in collaboration with Helmholtz-Zentrum Hereon, promises new advances in understanding coastal ocean carbon cycle dynamics. Increased turnaround of HAMOCC due to concurrency (ongoing work by Leonidas Linardakis) is promising for high resolutions.

2.2 Implications of ongoing and future climate change

One negative side-effect of the ocean's role as a major carbon sink for rising anthropogenic CO₂ is ocean acidification. This phenomenon, often called "the other CO₂ problem," is a result of the dissolution of fossil fuel carbon in seawater leading to a decrease in carbonate ion concentration and lowering of seawater pH, with a number of negative impacts for many marine organisms. A decrease in seawater pH is already detectable; moreover it is accelerating. Observations from different locations in the ocean, available from long-term biogeochemical time-series sites, reveal decreasing trends in ocean pH between 0.0015 and 0.0024 pH units per year (Tanhua et al., 2015). In the context of Earth's history, this ongoing change in seawater pH is probably the fastest in the last 300 million years (Hönisch et al., 2012). Rather dreadful is the realization, supported by geological evidence, that the fastest known natural acidification event, occurring during the PETM 55 million years ago which was associated with a severe extinction of benthic organisms, was probably ten times slower than the ongoing acidification caused by human activities.

Carbonate chemistry processes quantifying the global response of inorganic carbon cycle to the ocean's invasion by anthropogenic CO₂ from the atmosphere is relatively well constrained (Bopp et al., 2013). My earlier projections of changes in ocean biogeochemistry with HAMOCC (Ilyina et al., 2010) showed that, if CO₂ emissions follow the business-as-usual (at that time) emission scenario A1B, by the year 2100, ocean pH may drop by up to 0.6 units at the surface ocean that

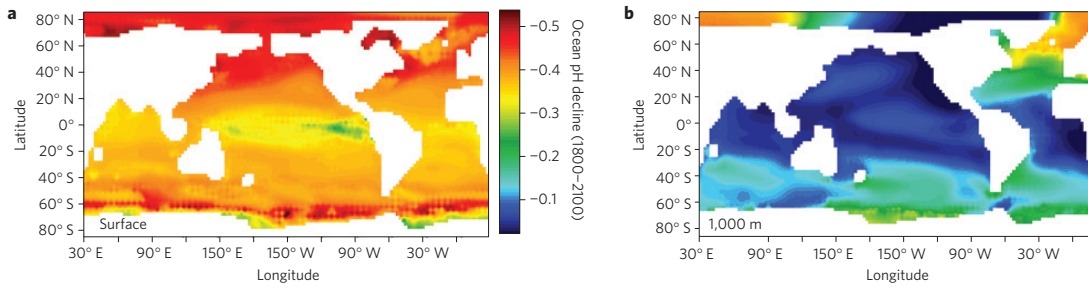


Figure 2.6: Projected changes in seawater pH in 2100 at the surface (a) and at a depth of 1000 m (b) in emission scenario A1B; (Ilyina et al., 2010).

continually absorbs atmospheric CO_2 . At depth of 1000 m, a lower decrease by about 0.2-0.4 units is projected (Fig.2.6). Corresponding decreases in seawater pH value in a more conservative (regarding fossil fuel emissions) B1 scenario are 0.4 and 0.2 units, and 0.7 and 0.5 units in a fossil-fuel-intensive A1FI scenario, respectively. These projections indicate a high sensitivity of ocean carbon chemistry to policy change, as well as the importance of curbing anthropogenic CO_2 to avoid dangerous ocean acidification. In all considered climate change scenarios, high latitudes where the major carbon sink regions are located, including the Southern Ocean, North Atlantic, and Arctic Ocean, emerged as hot spots for changes in seawater pH.

Together with my group and in collaboration with international colleagues, I continuously investigate the extent to which ocean biogeochemical cycles can accommodate perturbations brought about by anthropogenic activities or natural forcings, as well as their influence on and response to ongoing and future climate change. With the HAMOCC model in the framework of MPI-ESM, I network within numerous international and national projects and contribute to the design of coordinated simulations, i.e. CMIP within the number of topical MIPs and GCB. Thereby I have established a broad international network and taken part in academic collaborations resulting in numerous scientific publications featuring the implications of climate change on ocean biogeochemistry and carbon feedbacks in the climate system.

This engagement led to major assessments framing the state of ocean biogeochemistry and the range of change in response to climate change scenarios in CMIP5 (Bopp et al., 2013; Arora et al., 2013; Andrews et al., 2013; Séférian et al., 2016; Vancoppenolle et al., 2013) and CMIP6 (Arora et al., 2020; Kwiatkowski et al., 2020; Séférian et al., 2020) simulations. Important in this context is a critical assessment of HAMOCC performance in the family of other analogous models. For instance, (Séférian et al., 2016) found that due to the longest spin-up in comparison to other CMIP5 models, HAMOCC had the lowest drift in oxygen concentration at the depth of 2000m. The study furthermore suggests that differences in spin-

up protocols could explain a substantial part of model disparities, constituting a source of model-to-model uncertainty.

These activities provide a source of continuous inspiration to my research and an opportunity to make an impact on future directions in my discipline, and to impact policy. On the latter aspect, in collaboration with Damon Matthews and other colleagues, we presented a methodology on how to properly calculate the remaining carbon budgets (Matthews et al., 2020). This is commonly interpreted as measure of the total remaining CO₂ that may be still emitted to limit a warming level, such as meeting the Paris Agreement target. Furthermore, under the auspices of Future Earth, I contributed to identifying and shaping the ten new insights in climate science 2020 (Pihl et al., 2021) launched at the UNFCCC policy report. Moreover, I strive to push the boundaries of CMIP, by running a large ensemble of CO₂ emission-driven simulations enabling the interactive carbon cycle, whereas the status quo is that currently most simulations run with prescribed atmospheric CO₂ concentrations. For instance, in the recent CovidMIP (Jones et al., 2021) our model was the only one which ran with an interactive carbon cycle. Such simulations allow us to address a number of questions that are not possible with concentration-driven simulations and enables direct studies of the role of different climate policies on carbon feedbacks.

2.2.1 Impacts of ocean biogeochemistry outside its realm

Changes in ocean biogeochemistry brought about by rising atmospheric CO₂, referred to as ocean acidification, are commonly considered a purely ocean chemistry problem. As a result, climate change and ocean acidification (i.e. the decrease in seawater pH) have widely been treated as uncoupled consequences of the anthropogenic CO₂ perturbation. We showed that ocean acidification itself could have an effect on climate. In a study Six et al. (2013) supervised by me, data from mesocosm experiments was implemented into the HAMOCC model, showing that phytoplankton produces 20% less DMS, a precursor to sulfate aerosol in the atmosphere, under lower values of seawater pH. Running the MPI-ESM with this new parameterization, in a future climate change scenario (A1B), we projected a decrease in atmospheric DMS emissions of about 18%. The resulting additional radiative forcing would accelerate global warming characterized by an equilibrium temperature rise between 0.23 and 0.48K by 2100 (Fig.2.7). This work has inspired further research proposals. Additionally, the developed model parameterization is being further used in the Norwegian ESM (Nor-ESM; Schwinger et al. (2017)) which includes an interactive aerosol model.

In my work, I also addressed another rather unexpected effect of changing seawater carbonate chemistry brought about by ocean acidification, the effect on ocean acoustics (Ilyina et al., 2010). One of the mechanisms driving attenuation

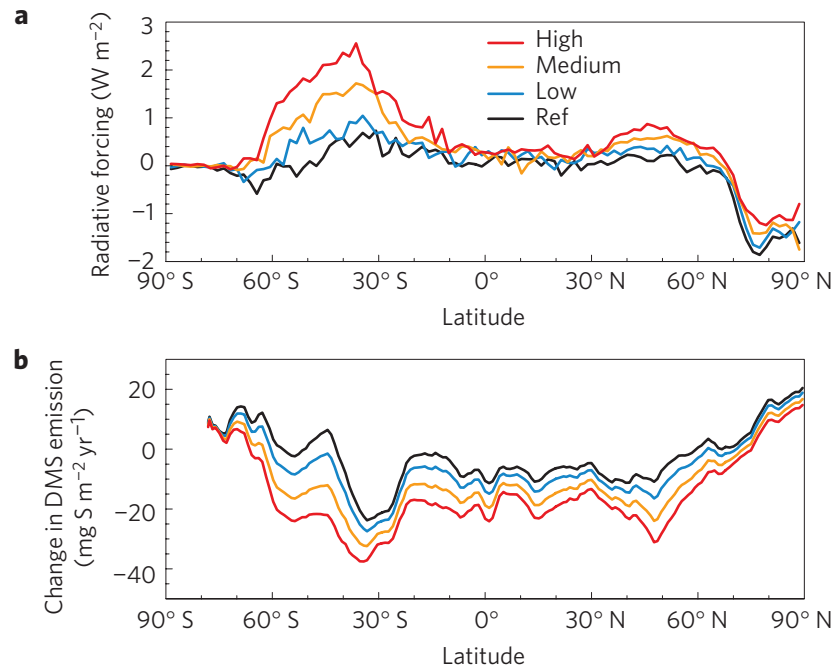


Figure 2.7: Changes in the annual zonal mean of (a) top-of-the-atmosphere radiative forcing and (b) DMS emissions between the years 2090–2099 and 1865–1874. Results are shown for the reference run (Ref) and three pH-sensitive runs (low, medium and high); (Six et al., 2013).

of low frequency sound in seawater is due to the chemical resonances of some constituents of sea water, such as magnesium sulphate and the boric acid / carbonate system. The pH-dependent chemical relaxation from the borate/carbonate system affects low frequencies, primarily between 100 Hz and 10 kHz. I performed calculations of the effects of changing pH on the low-frequency sound absorption in the future ocean using HAMOCC. The concentration of dissolved borate ion and boric acid absorbing sound near 1 kHz depends on seawater pH. In model projections of future ocean acidification, I quantified, for the first time, that a pH decrease of 0.6 leads to a drop in the low frequency sound absorption coefficient by more than 60% (Fig.2.8). This can have implications for marine life and naval applications that are based on ocean acoustics.

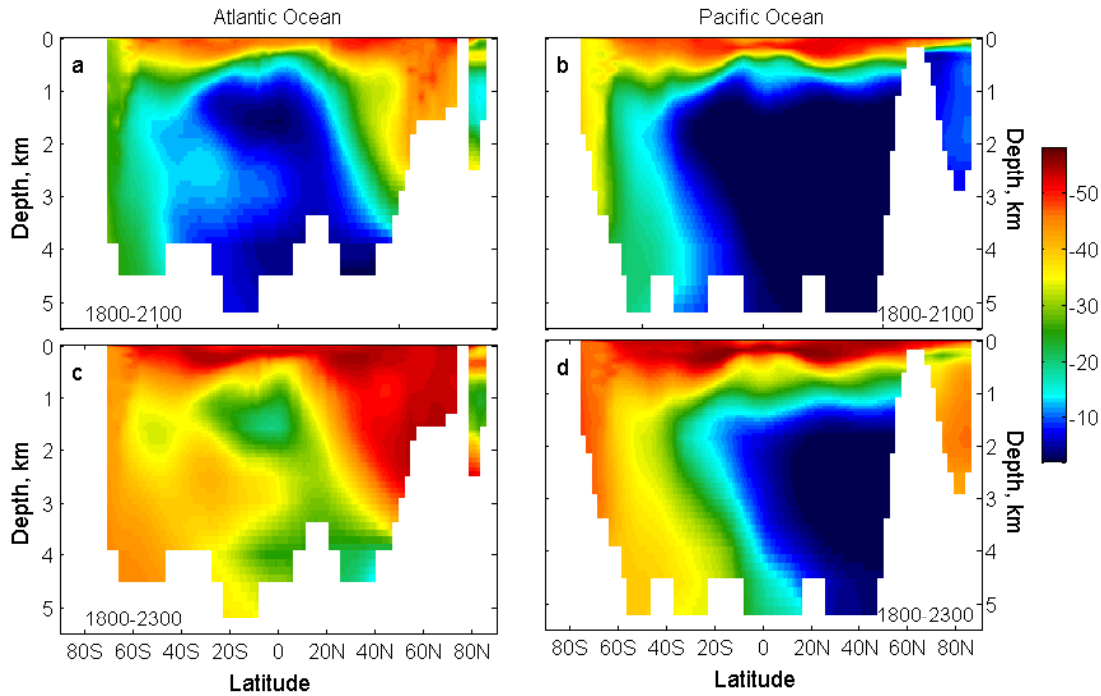


Figure 2.8: Changes in the zonally averaged vertical distributions of the sound absorption coefficient (%) at 200 Hz, (a–d) in the Atlantic Ocean (a,c) and in the Pacific Ocean (b,d) projected for the years 2100 (a,b) and 2300 (c,d) (Ilyina et al., 2010).

2.2.2 Total alkalinity as a tracer for shifts in the carbon cycle

Seawater Total Alkalinity (TA), determined by the charge imbalance of the conservative ions in seawater together with Dissolved Inorganic Carbon (DIC) represented by the sum of carbon species, controls the variations of partial pressure of CO_2 ($p\text{CO}_2$) in seawater, which in turn directly determines the air-sea exchange of CO_2 . Because TA and DIC are conserved during mixing and are unaffected by changes in temperature and pressure (Zeebe and Wolf-Gladrow, 2001), they are key parameters of the marine carbonate system and are used as state variables in models of ocean biogeochemistry. Oceanic TA is altered by three main processes, being (i) changes in freshwater fluxes, such as precipitation/evaporation, riverine discharge of fresh water, ice growth and melting; (ii) production of CaCO_3 by calcifying organisms (e.g. coccolithophorids, corals, foraminifera) and CaCO_3 dissolution in the water column and deep-sea sediments; and (iii) production and remineralization of organic matter by microalgae. Increasing the surface ocean TA enhances the oceanic uptake of atmospheric CO_2 , while decreasing TA lowers the

oceanic capacity to take up and store carbon. Changes in seawater TA by a variety of mechanisms have been proposed to modulate the variations of atmospheric CO_2 along glacial-interglacial timescales (Heinze et al., 1991; Archer and Maier-Reimer, 1994; Rickaby et al., 2010), as well as a means of deliberate manipulation of climate (Ilyina et al., 2013b; Köhler et al., 2013). Therefore, understanding the spatiotemporal distribution of TA changes is critical to grasp the oceanic capacity to uptake and store carbon. Furthermore, while TA does not change when CO_2 is dissolved in seawater, the processes controlling its cycling do. Hence, it is also interesting to study TA in the context of climate change, i.e. in a rising CO_2 ocean (Fig.2.9).

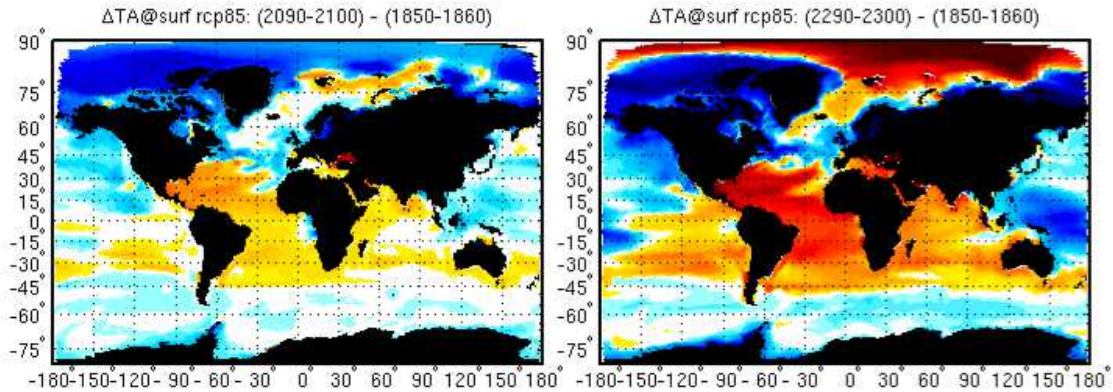


Figure 2.9: Changes in TA $\mu\text{mol kg}^{-1}$ at the ocean surface for the scenario RCP8.5 in 2090-2100 relative to 1850-1860 (Ilyina, 2015).

In my earlier work I focused on designing model scenarios in which the production and dissolution of CaCO_3 is treated as a function of carbonate ion saturation (Ilyina et al., 2009; Ilyina and Zeebe, 2012). Back then, only a few models accounted for this dependency. This allowed me to examine the effects of changes in marine CaCO_3 production in response to ocean acidification on TA in the ocean. Projections of TA over the historical time period were evaluated taking into account the natural variability in ocean carbonate chemistry, as derived from repeat hydrographic transects. In this study (Ilyina et al., 2009) we hypothesized that if ocean acidification leads to a decrease in CaCO_3 production, the surface ocean would have a higher abundance of carbonate ion (CO_3^{2-}) which could not be used during calcification. Changes in CO_3^{2-} concentration would then induce a change in ocean TA, which could eventually be measured. The study concluded that the data currently available does not allow discerning significant trends in TA due to changes in pelagic calcification caused by ocean acidification. Given different calcification scenarios, our model calculations indicated that the TA increase over time will start being detectable by the middle of the current century, increasing by 5-30 mmol kg^{-1} compared to the present-day values. In a scenario of extreme reductions

in calcification, large TA changes relative to preindustrial conditions would have occurred at present, which we consider very unlikely. The real novelty of this work was to propose monitoring the changes in TA for early detection of ocean acidification effects. However, the time interval of reliable TA observations is too short to disregard this scenario. Moreover, these model simulations, based on single model realizations in each scenario, could not represent the range of ICV. This deficiency sparked my interest to study the effects of ICV on ocean biogeochemistry.

Follow up studies (Ilyina, 2015; Carter et al., 2016) found that detection can be hampered by substantial seasonal variability of TA, as well as due to the concomitant effects on TA of changes in carbonate chemistry, marine biology, and ocean circulation. Interestingly, however, the production of CaCO_3 is linked to the concentration of radionuclide thorium (^{230}Th) in the ocean water column. An increase of ^{230}Th concentration with depth takes place due to scavenging and a downward particle flux of CaCO_3 . Therefore, in collaboration with Christoph Heinze, we further employed the design of the CaCO_3 production scenarios to test the potential of using ^{230}Th as an additional line of evidence for detection of ocean acidification (Heinze et al., 2018). We confirmed that the time of emergence of signals in dissolved ^{230}Th due to ocean acidification is likely on the same order of magnitude as for TA measurements found in the earlier study (Ilyina et al., 2009).

While the effects of ocean acidification on the production of CaCO_3 could become detectable via TA changes over the next decades, the response of CaCO_3 dissolution in the water column and sediments would take a substantially longer time (Ilyina and Zeebe, 2012), with an inhomogeneous response among different ocean basins, being earlier in the Atlantic Ocean than in the Pacific Ocean. We show that different model assumptions regarding CaCO_3 dissolution rates have little impact on future projections of atmospheric CO_2 . Instead, anthropogenic CO_2 emissions overwhelmingly control the degree of perturbation in ocean chemistry. On longer time scales, as anthropogenic CO_2 penetrates into the subsurface ocean, it will be neutralized by the dissolution of carbonates in the water column and in the sediments (Broecker and Peng, 1982), thereby mitigating atmospheric CO_2 and ocean acidification. Our study (Ilyina and Zeebe, 2012) also arrived to the conclusion that ocean carbonate dissolution has insignificant potential in mitigating atmospheric CO_2 and ocean acidification in the next millennia.

2.3 Ocean carbon cycle during ancient warming

Paleo records show strong co-variances between climate and the carbon cycle, which can be used to infer the sensitivity of the global carbon cycle to climate change. While my previous work mostly addressed the global carbon cycle under ongoing climate change, I find that ancient warmings are useful testbeds to confront our

models with a wider (or a rather extreme) range of environmental conditions. Such simulations contribute to the assessment of current and future risks related to climate change from an ecological and a biogeochemical perspective defining Earth's habitability. Such approaches are also useful to constrain future centennial sensitivity of numerous biogeochemical processes in ESMs. Therefore, throughout my research, together with my PhD students, I took opportunities to investigate extreme ancient warming events during the PETM (about 55 million years ago) and PTB (about 252 million years ago). Available paleo records from these two periods suggest a strong warming and perturbations in the ocean carbon cycle associated with atmospheric emissions of carbon. Moreover, they were also accompanied by mass extinction events.

A carbon-induced global warming of the PETM is considered to be the closest analog to ongoing climate change. Impacts of a decrease in deep water formation during the onset of the PETM suggested by proxy data on the carbon cycle have remained unexplored. In a PhD thesis by Mathias Heinze (Heinze, 2015), which I supervised, we addressed this knowledge gap. Our simulations with HAMOCC were a first projection of the ocean biogeochemical state during the warm and stable climate conditions of the late Paleocene based on a comprehensive 3D ocean biogeochemistry model (Heinze and Ilyina, 2015). Our outcomes, in agreement with proxy, produced a warm ocean state with a rather stagnant ocean circulation, indicating that a 3 dimensional ocean circulation is a prerequisite to reconstruct the marine biogeochemistry. The sluggish circulation slows the transport of carbon into the ocean interior, resulting only in moderate carbonate sediment dissolution. Weakening of the overturning circulation (Fig.2.10) depletes nutrient concentrations in the surface ocean and reduces global primary production by 25%. Important in this context is the production and dissolution of CaCO_3 , the two main processes that alter seawater TA. Because TA determines the ocean's capacity to take up atmospheric CO_2 , changes in the CaCO_3 cycle also have the potential to affect the ocean carbon sink and climate. Therefore, in this study model parameterizations, in which the production and dissolution of CaCO_3 is treated as a function of carbonate ion saturation (Ilyina et al., 2009; Ilyina and Zeebe, 2012), were further tested in the framework of the PETM model setup.

Further using MPI-ESM, we found that changes in overturning circulation drive the strong deoxygenation and carbonate dissolution changes that are found in the sediment record during PETM. We suggested the following mechanism (Ilyina and Heinze, 2019) overseen in previous studies. Weakening of the Southern Ocean deep water formation and enhancement of ocean stratification driven by global warming cause an asymmetry in carbonate dissolution between the Atlantic and Pacific basins (calcite saturation state (Ω) in Fig.2.10). Furthermore, reduced ventilation results in accumulation of remineralization products (CO_2 and nutrients) in

intermediate waters. This process leads to a lowering of O_2 and an increase of CO_2 concentrations. As a result, carbonate dissolution is triggered throughout the water column, which is stronger in the Atlantic Ocean and weaker in the Pacific Basin (as opposed to the modern ocean). The ocean surface remains thereby supersaturated with respect to $CaCO_3$. This feature is also suggested by proxy data (Zeebe and Zachos, 2007), raising the question about the possible mechanism driving such CO_3^{2-} asymmetry between ocean basins. However, previous modeling studies based on box or intermediate complexity models were unable to demonstrate this driving role of changes in the meridional overturning circulation.

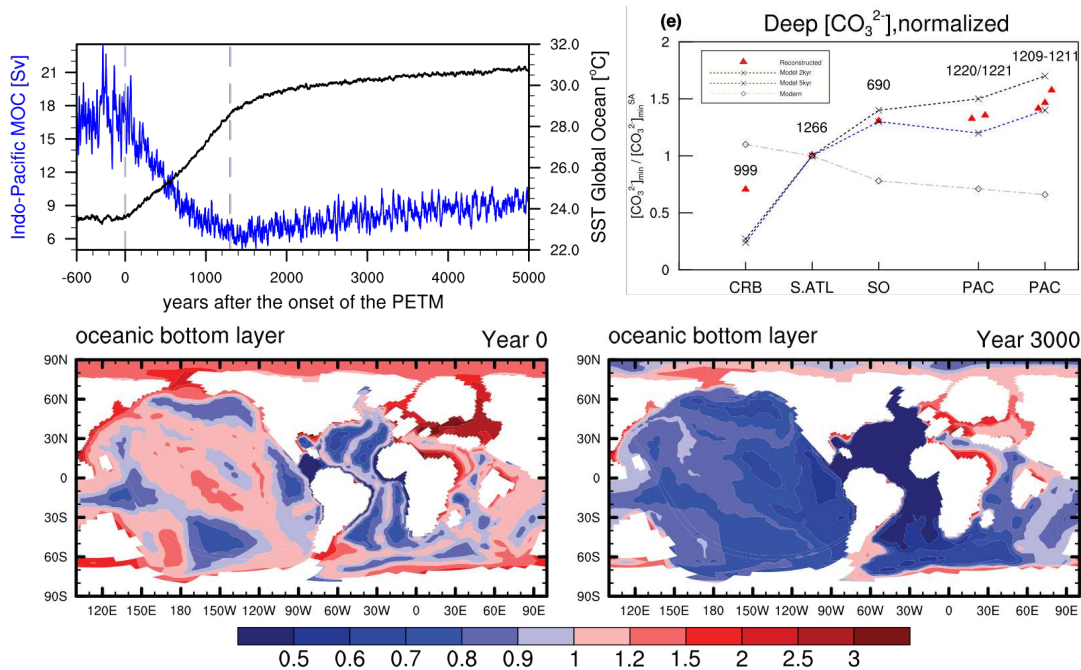


Figure 2.10: Upper left panel: Response of the meridional overturning circulation and sea surface temperature to PETM warming. Upper right panel: Simulated deep-sea CO_3^{2-} basin gradient at 2 and 5 kyr after the onset of PETM compared to geological reconstructions (Zeebe and Zachos, 2007); CO_3^{2-} normalized to S.ATL site. CRB = Caribbean; S.ATL = South Atlantic Ocean; SO = Southern Ocean, PAC = Pacific Ocean. Lower panels: $CaCO_3$ saturation state Ω in the oceanic bottom layer for year 0 (left) and year 3000 (right) after the onset of PETM. Modified from Ilyina and Heinze (2019); Heinze (2015)

Our results support the hypothesis that the PETM perturbation was likely accompanied by a rather moderate increase in atmospheric CO_2 concentration that is consistent with recent proxy interpretations (Hönisch et al., 2012). Furthermore, these findings contribute to understanding the long-term response of the carbon

cycle to climate change, nurturing my scientific curiosity. We furthermore suggest that such reorganization of the ocean circulation and concomitant metabolic CO_2 accumulation will likely become increasingly important in the future warming climate, on centennial to millennial timescales. However, they are not yet inferable in shorter CMIP simulations that typically only run until the year 2100.

Our finding in Ilyina and Heinze (2019) about the key role of a changing overturning circulation in driving the deoxygenation and carbonate dissolution record of the PETM inspired me to study another warm ancient event. Also for this period in Earth's history, overturning circulation might have played a key role in shaping biogeochemical changes, hypoxia, and a shift the oceanic nitrogen cycle from a nitrate-dominated state to an ammonium-dominated state (Sun et al., 2019). In an ongoing PhD project by Daniel Burt, which I supervise, within the Deutsche Forschungsgemeinschaft (DFG) project TERSANE, we aim at reconstructing ocean biogeochemical conditions that accompanied the mass extinction of the PTB. One particular knowledge gap that needs to be addressed here is how a wide-spread ocean hypoxia could produce a shift in the nitrogen cycle from a nitrate-dominant to a toxic ammonium-dominant ocean-state. The simulations with HAMOCC in the framework of MPI-ESM need to resolve the nitrogen cycle to determine what was the dominant nitrogen species in the ocean under the climate conditions of PTB. Hence, lessons learned from the ongoing PTB study will be important to constrain nitrogen-carbon cycle feedbacks under current and future climates.

2.4 Biogeochemistry of the glacial ocean

The glacial-interglacial historical record is full of modes of variability in the climate system with clear impacts on the carbon cycle (Fig.1.1). I have a chance to study this very exciting period in Earth's history within the the Federal Ministry of Education and Research (BMBF) project PalMod (short for Paleo Modeling). PalMod addresses some long-standing scientific gaps in our understanding of the dynamics and variability of the climate system during the last glacial cycle. The overall ambition spanning Phase I and Phase II (in which I am project coordinator together with Mojib Latif and Michael Schultz) is to simulate Earth's climate and biogeochemistry over the full last glacial cycle with comprehensive ESMs. Furthermore, using new insights into glacial Earth system dynamics, PalMod additionally aims to make projections into the future over the next few millennia. The MPI-M with colleagues from two departments, the Ocean in the Earth System and the Land in the Earth System, plays a key scientific role in PalMod, with the MPI-ESM being the most important workhorse for glacial simulation and a platform for testing missing processes that are critical for the glacial times. One novel feature is the introduction of interactive ice sheets, by coupling MPI-ESM to an ice

sheet model with fully automatic adaptation of land and ocean topography with evolving land-sea masks and river pathways, enabling it to address the response of the climate system to changes in ice sheets (Ziemen et al., 2019; Kapsch et al., 2021). Another feature is the new MPI-ESM component for terrestrial methane emissions and rapid atmospheric methane degradation, enabling unique interactive simulations of atmospheric methane in the context of paleo simulations (Kleinen et al., 2020).

The work in my group focuses on the modeling of the glacial ocean biogeochemical mechanisms regulating the ocean carbon sink and their sensitivity to climate variations. One big scientific challenge in this context is to make the ocean out-gas CO_2 during deglaciation. The global ocean is a major carbon sink today, but during deglaciation, it was largely the ocean (with the help of land) that vented substantial amounts of CO_2 to increase its content in the atmosphere and heat the climate (Broecker et al., 1985; Stocker, 2000). While the terrestrial carbon cycle seemingly easily changes its role as a source or sink of carbon, for the ocean it seems to be less straightforward to give up the stored carbon. Note that this is not a special feature of the MPI-ESM, but rather a long-standing scientific challenge for ESMs based on the atmospheric and ocean general circulation models. There are a number of hypotheses about the mechanisms that enabled oceanic carbon release during deglaciation, including coral regrowth and changes in the biological carbon pump Kohfeld and Chase (2017). Yet, while they assist to steer the ocean in the right direction, the key role is played by the reorganization of the ocean circulation (Schmittner et al., 2008), manifested in changes of the overturning circulation. We faced this challenge during the Holocene simulations with MPI-ESM (Brovkin et al., 2019) when the ocean released carbon in accordance with proxy records only after artificially decreasing TA in HAMOCC.

The work of my group within PalMod showed that changes in ocean circulation, as well as its interaction with the ocean carbon cycle, are crucial for the glacial CO_2 sink. In order to quantify sequestration mechanisms of atmospheric CO_2 in the glacial ocean and to enable a direct comparison of model results to $\delta^{13}\text{C}$ records from deep sea sediment, the oceanic biogeochemistry model HAMOCC was extended to include a comprehensive representation of carbon isotope ^{13}C , which is indispensable for constraining marine ventilation and biogeochemistry (Liu et al., 2021). This new scheme explicitly represents ^{13}C in all carbon pools and includes a temperature-dependent fractionation during the air-sea exchange and photosynthesis. The scheme was tested in model configurations representing the LGM and the pre-industrial climate. While the model results generally agree well with the carbon isotope ratios derived from the proxy data, they also indicate a high sensitivity of marine biogeochemical tracers to changes in freshwater flows, as demonstrated in the sensitivity experiments with fresh water hosing.

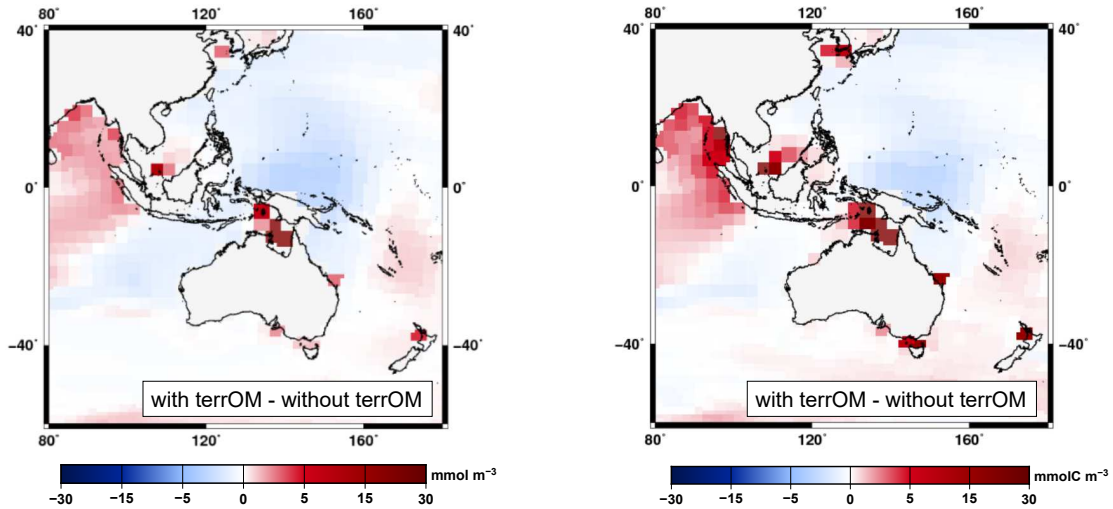


Figure 2.11: Anomaly of the mean surface TA (left) and surface DIC (right), with a focus over Indonesia, between the two simulations with and without terrestrial organic matter fluxes averaged over Melt Water Pulse 1a, occurring between 15-14 ka; after (Extier et al., 2022).

Another focus of my group in the context of glacial ocean biogeochemistry is to address the role of the land-ocean transfer of carbon. For this we developed a system for the transfer of terrestrial carbon, its stable isotopic signal, and nutrients into the marine domain in the course of sea-level changes enabled by previous PalMod studies at the MPI-M, providing a fully interactive adaptation of the ocean bathymetry with corresponding changes of the land-sea distribution (Meccia and Mikolajewicz, 2018) and a transient river routing (Riddick et al., 2018). Such a coupling between JSBACH and HAMOCC enables, for the first time, a consistent assessment of the global carbon cycle, taking into account the transfer of substances between land and sea in MPI-ESM simulations on glacial time scales (Extier et al., 2022).

Our results suggest that during a deglacial flooding event, additional carbon and nutrients entering the ocean with the input of terrestrial organic matter result in an increase of the surface TA and DIC once the terrestrial organic matter has been remineralized (Fig. 2.11). Thereby, oceanic CO_2 outgassing is triggered, however, only on a regional scale, with a hotspot around Indonesia. This regional outgassing of CO_2 in the Indonesian region is mainly maintained by wood inputs during flooding. This is supported by observational evidence suggesting that prior to this meltwater pulse event, the tropical forest that developed in this region favored storage of carbon-rich materials on land, becoming available for the ocean during deglacial flooding. This novel approach furthermore provides an important

step forward towards a fully coupled carbon cycle in ESM simulations that we strive to achieve in PalMod.

Chapter 3

Variability and predictability of the ocean carbon sink

3.1 Decadal variability of the ocean carbon sink

The oceans currently absorb about 25% of anthropogenic emissions of carbon (Friedlingstein et al., 2020), with the Southern Ocean being the largest contributor. On multi-decadal to centennial time-scales, the growth in the ocean carbon sink follows rising emissions. By contrast, the year-to-year and decadal variations are largely driven by internal variations in the climate system due to the non-linear, chaotic nature of the Earth system. Observationally-driven studies reveal pronounced shifts in ocean carbon sink regimes, with a substantially different variability in different oceanic regions (Landschützer et al., 2015; Fay and McKinley, 2013; Schuster and Watson, 2007). This appeared puzzling to scientists as the overall expected growth in the major ocean sink areas either did not follow the pace of growing carbon emissions, or even slowed down. As a result, ICV has been identified as one of the drivers of the imbalance in the GCB (Le Quéré et al., 2018), and understanding the role of natural climate variability for the ocean carbon sink has been identified as a major scientific challenge (Ilyina and Friedlingstein, 2016).

Together with my group and colleagues, I contributed to process understanding and quantification of the range of ICV-driven variability in the ocean carbon cycle. In particular, how these hidden trends (Ilyina, 2016) modulate the estimates of the ocean carbon sink. In a study by Landschützer et al. (2019) using a neural network-based estimate of the sea surface $p\text{CO}_2$ derived from measurements, we found that most of the observed variability in oceanic carbon in the upper ocean takes place on decadal timescales and longer. However, observationally-based data products currently do not extend long enough in time to robustly capture long-term variations and modes of the surface ocean carbon content. Analogously, another

study with my contribution demonstrates that data sparsity in space and time poses a fundamental uncertainty for addressing decadal variability and trends in the oceanic uptake of carbon (Gloege et al., 2021) and oxygen (Takano and Ilyina, 2021).

Ocean biogeochemistry models show an overall consistency in representing the global carbon sink, but largely differ in the representation of regional carbon uptake and temporal variability, as shown in recent studies with my contribution, focusing on a multi-model assessment of ocean carbon sink estimates in GCB models (Hauck et al., 2020; DeVries et al., 2019). In particular, models seem to miss the substantial decrease in the global ocean carbon sink during the last decade of the 20th century found in observationally-based studies (Landschützer et al., 2015).

I hypothesize that while producing positive trends (indicating increasing uptake) might be more natural in model simulations, given rising CO₂ emissions, capturing decadal negative trends (decreasing uptake) occurring in observations is a challenge associated with poorly represented ICV in single model realizations. We test this hypothesis in the framework of the Max Planck Institute Grand Ensemble (MPI-GE) with 100 members for the historical simulations (1850-2005) and four climate change scenarios (Maher et al., 2019), which offered an unprecedented opportunity. Using the MPI-GE we determine (Li and Ilyina, 2018) that on decadal time scales over the historical time period and in future climate change projections, internal variability (represented by ensemble spread) is as large as the forced variability (represented by ensemble mean). This indicates that decadal trends in oceanic carbon uptake are dominated by ICV. The MPI-GE simulations are able to capture the range of uncertainty suggested by observations. However, a large number of ensemble members is needed to capture ICV in the hotspots of variability in the Southern Ocean, the North Pacific, and the North Atlantic. Interestingly, the number of ensemble members necessary to reproduce the forced decadal trends increases (up to 79 in the Southern Ocean) in future decades as the carbon emission trajectory changes (Fig.3.1).

In collaboration with Sarah Schlunegger during her academic stay in my group, we extended the interpretation of our MPI-GE for further key biogeochemical variables and other available large ensembles focusing on the time of emergence. Previous studies, to which I contributed, showed long and vastly different time scales of the emergence of anthropogenic signals (Friedrich et al., 2012; Dobrynin et al., 2015; Henson et al., 2017), estimated based on either the noise from a preindustrial control run of a single ESM or an average across single ensemble members from multiple ESMs. Hence, with Sarah Schlunegger, we took the opportunity offered by the large ensembles to constrain the emergence of trends in ocean biogeochemistry in a unified and consistent framework. We found that changes in, for instance, the biological carbon pump emerge on timescales longer than 50 years

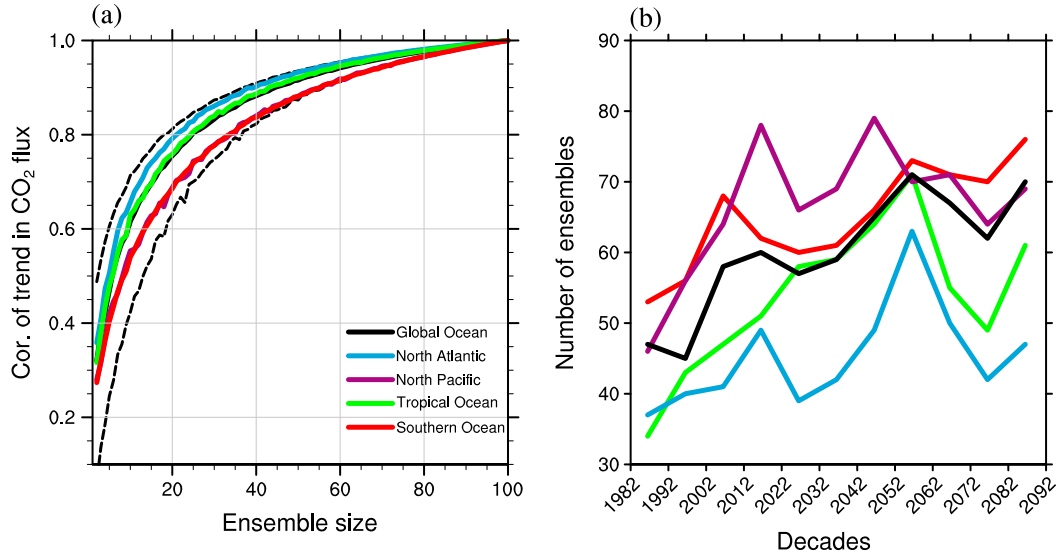


Figure 3.1: (a) Spatial correlation of the mean trend in the CO₂ flux for different ensemble size against a 100-member ensemble mean trend in the global (black line) and different ocean regions (colored lines) during the decade from 1992 to 2001. For each ensemble size, the correlation coefficient is calculated 1,000 times using a bootstrap resample method. The solid lines show the mean results. Here we only show the 90% confidence interval (i.e., 5–95% of the ranked correlations from the 1,000 resampled results) for the global ocean. (b) Temporal evolution of the ensemble members required to produce high spatial correlation of 0.9 with the 100-member mean trend pattern in different ocean regions. The x-axis shows the consecutive decades, and the y-axis shows the necessary ensemble members for the respective decade; (Li and Ilyina, 2018).

in the presence of ICV, highlighting the necessary duration and spatial coverage of marine observing systems for the robust detection of anthropogenic signals in ocean biogeochemistry (Schlunegger et al., 2020).

Intrigued by an apparent link between changing emissions and the ensemble size needed to capture the response of the ocean carbon uptake, Aaron Spring, a PhD student supervised by me, further explored the power of MPI-GE to address the variability of the ocean and terrestrial carbon sinks featuring implications for atmospheric CO₂ growth. Using a causation framework applied earlier for surface temperature by Marotzke (2019), we addressed the question of how long it would take to attribute changes in atmospheric CO₂ concentrations to changes in emissions (Spring et al., 2020). Our study found that a certainty of causation that carbon emission reductions cause a reduction in atmospheric CO₂ growth is delayed due to ICV in atmospheric CO₂ by 10–16 years, depending on the emission pathway. This makes the attribution of a reduction in the atmospheric CO₂

growth rate to carbon emission reductions induced by a policy change (or lockdown measures during the ongoing Covid19 pandemic) unclear for the next several years.

3.2 Predictability of the ocean carbon sink

The substantial impact of ICV on decadal trends in the ocean carbon sink demonstrated in our paper Li and Ilyina (2018), and the recent progress in developing a decadal prediction system based on MPI-ESM in the Ocean in the Earth System Department at MPI-M, motivated me to start working on the development of ESM-based systems for decadal predictions that include the carbon cycle.

Decadal prediction systems based on ESMs, by construction, exploit both the sources of predictability from external radiative forcings and from ICV. This enables them to provide the best possible estimates of climate system evolution for the next decade. In such systems, external forcing is represented in the same way as in coupled climate projections, whereas ICV is achieved by initializing the climate model from observational estimates following different initialization and data assimilation techniques.

Recent initialized predictions of the near-term future climate have proven successful, suggesting robust predictive skills for a number of the physical climate's phenomena, such as Atlantic multi-decadal variability, Atlantic Meridional Overturning Circulation (AMOC), and Earth's global surface temperature (e.g. summarized in Marotzke et al. (2016); Merryfield et al. (2020)). However, predictability of variations in the oceanic carbon uptake related to ICV has not been addressed previously. Therefore, at first my focus was on establishing whether near-term variability in the ocean carbon uptake is predictable. The working hypothesis here was that given the predictability of some elements of the physical climate system, their effects in the ocean carbon cycle should be predictable as well. In this context, within the BMBF project MiKlip II, based on MPI-ESM simulations, with Hongmei Li, at that time a postdoc supervised by me, we started to work on the predictability of the air-sea CO₂ flux in the North Atlantic, a region prone to substantial decadal variability. Our first paper on this topic (Li et al., 2016), which was also the first one worldwide on the predictability of the ocean carbon uptake, reveals significant inter-annual and decadal variations in CO₂ uptake in the western sub-polar gyre region. Moreover, we demonstrated that the potential prediction skill of the air-sea CO₂ flux variation is up to 4-7 years in this region. In a seasonal analysis we showed that the predictive skill in the air-sea CO₂ is mainly maintained in winter. This is related to the improvement of the ocean physical state and circulation due to initialization of the ESM.

We made a step forward with Hongmei Li to work towards understanding the sources of predictability of the global ocean carbon sink. We found in our next

paper (Li et al., 2019), being the first one worldwide on the global ocean carbon sink predictability assessed against an observational product, that variations of the ocean CO₂ uptake are predictable up to 2 years in advance globally, albeit there is evidence for a higher predictive skill up to 5 years regionally. We moved further to separate the contributions of the thermal and nonthermal components of ocean surface pCO₂. This analysis enabled us to quantify that while temperature variations largely determine shorter-term (<3 years) predictability, nonthermal drivers are responsible for longer-term (>3 years) predictability, especially at high latitudes (Fig.3.2).

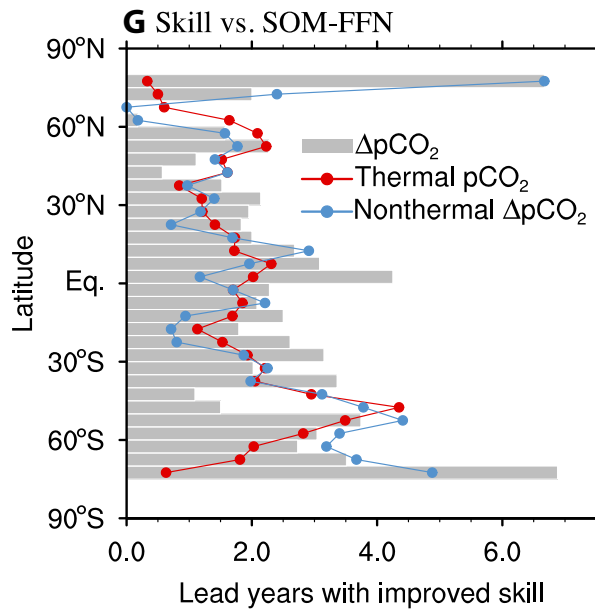


Figure 3.2: Zonal mean of lead years with improved predictive skill of $\Delta p\text{CO}_2$ (gray bars) and its thermal and non-thermal components (red and blue dotted lines, respectively) against SOM-FFN estimates; Li et al. (2019).

3.3 Towards predictability of the atmospheric CO₂ growth rate

The next obvious step, given the predictability of the natural carbon sinks in the ocean and on land, is to establish the predictability of atmospheric CO₂ variations. On interannual to decadal time-scales, the growth rate of atmospheric CO₂ exhibits substantial variations (see highlighted zoomed panel in Fig.1.1) associated to varying strengths of the land and ocean carbon sinks; these variations have been

linked to ICV (Friedlingstein et al., 2020; Landschützer et al., 2019; Peters et al., 2017; Bacastow, 1976; Keeling et al., 1976). Variability of the ocean carbon sink is associated with major carbon uptake regions in the Southern Ocean and the North Atlantic (Landschützer et al., 2019; Hauck et al., 2020). Variations of the land carbon sink on inter-annual time scales are primarily driven by the terrestrial biosphere response to El Niño Southern Oscillation (ENSO) (Ropelewski and Halpert, 1987; Jones et al., 2001). Our work has shown the predictability of the global ocean carbon sink of up to 2 years (Li et al., 2019). On the land side, a potential prediction skill of 2 years was established for terrestrial net ecosystem production Lovenduski et al. (2019), but only of 9 months for tropical land-atmosphere carbon flux Zeng et al. (2008).

Since we started to work on carbon cycle predictability in my group, more studies on carbon cycle sinks based on various prediction systems emerged, offering an opportunity for the analysis of the global carbon cycle predictability in different systems. I took this opportunity, using a multi-model framework comprising prediction systems initialized by the observed state of the physical climate (Ilyina et al., 2021). In this paper, a predictive skill for the global ocean carbon sink of up to 6 years is found for some models which run with a larger number of ensemble members. Consistently across models, longer regional predictability horizons are found as compared to global predictability. On land, a predictive skill of up to 2 years is primarily maintained in the tropics and extra-tropics, enabled by the initialization of the physical climate.

The novelty of this paper was, for the first time, to quantify the predictability of the atmospheric CO₂ growth rate from the various decadal prediction systems. We show that anomalies of the atmospheric CO₂ growth rate inferred from natural variations of the land and ocean carbon sinks are predictable at lead time of 2 years, and the skill is limited by the land carbon sink predictability horizon (Fig.3.3).

All previous prediction studies were based on concentration-driven simulations, in which the model is forced by prescribed atmospheric CO₂ concentration without an interactive impact from the land and ocean carbon cycle. Yet, to address the predictability of the global carbon cycle with the year-to-year wiggles in atmospheric CO₂ (Fig.1.1), emission-driven simulations are necessary. With this objective in mind, Aaron Spring, within his PhD thesis (Spring, 2021), set-up an idealized emission-driven perfect-model framework to investigate the sources of predictability of atmospheric CO₂ and carbon sinks.

Aaron Spring's work led to a number of novel results. The most interesting to me was that by disentangling the origins of variations in atmospheric CO₂ (Spring and Ilyina, 2020), it was shown that if only the ocean would be driving atmospheric CO₂ variations, they would be predictable up to 12 years in advance. Effects of the land carbon sink dampen atmospheric CO₂ predictability to max. 5 years

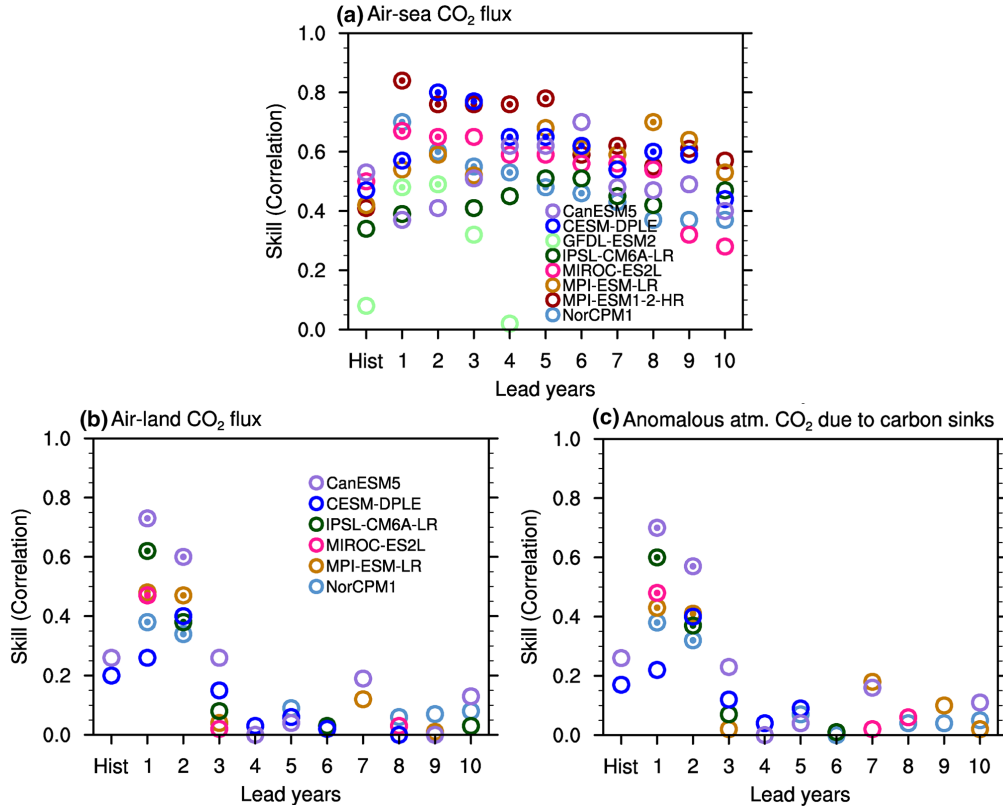


Figure 3.3: Predictive skill of the detrended CO₂ flux into the ocean (a), CO₂ flux into the land (b), and variations in the inferred atmospheric CO₂ growth rate (c). Predictive skill is quantified as anomaly correlation coefficients of the model simulations with the SOM-FFN observation-based product for the air-sea CO₂ fluxes, and with GCB2019 for the air-land CO₂ flux and anomalous atmospheric CO₂. Significantly improved predictive skill at 95% level for initialized over uninitialized simulations are marked with filled dots. Hist represents the uninitialized simulations; modified after Ilyina et al. (2021).

(Fig.3.4). Furthermore, the predictive horizon for the ocean carbon sink quantified in this idealized framework was 2 years for the global oceanic CO₂, with regional predictability up to a decade. The global land CO₂ flux predictability is 2 years and is maintained by the tropical regions. Finally, global annual variations in atmospheric CO₂ are potentially predictable up to 3 years in advance.

One potential limitation of the prediction systems is that in the absence of comprehensive biogeochemical reanalysis products, they only assimilate the physical state variables; biogeochemistry thereby adjusts to the state acquired by such assimilation. Such an approach is pragmatic, as it does not require extended assimilation of further variables. But what are the implications on the global CO₂ flux and atmospheric CO₂? Aaron Spring addresses this question by comparing

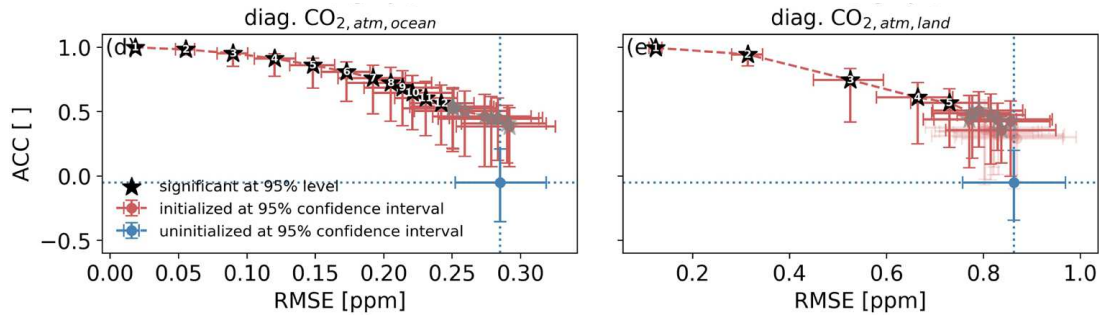


Figure 3.4: Comparison of the mean potential prediction skill of the initialized ensemble (red) versus random uninitialized ensembles (blue) in global annual surface quantities of the carbon cycle with the anomaly correlation coefficient (ACC) on the y-axis and root-mean-square-error (RMSE) on the x-axis for lead years represented as dots: (left) diagnosed atmospheric CO_2 based on the oceanic carbon sink and (right) diagnosed atmospheric CO_2 based on the global terrestrial carbon sink. Error bars show 95% confidence intervals based on bootstrapping with replacement ($N = 5,000$). The last lead year with a bootstrapped p-value (which represents that uninitialized ensembles beat initialized ensembles) lower than 5% marks the predictability horizon. Black stars with white integers denote significant lead years in ACC and RMSE, gray stars if only one metric is significant, and lead years nonsignificant in both metrics are blurred; modified after Spring and Ilyina (2020).

direct vs. indirect reconstruction of the carbon cycle, i.e. with and without direct assimilation of biogeochemical state variables in an idealized perfect model setup (Spring et al., 2021). The so-called assimilation in this approach is based on the assumption that the model represents a 'perfect' biogeochemical state. The study shows that direct carbon cycle reconstruction adds rather little improvement in the global carbon cycle. Apparently, uncertainties in the effects of reconstruction, induced by the physical climate state, impede better biogeochemical reconstruction. This finding adds confidence to the current practice of indirect reconstruction for predictions of the global carbon cycle. Yet, we conclude that on a regional scale, or if other biogeochemical state variables are a target for predictions, our study does not provide full answers.

Overall, with the work initiated in my group, we gained novel insights on horizons and sources of predictability in the global carbon cycle. This work enables us to address the predictability of atmospheric CO_2 in the framework of emission-driven models and to discern the pathways of anthropogenic carbon in the Earth system. Such information is of emerging importance to support CO_2 monitoring campaigns in verification of the effectiveness of fossil fuel emission reduction measures.

Chapter 4

The potential of ocean alkalinity enhancement to mitigate climate change and ocean acidification

4.1 Effects on ocean biogeochemistry and the Earth system

As anthropogenic CO₂ continues to rise, i.e. over the past decade at a rate of about 2.5 ppm/yr (Friedlingstein et al., 2019), causing dangerous climate change, climate engineering methods, such as CDR and Stratospheric Aerosol Injection (SAI) are being proposed. An ocean-based CDR method of AOA assumes enhancement of ocean alkalinity by adding processed minerals such as lime (Ca(OH)₂) and olivine (Mg₂SiO₄) to the surface ocean. These additions would increase the ocean's capacity to buffer CO₂, thereby strengthening the oceanic CO₂ uptake and decreasing seawater acidity. The latter is a nice side-effect to counteract ocean acidification, characterized by the sinking pH of seawater. As discussions on the addition of alkalinity enhancing minerals were going on, I was astonished (and still am) that they had a very insufficient knowledge base about the potential implications for ocean biogeochemistry and in the Earth system. Here, models offered a handy tool to address some of the critical knowledge gaps. While I am highly skeptical that any climate engineering method can offer a sound global alternative to reducing emissions, it is important to provide compelling scientific evidence on their Earth system impacts. That is why I started to study the topic of ocean alkalinity enhancement.

My paper Ilyina et al. (2013b), exploring the effectiveness of AOA scenarios was the first one testing the effects of calcium-based AOA in a three-dimensional ocean biogeochemistry model. This paper shows that only scenarios in which

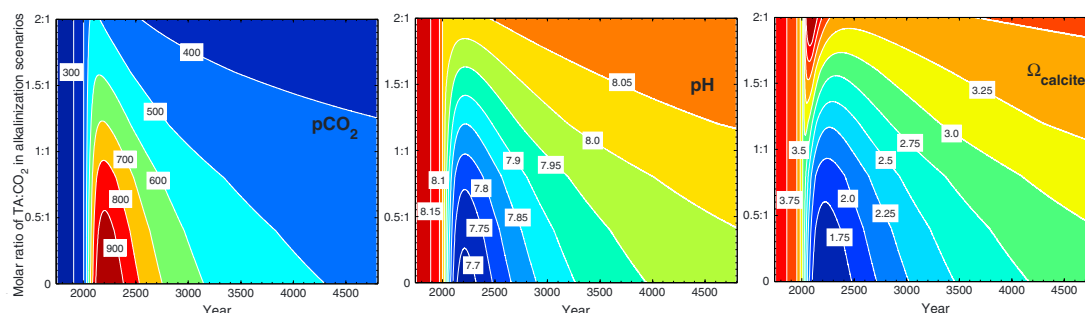


Figure 4.1: Mitigation potential of AOA: atmospheric CO_2 concentration (in ppm), sea surface pH, and Ω are shown by white contour lines for different AOA scenarios (represented in molar ratios $\text{TA}:\text{CO}_2$) as a function of time.; modified after Ilyina et al. (2013b).

large amounts of alkalinity (e.g., in a ratio of 2:1 with respect to emitted CO_2) are added over large ocean areas can mitigate the rising atmospheric CO_2 and avoid further ocean acidification under fossil-based economies (Fig.4.1). This would elevate some key biogeochemical parameters significantly above preindustrial levels, causing unintended effects on marine life.

Yet, with this first paper, only the ocean biogeochemistry realm was addressed, leaving the Earth system effects unexplored and my scientific curiosity unsatisfied. With Miriam Ferrer González, a PhD student supervised by me, we addressed the effects of AOA in MPI-ESM with a scenario based on the Representative Concentration Pathway (RCP) framework (González, 2017) within the DFG's SPP on Climate Engineering. We quantified that an addition of 114 Pmol of alkalinity to the surface ocean stabilizes atmospheric CO_2 concentration to RCP4.5 levels under RCP8.5 emissions (González and Ilyina, 2016). This scenario removes 940 GtC from the atmosphere and mitigates 1.5 K of global warming within this century. The climate adjusts to the lower CO_2 concentration, preventing the loss of sea ice and high sea level rise. Seawater pH and the carbonate saturation state Ω rise substantially above levels of the current decade (Fig.4.2).

As our scenario targeted mitigating climate change effects under an intensive fossil fuel scenario, substantial amounts of alkalinity were necessary. Thus, we conclude that the CO_2 mitigation potential of intensive AOA comes at a price of an unprecedented ocean biogeochemistry perturbation with unknown ecological consequences. Rather less expected was the finding in our further paper (Sonntag et al., 2018), comparing the CDR methods of afforestation and AOA, that due to compensating processes such as the biogeophysical effects of afforestation, more carbon needs to be removed from the atmosphere by afforestation than by AOA to reach the same global warming reduction.

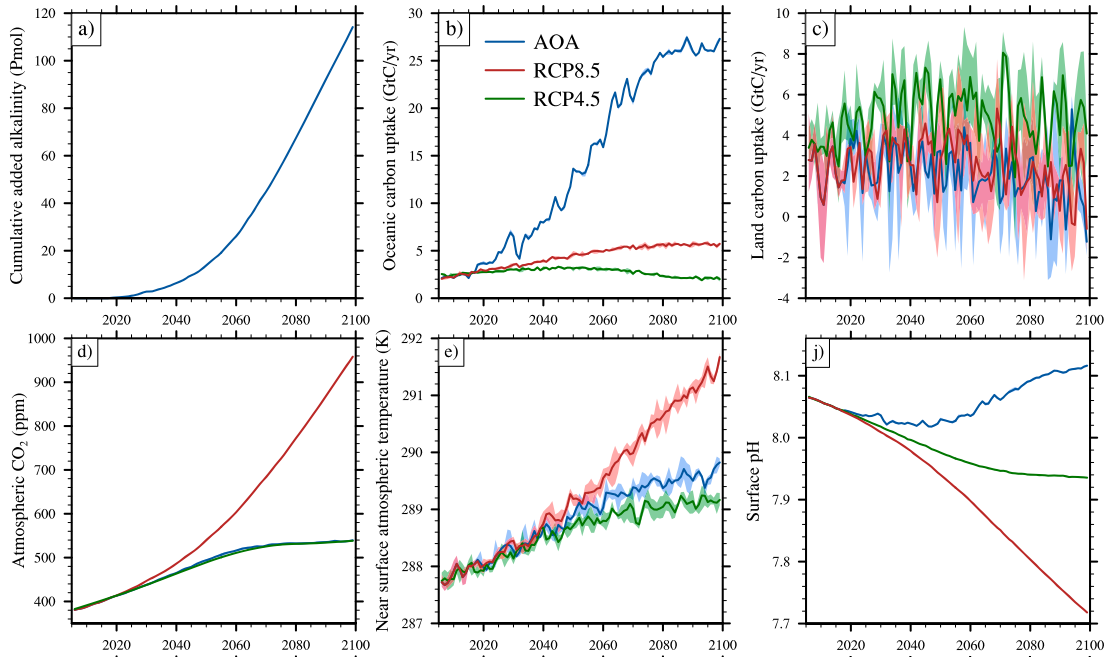


Figure 4.2: Temporal evolutions of various Earth system variables in different scenarios. Solid lines depict 3 year running means under the scenarios RCP8.5 (red), AOA (blue), and RCP4.5 (green). (a) Cumulative added alkalinity (Pmol), (b) total ocean carbon uptake per year (Gt/yr), (c) total terrestrial carbon uptake per year (Gt/yr), (d) global annual mean of atmospheric CO_2 (ppm), (e) global annual mean of near-surface atmospheric temperature (K), (f) global annual mean of surface seawater pH. Colored area is model internal variability including three ensemble members. Modified after González and Ilyina (2016).

We further challenged the common assumption that the termination effects of AOA pose low to no risk to the environment (Shepherd, 2009). Analyzing the rate at which the environment changes after termination of AOA, we found that the abrupt termination of large-scale implementation of AOA leads to regional rates of surface warming and ocean acidification, which largely exceed the pace of change that the implementation of AOA was intended to alleviate (González et al., 2018). This enhanced rate of environmental change would restrict even more the already limited adaptive capacity of vulnerable organisms and ecosystems.

One recurring feature of our AOA model simulations was the occurrence of pronounced differences in sensitivities to alkalinity enhancement in the different ocean regions, determined by physical regimes and marine carbonate system states. Therefore, within the MSc project of Daniel Burt, supervised by me, we addressed the sensitivity of the carbonate system to regional AOA implementation. The

guiding question here was whether a regional targeted and less intensive AOA could be similarly efficient in enhancing the ocean carbon sink, but at a lower price of having negative impacts on ecosystems. Indeed, in Burt et al. (2021) we show that the Southern Ocean application of AOA is most efficient, sequestering 12% more carbon than the experiment with a global application, despite being applied across a surface area 40 times smaller. Furthermore, different carbon uptake potentials are driven by the surface pattern of TA redistributed by physical regimes across areas of different carbon uptake efficiencies. We also show that while the marine carbonate system becomes less sensitive to alkalinity enhancement in all experiments globally, regional responses to enhanced alkalinity vary depending upon the background concentrations of DIC and TA.

In summary, our work on AOA has taught us valuable lessons on carbonate chemistry and its role in regulating the ocean carbon sink. Moreover, my methodology to relate changes in ocean alkalinity and atmospheric CO_2 first suggested in Ilyina et al. (2013b) has been further applied to adjust the strength of the global ocean carbon sink in Holocene simulations with MPI-ESM (Brovkin et al., 2019).

4.2 Challenges for verification in the presence of climate variability

The success or failure of AOA would eventually be measured by its effects on ocean biogeochemistry, atmospheric CO_2 concentration, and climate. In the presence of ICV, how can we verify the effectiveness of AOA or any other CDR strategy? A real challenge for monitoring the success of CDR would be the detection and attribution of its effects. Friederike Froeb, a postdoc supervised by me, addressed this challenge using regularized optimal fingerprinting with a stationary and nonstationary (regarding the statistics of the climate) null hypothesis in the framework of AOA and SAI scenarios with an interactive carbon cycle performed with MPI-ESM, along with the 100 ensemble members available from MPI-GE simulations to quantify ICV.

Fröb et al. (2020) found that while global signals of AOA and SAI are detected earlier because patterns of ICV that may compete on local scales are averaged, regional detection time scales are much longer. For AOA, local detectability of temperature is up to several decades (Fig.4.3), depending on the physical, chemical, and radiative impacts of CDR forcing on the climate system, as well as on patterns of internal variability. For pH, shorter detection timescales are found. This is because by methodology AOA assumes a direct intervention in the carbonate system of seawater, making it detectable within the first years after its deployment. Generally, detection can be claimed earlier and the results are more robust under

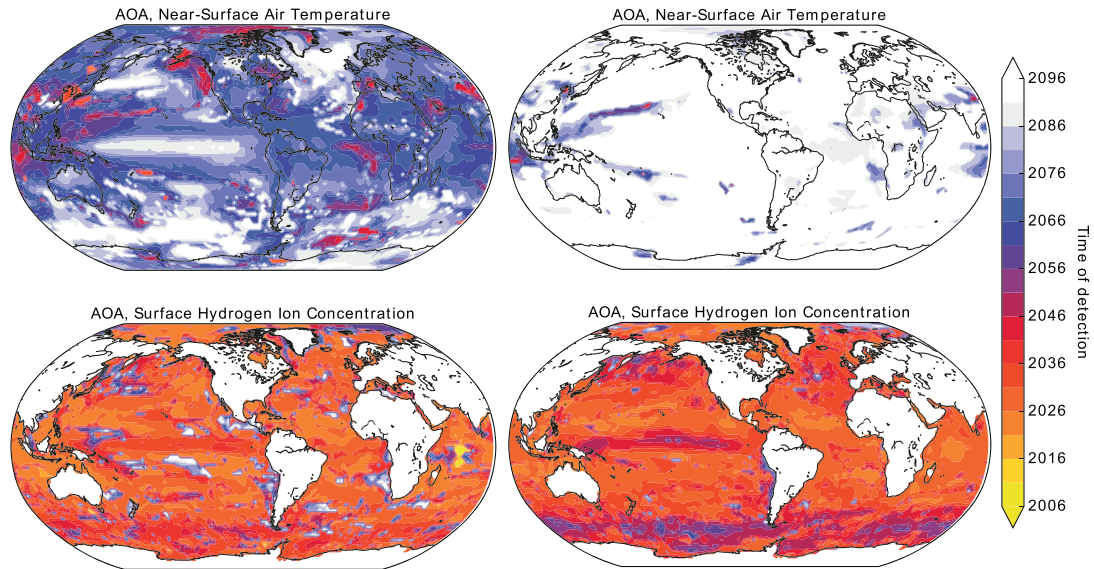


Figure 4.3: Local detectability for temperature (upper panel) and hydrogen ion concentration (bottom panels) in AOA simulations. Regularized optimal fingerprinting was applied to every grid point assuming a nonstationary (left panels) and stationary (right panels) control climate respectively; modified after Fröb et al. (2020).

the assumption of a transient background climate state (nonstationary) instead of a stationary null hypothesis.

Deployment of AOA on the spatial and temporal scales for mitigating climate change without reducing emissions is currently technically infeasible, as concluded in the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) Canadell et al. (2021). Moreover, it yields the elevation of some key biogeochemical parameters significantly above their 'normal' levels with a risk of causing unintended effects on marine life Ilyina et al. (2013b); González and Ilyina (2016). Policies to mitigate dangerous climate changes, i.e. the European Green Deal, inevitably assume negative CO_2 emissions and hence the implementations of some CDR strategies are being considered. In this context, our work is valuable in highlighting that along with the challenges related to potential implementations of large-scale CDR strategies, their verification, including the range of various feedbacks in the Earth system and ICV, would be an even bigger and unavoidable challenge. This makes me believe that discussions on carbon removal promising fast and cheap solutions are quite distractive from the actions needed to cut fossil fuel carbon emissions.

Chapter 5

Summary and Outlook

5.1 Summary of main research achievements

As summarized in this essay, my research has spanned the areas of the global ocean carbon cycle, its variability, predictability, and relation to Earth's climate. I have investigated the extent to which ocean biogeochemistry can accommodate perturbations brought about by anthropogenic activities or natural forcings, as well as its influence on and response to climate variations.

The ocean carbon cycle has been fascinating to me due to its various roles in the Earth system. First, being the largest climate-relevant repository of carbon, the ocean regulates atmospheric CO₂ variations. It is a sink for anthropogenic CO₂ today and in future projections of climate change, but during deglaciations it was acting as a source of carbon to the atmosphere. This capacity to take up anthropogenic CO₂, which mitigates climate change to some extent, comes at a price of ocean acidification with harmful effects for marine life. Second, the longer-term sink/source behavior of the ocean carbon sink is determined by the concentration difference of CO₂ in the surface water and the overlaying atmosphere. This makes the ocean follow the change in fossil fuel carbon emissions on multi-decadal time scales. However, on shorter time scales, i.e. interannual to decadal, this relationship is obscured by the presence of natural climate variability. Third, unlike other gases, CO₂ in the ocean reacts with seawater, governed by reversible reactions of the carbonate system. These chemical reactions, transferring dissolved CO₂ into bicarbonate ion, regulate the ocean's capacity to absorb and store carbon, as well as provide a buffering capacity to acidification. Possible manipulation of this buffering capacity feeds thought experiments on artificially enhancing the ocean carbon sink.

These three broad aspects of the ocean's role in the Earth system have largely guided my research contributions. I have focused my research on addressing major

scientific challenges in this context, which is to quantify both the shorter-term (i.e. interannual to decadal) and longer-term (i.e. centennial to millennial) feedbacks, as well as their susceptibility to climate change. For both time scales, my approach has been to address the ocean carbon cycle as an interactive component of the Earth system. This enabled me to study changes in the ocean carbon cycle that are intimately coupled to changes in circulation and climate, both in the past and under ongoing climate change. My choice to focus on these topics was driven by a scientific curiosity to address questions for which I didn't know the answers and by the ambition to contribute to major knowledge gaps that existed in the discipline. My research contributions led to new scientific knowledge on these topics, and the key scientific results are summarized below:

1. Future changes in ocean biogeochemical cycles brought about by rising atmospheric CO_2 , referred to as ocean acidification, have some surprising implications beyond ocean chemistry that were not quantified before. First, ocean acidification itself could affect climate warming: Marine phytoplankton produces less DMS (a precursor to sulfate aerosol in the atmosphere) under lower values of seawater pH. Running MPI-ESM with the new parameterization linking DMS production and pH in a future climate change scenario, projects a decrease in atmospheric DMS emissions resulting in additional radiative forcing that would accelerate global warming. Second, changes in seawater pH affect ocean acoustics. In model projections of future ocean acidification, I quantified that a pH decrease projected under future climate changes scenarios leads to a drop in the low frequency sound absorption coefficient, identifying hotspots where these changes would be largest. This can have implications for marine life and naval applications that are based on ocean acoustics.
2. In the context of activities to monitor ongoing ocean acidification, my work showed, for the first time, that changes in seawater total alkalinity could be used to track changes in carbonate chemistry. This would help to detect changes in CaCO_3 that resulted from the shifts in biological production and dissolution, that are otherwise are difficult to estimate.
3. During the climate perturbation associated with PETM, changes in the ocean biogeochemical cycles, including deoxygenation and carbonate dissolution changes that are found in the sediment record, were largely driven by changes in the overturning circulation. Weakening of the Southern Ocean deep water formation and enhancement of ocean stratification driven by global warming cause an asymmetry in carbonate dissolution between the Atlantic and Pacific basins, suggested by proxy data. Reduced ventilation results in the

accumulation of remineralization products (CO_2 and nutrients) in intermediate waters, thereby lowering O_2 and increasing CO_2 . As a result, carbonate dissolution is triggered throughout the water column, while the ocean surface remains supersaturated. This mechanism, suggested in our work, has been largely overlooked in previous studies. I furthermore suggested that reorganization of ocean circulation and concomitant metabolic CO_2 accumulation will likely become increasingly important in the future warming climate, on centennial to millennial timescales.

4. During deglaciation, changes in ocean circulation are critical to shape the distribution of the ocean biogeochemical variables found in proxy data. Only with a weaker and shallower AMOC than today is it conceivable to make the ocean outgas CO_2 during deglaciation. Other processes, including the novel component to represent carbon and nutrient input from land during flooding, invoke regional CO_2 outgassing, which is insufficient to affect the global pattern. This ongoing work in my group lays a cornerstone for a first transient deglacial interactive carbon cycle simulation with MPI-ESM, including the integration of carbon fluxes across the land-sea continuum and fully coupled carbon isotope representation.
5. The ocean carbon cycle is prone to substantial variability, driven by ICV. My work enabled us to conclude that shifts in decadal trends in the recent ocean carbon sink were largely determined by ICV, as inferred from the novel simulations with MPI-GE. Despite continuously rising atmospheric CO_2 concentrations, assumed in climate change scenarios, both negative (indicating decreasing uptake) and positive (indicating increasing uptake) decadal trends in the global ocean carbon sink are possible, implying a dominant role of ICV. The largest internal variability in the ocean carbon uptake is found in the major carbon sink regions, i.e., the Southern Ocean, the North Pacific, and the North Atlantic. Due to the large internal variability, major ocean carbon sink areas, such as the Southern Ocean, require the most ensemble members to reproduce the forced trend.
6. A novel approach extending the existing decadal prediction system with the carbon cycle components enabled me to establish that variations in the global ocean carbon sink brought about by the presence of ICV can be predicted a few years in advance, with longer regional predictability. The predictive skill in the ocean is mainly maintained in winter, and is attributed to the improvement of the ocean's physical state and circulation by initialization of the ESM. Furthermore, while thermal processes govern shorter-term predictability of <3 years, longer-term predictability >3 years is enabled by non-thermal processes. Another important finding of this work is that improvement of the

physical ocean state alone substantially improves the representation of the ocean carbon cycle.

7. The next and obvious step forward in carbon predictions is to establish the predictability of atmospheric CO₂ growth. The novel work in my group shows promising results. An interesting feature emerging in this regard is that the ocean carbon sink acts to enable atmospheric CO₂ predictability, whereas the land carbon sink dampens it. I demonstrated, for the first time, an emerging causal explanatory capacity of ESMs for skillful predictions of near-term variations in the natural carbon sinks and atmospheric CO₂. This work endowed a corresponding section in the Sixth Assessment Report of the IPCC (within WG1 Chapter 5).
8. The potential of an artificially enhanced ocean carbon sink by adding alkalinity to take up atmospheric CO₂ is high. This comes, however, at a price of unprecedented perturbations in the marine carbonate system, with unknown implications for marine life when large-scale additions of large amounts of alkalinity are considered.
9. While a number of CDR strategies are being considered as climate mitigation options, it is commonly overlooked that, as shown in our research, the detection and attribution of their effects will be largely obscured due to the presence of ICV.

Understanding the variation and variability of the ocean carbon cycle has become a common thread that ties my work together. My findings contributed to the overall understanding of the implications of the ongoing climate change on the global carbon cycle which influenced the discipline. Specifically, carbon cycle predictions, enabled through my work, are now becoming an integral part of decadal prediction systems. Owing to my co-leadership of the WCRP's Grand Challenge on Carbon Feedbacks in the Climate System, the topic of carbon cycle predictions has been identified as a key area of interest to the WCRP and the Global Carbon Project. This research focus might have far-reaching implications, because discerning the pathways of anthropogenic carbon in the Earth system is necessary to verify the effectiveness of mitigation measures related to the operationalization of the Paris Agreement. Here, the capability to predict where the atmospheric carbon would go could become very handy in supporting CO₂ monitoring campaigns and policy.

One limitation of the previous approaches addressing the ocean carbon sink that became apparent to me was that they were largely based on CO₂ concentration-driven simulations with prescribed atmospheric CO₂ concentrations. In such simulations the land and ocean carbon cycle do not have an impact on atmospheric

CO₂. While such simulations show to be sufficient for projecting the impact of climate change, they are of limited interest for studying the carbon cycle feedbacks in the climate system. On the contrary, in emission-driven simulations, in which CO₂ emissions are prescribed directly, the atmospheric CO₂ is computed prognostically. This nears the real world as in nature, atmospheric CO₂ is modulated by carbon emissions and the strength of the sinks. Unfortunately, a vast majority of CMIP simulations including those with MPI-ESM, still tend to prescribe atmospheric CO₂ instead of emissions, likely due to simplicity. I try to change this paradigm, at least within the scope of simulations performed in my group, because concentration-driven simulations are insufficient to fully address my scientific questions.

My research inspired and guided new developments in the model HAMOCC. With a plethora of processes I'd like to have in the model, confronted by the reality of ever insufficient computational resources, my approach has been to prioritize those model developments that can have essential first-order effects in the framework of our representation of the Earth system. Furthermore, the ultimate bottleneck for our model development efforts has been to ensure that HAMOCC is capable of running within feasible real time to allow a length of simulations that is sufficient for a proper model spinup and for performing centennial to millennial coupled climate simulations. This "natural selection" limited the number of advective tracers that could be included in the model, and to a large degree also constrained our ambitions regarding the complexity of represented processes. The latter, in particular, refers to the decisions with respect to representation of marine ecosystem processes in HAMOCC, whose enhancement would inevitably require more tracers. With such restrictive model development tactics within my group, a number of HAMOCC components were addressed and the model kept at the frontiers of ocean biogeochemical modeling. Thereby I contributed to the development of new approaches and concepts in modeling ocean biogeochemistry in the context of ESMs, striving to advance our current understanding of ocean biogeochemical feedbacks in the Earth system.

5.2 Avenues for future work

On multi-decadal to centennial time-scales, the growth in the ocean carbon sink follows rising emissions. By contrast, the year-to-year and decadal variations are largely driven by ICV. In the coming years, I plan to further increase the impact of my research by addressing major knowledge gaps associated with these two time horizons of carbon feedbacks in the climate system. To this end I will follow two research lines, dedicating one of them to each area:

- **Near-term variability and predictability of the global carbon cycle**

My previous research showed that ICV determines decadal variations of the global carbon cycle and the atmospheric CO₂ growth. Moreover, my own and my group's papers for the first time showed that these variations and the associated changes in atmospheric CO₂ can be predicted several years in advance with ESM-based prediction systems enhanced by the interactive carbon cycle. This novel research, pioneered by my group (within the past BMBF project MIKLIP and the ongoing EU H2020 project 4C), on constraining and predicting variations in atmospheric carbon growth in the next decades currently gains political and societal relevance, especially in the context of the net-zero climate targets.

I plan to advance my research on investigating the contribution of ICV-driven changes to the strength of the land and ocean carbon sinks, and implications for atmospheric CO₂ in the framework of emission-driven simulations. One timely task here will be to predict to which extent the near-term variations of CO₂ growth rate are attributable to a policy change and associated change in emissions or to the strength of the carbon sinks arising from an interplay between the dominant modes of climate variability and biogeochemical feedbacks. This will enable me to predict to which extent the effects of negative emissions and potential CDR techniques will be verifiable on near-term time scales relevant for the global stocktake. This work will link to activities on carbon management and monitoring, bringing added value for verifying climate mitigation efforts.

- **Longer-term evolution of the ocean carbon cycle in response to transient climate change**

Determining where anthropogenic carbon will go in the current century and beyond is critical to inform climate policy. I will continue building the next generation of ESMs by enabling and exploring new couplings between the components of the global carbon cycle for future climate projections (this work is currently supported by the newly started EU H2020 project ESM2025). I am interested in developing new capabilities allowing us to study mesoscale and even submesoscale processes regulating the ocean carbon sink from the point of view of the ocean general circulation and the climate system as a whole. This will reduce the scope of poorly constrained model assumptions, and links more naturally to observations.

As to past climates, I find that the glacial-interglacial is probably the most exciting period, as it is full of modes of variability in the climate system, with distinct impacts on the carbon cycle. Using ESMs, I will continue addressing the glacial- interglacial variations of the ocean carbon sink with

its regulative role on climate. I am already strengthening my expertise in this topic within the BMBF project PalMod (now in phase II). One specific long-standing challenge for ESMs is to make the global ocean outgas of CO₂ in transient deglaciation simulations. While the ocean circulation is key to determine the dynamics of the carbon cycle, the interplay of biological and chemical processes presents an interesting puzzle. I plan to assemble the pieces of this puzzle by conducting glacial sensitivity simulations including some novel features that are being currently developed in my group. I will use these simulations as a platform for testing the effects and sensitivity of some key processes that are critical for the glacial times in a transient mode (as opposed to time-slices). Furthermore, combining simulations with the interactive carbon cycle that span the last glacial cycle and extending them into the future will enable me to determine which elements of future climate change projections are robust when using models that are evaluated against the paleoclimatic record.

- **Towards exascale Earth system computing for realistic representation of the ocean carbon sink**

As of now, global ocean biogeochemical models suffer from a number of long-standing problems related to uncertainties in representing effects of ocean circulation and climate on biogeochemistry due to a too coarse spatial resolution of ESMs. A number of studies demonstrated added values of increasing spatial resolution. For instance, by transferring from an eddy parameterized (common for most CMIP6 ESMs) to eddy-permitting resolutions improves the representation of vertical structures in ocean oxygen and nutrients (Ilyina et al., 2013a). However, this is not enough. The poor, or often absent, representation of mesoscale (2 km to 200 km) circulations in present climate models limits the ability to explore important Earth system questions with any fidelity. For instance, CMIP6 models do not capture the intensity and the spatial structure of the oxygen minimum zones (Kwiatkowski et al., 2020), a problem related to coarse resolutions. This leaves our understanding of the future evolution of ocean oxygen under climate change rather illusive. By resolving the circulation systems that are decisive for these ocean biogeochemistry processes, it is critical to study their impacts in new ways, even with relatively short (decadal to multi-decadal) simulations.

Mesoscale and sub-mesoscale processes play a fundamental role for ocean dynamics by modulating movements in the ocean at the scales ranging from hundreds of meters to hundreds of kilometers via the presence of eddies, fronts, or density filaments among others. These processes inevitably affect biogeochemical cycles as they shape the vertical and horizontal distribution

of nutrients and carbon, including their transport to the euphotic zone. This in turn affects the capacity of the ocean to take up and store anthropogenic carbon under changing climate.

Characterizing and quantifying the role of these processes in the ocean carbon cycle on inter-annual to decadal time scales is still an immense challenge, largely constrained by the availability of computational resources. The added value of enhanced resolution and greater realism will allow me to explore a set of new scientific questions at the center of climate science. Furthermore, I will study opportunities of using Machine Learning in the context of exascale Earth system computing to expand horizons of my expertise.

Bibliography

- Andrews, O. D., Bindoff, N. L., Halloran, P. R., **Ilyina, T.**, and Le Quéré, C. (2013). Detecting an external influence on recent changes in oceanic oxygen using an optimal fingerprinting method. *Biogeosciences*, 10(3):1799–1813.
- Archer, D. and Maier-Reimer, E. (1994). Effect of deep-sea sedimentary calcite preservation on atmospheric co2 concentration. *Nature*, 367(6460):260–263.
- Arora, V. K., Boer, G. J., Friedlingstein, P., Eby, M., Jones, C. D., Christian, J. R., Bonan, G., Bopp, L., Brovkin, V., Cadule, P., Hajima, T., **Ilyina, T.**, Lindsay, K., Tjiputra, J. F., and Wu, T. (2013). Carbon-Concentration and Carbon-Climate Feedbacks in CMIP5 Earth System Models. *J. Climate*, 26(15):5289–5314.
- Arora, V. K., Katavouta, A., Williams, R. G., Jones, C. D., Brovkin, V., Friedlingstein, P., Schwinger, J., Bopp, L., Boucher, O., Cadule, P., Chamberlain, M. A., Christian, J. R., Delire, C., Fisher, R. A., Hajima, T., **Ilyina, T.**, Joetzjer, E., Kawamiya, M., Koven, C., Krasting, J., Law, R. M., Lawrence, D. M., Lenton, A., Lindsay, K., Pongratz, J., Raddatz, T., Séférian, R., Tachiiri, K., Tjiputra, J. F., Wiltshire, A., Wu, T., and Ziehn, T. (2020). Carbon-concentration and carbon-climate feedbacks in CMIP6 models, and their comparison to CMIP5 models. *Biogeosciences*, 17(16):4173–4222.
- Bacastow, R. (1976). Modulation of atmospheric carbon dioxide by the southern oscillation. *Nature*, 261(5556):116–118.
- Bopp, L., Resplandy, L., Orr, J. C., Doney, S. C., Dunne, J. P., Gehlen, M., Halloran, P., Heinze, C., **Ilyina, T.**, Séférian, R., Tjiputra, J., and Vichi, M. (2013). Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. *Biogeosciences*, 10(10):6225–6245.
- Broecker, W. S. and Peng, T.-H. (1982). *Tracers in the Sea*. Lamont-Doherty Geological Observatory, Columbia University Palisades, New York.

- Broecker, W. S., Peteet, D. M., and Rind, D. (1985). Does the ocean–atmosphere system have more than one stable mode of operation? *Nature*, 315(6014):21–26.
- Brovkin, V., Lorenz, S., Raddatz, T., **Ilyina, T.**, Stemmler, I., Toohey, M., and Claussen, M. (2019). What was the source of the atmospheric CO₂ increase during the holocene? *Biogeosciences*, 16(13):2543–2555.
- Burt, D. J., Fröb, F., and **Ilyina, T.** (2021). The sensitivity of the marine carbonate system to regional ocean alkalinity enhancement. *Frontiers in Climate*, 3.
- Canadell, J. G., Monteiro, P. M., Costa, M. H., Cotrim da Cunha, L., Cox, P. M., Eliseev, A. V., Henson, S., Ishii, M., Jaccard, S., Koven, C., Lohila, A., Patra, P. K., Piao, S., Rogelj, J., Syampungani, S., Zaehle, S., and Zickfeld, K. (2021). Global carbon and other biogeochemical cycles and feedbacks. In *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, pages 465–570. Cambridge University Press, in press.
- Carter, B. R., Frölicher, T. L., Dunne, J. P., Rodgers, K. B., Slater, R. D., and Sarmiento, J. L. (2016). When can ocean acidification impacts be detected from decadal alkalinity measurements? *Global Biogeochemical Cycles*, 30(4):595–612.
- Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A., DeFries, R., Galloway, J., Heimann, M., et al. (2013). Carbon and other biogeochemical cycles. In *Climate change 2013: the physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, pages 465–570. Cambridge University Press.
- DeVries, T., Le Quéré, C., Andrews, O., Berthet, S., Hauck, J., **Ilyina, T.**, Landschützer, P., Lenton, A., Lima, I. D., Nowicki, M., et al. (2019). Decadal trends in the ocean carbon sink. *Proceedings of the National Academy of Sciences*, 116(24):11646–11651.
- Dobrynin, M., Murawski, J., Baehr, J., and **Ilyina, T.** (2015). Detection and attribution of climate change signal in ocean wind waves. *Journal of Climate*, 28(4):1578–1591.
- Extier, T., Six, Katharina, D., Liu, B., Paulsen, H., and **Ilyina, T.** (2022). Local oceanic CO₂ outgassing triggered by terrestrial organic carbon fluxes during deglacial flooding. *Climate of the Past*, 18:273–292.
- Fay, A. and McKinley, G. (2013). Global trends in surface ocean pCO₂ from in situ data. *Global Biogeochemical Cycles*, 27(2):541–557.

- Foote, E. (1856). Art. xxxi.—circumstances affecting the heat of the sun's rays. *American Journal of Science and Arts (1820-1879)*, 22(66):382.
- Friedlingstein, P., Jones, M. W., O'Sullivan, M., Andrew, R. M., Hauck, J., Peters, G. P., Peters, W., Pongratz, J., Sitch, S., Le Quéré, C., Bakker, D. C. E., Canadell, J. G., Ciais, P., Jackson, R. B., Anthoni, P., Barbero, L., Bastos, A., Bastrikov, V., Becker, M., Bopp, L., Buitenhuis, E., Chandra, N., Chevallier, F., Chini, L. P., Currie, K. I., Feely, R. A., Gehlen, M., Gilfillan, D., Gkritzalis, T., Goll, D. S., Gruber, N., Gutekunst, S., Harris, I., Haverd, V., Houghton, R. A., Hurtt, G., **Ilyina, T.**, Jain, A. K., Joetzjer, E., Kaplan, J. O., Kato, E., Klein Goldewijk, K., Korsbakken, J. I., Landschützer, P., Lauvset, S. K., Lefèvre, N., Lenton, A., Lienert, S., Lombardozzi, D., Marland, G., McGuire, P. C., Melton, J. R., Metzl, N., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., Neill, C., Omar, A. M., Ono, T., Peregon, A., Pierrot, D., Poulter, B., Rehder, G., Resplandy, L., Robertson, E., Rödenbeck, C., Séférian, R., Schwinger, J., Smith, N., Tans, P. P., Tian, H., Tilbrook, B., Tubiello, F. N., van der Werf, G. R., Wiltshire, A. J., and Zaehle, S. (2019). Global carbon budget 2019. *Earth System Science Data*, 11(4):1783–1838.
- Friedlingstein, P., O'Sullivan, M., Jones, M. W., Andrew, R. M., Hauck, J., Olsen, A., Peters, G. P., Peters, W., Pongratz, J., Sitch, S., Le Quéré, C., Canadell, J. G., Ciais, P., Jackson, R. B., Alin, S., Aragão, L. E. O. C., Arneeth, A., Arora, V., Bates, N. R., Becker, M., Benoit-Cattin, A., Bittig, H. C., Bopp, L., Bultan, S., Chandra, N., Chevallier, F., Chini, L. P., Evans, W., Florentie, L., Forster, P. M., Gasser, T., Gehlen, M., Gilfillan, D., Gkritzalis, T., Gregor, L., Gruber, N., Harris, I., Hartung, K., Haverd, V., Houghton, R. A., **Ilyina, T.**, Jain, A. K., Joetzjer, E., Kadono, K., Kato, E., Kitidis, V., Korsbakken, J. I., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Liu, Z., Lombardozzi, D., Marland, G., Metzl, N., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., Niwa, Y., O'Brien, K., Ono, T., Palmer, P. I., Pierrot, D., Poulter, B., Resplandy, L., Robertson, E., Rödenbeck, C., Schwinger, J., Séférian, R., Skjelvan, I., Smith, A. J. P., Sutton, A. J., Tanhua, T., Tans, P. P., Tian, H., Tilbrook, B., van der Werf, G., Vuichard, N., Walker, A. P., Wanninkhof, R., Watson, A. J., Willis, D., Wiltshire, A. J., Yuan, W., Yue, X., and Zaehle, S. (2020). Global carbon budget 2020. *Earth System Science Data*, 12(4):3269–3340.
- Friedrich, T., Timmermann, A., Abe-Ouchi, A., Bates, N., Chikamoto, M., Church, M., Dore, J., Gledhill, D., Gonzalez-Davila, M., Heinemann, M., **Ilyina, T.**, Jungclaus, J., McLeod, E., Mouchet, A., and Santana-Casiano, J. (2012). Detecting regional anthropogenic trends in ocean acidification against natural variability. *Nature Climate Change*, 2(3):167–171.

- Fröb, F., Sonntag, S., Pongratz, J., Schmidt, H., and **Ilyina, T.** (2020). Detectability of artificial ocean alkalization and stratospheric aerosol injection in mpi-esm. *Earth's Future*, 8(10):e2020EF001634. e2020EF001634 10.1029/2020EF001634.
- Giorgetta, M. A., Jungclaus, J., Reick, C. H., Legutke, S., Bader, J., Böttinger, M., Brovkin, V., Cruieger, T., Esch, M., Fieg, K., Glushak, K., Gayler, V., Haak, H., Hollweg, H.-D., **Ilyina, T.**, Kinne, S., Kornblueh, L., Matei, D., Mauritsen, T., Mikolajewicz, U., Mueller, W., Notz, D., Pithan, F., Raddatz, T., Rast, S., Redler, R., Roeckner, E., Schmidt, H., Schnur, R., Segschneider, J., Six, K. D., Stockhause, M., Timmreck, C., Wegner, J., Widmann, H., Wieners, K.-H., Claussen, M., Marotzke, J., and Stevens, B. (2013). Climate and carbon cycle changes from 1850 to 2100 in MPI-ESM simulations for the Coupled Model Intercomparison Project phase 5. *J. Adv. Model. Earth Syst.*, 5(3):572–597.
- Gloege, L., McKinley, G., Landschützer, P., Fay, A., Frölicher, T., Fyfe, J., **Ilyina, T.**, Jones, S., Lovenduski, N. S., Rodgers, K. B., Schlunegger, S., and Takano, Y. (2021). Quantifying errors in observationally-based estimates of ocean carbon sink variability. *Global Biogeochemical Cycles*, 35(4):e2020GB006788.
- González, M. F. (2017). *Climate engineering by enhancement of ocean alkalinity: impacts on the Earth system and a comparison with solar radiation management*, volume 193 of *Reports on Earth System Science*. Max-Planck-Institut für Meteorologie, Hamburg. PhD Thesis, Universität Hamburg.
- González, M. F. and **Ilyina, T.** (2016). Impacts of artificial ocean alkalization on the carbon cycle and climate in earth system simulations. *Geophysical Research Letters*, 43(12):6493–6502.
- González, M. F., **Ilyina, T.**, Sonntag, S., and Schmidt, H. (2018). Enhanced rates of regional warming and ocean acidification after termination of large-scale ocean alkalization. *Geophysical Research Letters*, 45(14):7120–7129.
- Hauck, J., Zeising, M., Le Quere, C., Gruber, N., Bakker, D. C. E., Bopp, L., Chau, T. T. T., Gürses, Ö., **Ilyina, T.**, Landschützer, P., et al. (2020). Consistency and challenges in the ocean carbon sink estimate for the global carbon budget. *Frontiers in Marine Science*, 7:852.
- Heinze, C., **Ilyina, T.**, and Gehlen, M. (2018). The potential of ^{230}Th for detection of ocean acidification impacts on pelagic carbonate production. *Biogeosciences*, 15(11):3521–3539.

- Heinze, C., Maier-Reimer, E., and Winn, K. (1991). Glacial pCO₂ Reduction by the World Ocean: Experiments With the Hamburg Carbon Cycle Model. *Paleoceanography*, 6(4):395–430.
- Heinze, M. (2015). *Modelling the Carbon Cycle during the Paleocene-Eocene Thermal Maximum*, volume 165 of *Reports on Earth System Science*. Max-Planck-Institut für Meteorologie, Hamburg. PhD Thesis, Universität Hamburg.
- Heinze, M. and **Ilyina, T.** (2015). Ocean biogeochemistry in the warm climate of the late Paleocene. *Climate of the Past*, 11(1):63–79.
- Henson, S. A., Beaulieu, C., **Ilyina, T.**, John, J. G., Long, M., Séférian, R., Tjiputra, J., and Sarmiento, J. L. (2017). Rapid emergence of climate change in environmental drivers of marine ecosystems. *Nature Communications*, 8(1):1–9.
- Hönisch, B., Ridgwell, A., Schmidt, D. N., Thomas, E., Gibbs, S. J., Sluijs, A., Zeebe, R., Kump, L., Martindale, R. C., Greene, S. E., et al. (2012). The geological record of ocean acidification. *science*, 335(6072):1058–1063.
- Ilyina, T.** (2007). *The fate of persistent organic pollutants in the north sea: multiple year model simulations of g-HCH, a-HCH and PCB 153*, volume 7. Springer Science & Business Media.
- Ilyina, T.** (2015). The combined effects of changes in ocean chemistry, biology, and hydrodynamics on alkalinity. In Sarnthein, M. and Haug, G. H., editors, *Deglaciation Changes in Ocean Dynamics and Atmospheric CO₂*, volume 408, pages 107–110. Nova Acta Leopoldina, Wissenschaftliche Verlagsgesellschaft Stuttgart.
- Ilyina, T.** (2016). Climate science: Hidden trends in the ocean carbon sink. *Nature*, 530(7591):426–427.
- Ilyina, T.** and Friedlingstein, P. (2016). Biogeochemical Cycles and Climate Change. White Paper on WCRP Grand Challenge. World Climate Research Programme, <https://www.wcrp-climate.org/gc-carbon-feedbacks>.
- Ilyina, T.** and Heinze, M. (2019). Carbonate dissolution enhanced by ocean stagnation and respiration at the onset of the paleocene-eocene thermal maximum. *Geophysical Research Letters*, 46(2):842–852.
- Ilyina, T.** and Hunziker, R. W. (2010). Scenarios of temporal and spatial evolution of hexabromocyclododecane in the north sea. *Environmental science & technology*, 44(12):4622–4628.

- Ilyina, T.**, Lammel, G., and Pohlmann, T. (2008). Mass budgets and contribution of individual sources and sinks to the abundance of γ -hch, α -hch and pcb 153 in the north sea. *Chemosphere*, 72(8):1132–1137.
- Ilyina, T.**, Li, H., Spring, A., Müller, W. A., Bopp, L., Chikamoto, M. O., Danabasoglu, G., Dobrynin, M., Dunne, J., Fransner, F., Friedlingstein, P., Lee, W., Lovenduski, N. S., Merryfield, W., Mignot, J., Park, J., Séférian, R., Sospedra-Alfonso, R., Watanabe, M., and Yeager, S. (2021). *Geophysical Research Letters*, 48(6):e2020GL090695.
- Ilyina, T.**, Pohlmann, T., Lammel, G., and Sündermann, J. (2006). A fate and transport ocean model for persistent organic pollutants and its application to the north sea. *Journal of Marine Systems*, 63(1-2):1–19.
- Ilyina, T.**, Six, K. D., Segschneider, J., Maier-Reimer, E., Li, H., and Núñez-Riboni, I. (2013a). Global ocean biogeochemistry model HAMOCC: Model architecture and performance as component of the MPI-Earth system model in different CMIP5 experimental realizations. *Journal of Advances in Modeling Earth Systems*, 5(2):287–315.
- Ilyina, T.**, Wolf-Gladrow, D., Munhoven, G., and Heinze, C. (2013b). Assessing the potential of calcium-based artificial ocean alkalization to mitigate rising atmospheric CO₂ and ocean acidification. *Geophysical Research Letters*, 40(22):5909–5914.
- Ilyina, T.** and Zeebe, R. E. (2012). Detection and projection of carbonate dissolution in the water column and deep-sea sediments due to ocean acidification. *Geophysical Research Letters*, 39(6):L06606.
- Ilyina, T.**, Zeebe, R. E., and Brewer, P. G. (2010). Future ocean increasingly transparent to low-frequency sound owing to carbon dioxide emissions. *Nature Geoscience*, 3(1):18–22.
- Ilyina, T.**, Zeebe, R. E., Maier-Reimer, E., and Heinze, C. (2009). Early detection of ocean acidification effects on marine calcification. *Global Biogeochemical Cycles*, 23(1).
- Jones, C. D., Collins, M., Cox, P. M., and Spall, S. A. (2001). The carbon cycle response to ENSO: A coupled climate–carbon cycle model study. *Journal of Climate*, 14(21):4113–4129.
- Jones, C. D., Hickman, J. E., Rumbold, S. T., Walton, J., Lamboll, R. D., Skeie, R. B., Fiedler, S., Forster, P. M., Rogelj, J., Abe, M., Botzet, M., Calvin, K., Cassou, C., Cole, J. N., Davini, P., Deushi, M., Dix, M., Fyfe, J. C., Gillett,

- N. P., **Ilyina, T.**, Kawamiya, M., Kelley, M., Kharin, S., Koshiro, T., Li, H., Mackallah, C., Müller, W. A., Nabat, P., van Noije, T., Nolan, P., Ohgaito, R., Olivie, D., Oshima, N., Parodi, J., Reerink, T. J., Ren, L., Romanou, A., Séférian, R., Tang, Y., Timmreck, C., Tjiputra, J., Tourigny, E., Tsigaridis, K., Wang, H., Wu, M., Wyser, K., Yang, S., Yang, Y., and Ziehn, T. (2021). The climate response to emissions reductions due to covid-19: Initial results from covidmp. *Geophysical Research Letters*, 48(8):e2020GL091883. e2020GL091883 2020GL091883.
- Jungclaus, J. H., Lorenz, S., Schmidt, H., Brovkin, V., Brüggemann, N., Chegini, F., De-Vrese, P., Gayler, V., Giorgetta, M., Gutjahr, O., Haak, H., Hagemann, S., Hanke, M., **Ilyina, T.**, Korn, P., Kröger, J., Linardakis, L., Mehlmann, C., Mikolajewicz, U., Müller, W., Nabel, J., Notz, D., Pohlmann, H., Putrasahan, D., Raddatz, T., Ramme, L., Redler, R., Reick, C., Riddick, T., Sam, T., Schneek, R., Schnur, R., Schupfner, M., von Storch, J.-S., Wachsmann, F., Wieners, K.-H., Ziemer, F., Stevens, B., Marotzke, J., and Claussen, M. (2022). The icon earth system model version 1.0. *Journal of Advances in Modeling Earth Systems*, 14(4):e2021MS002813.
- Kapsch, M.-L., Mikolajewicz, U., Ziemer, F. A., Rodehacke, C. B., and Schannwell, C. (2021). Analysis of the surface mass balance for deglacial climate simulations. *The Cryosphere*, 15(2):1131–1156.
- Keeling, C. D., Bacastow, R. B., Bainbridge, A. E., Jr., C. A. E., Guenther, P. R., Waterman, L. S., and Chin, J. F. S. (1976). Atmospheric carbon dioxide variations at mauna loa observatory, hawaii. *Tellus*, 28(6):538–551.
- Kleinen, T., Mikolajewicz, U., and Brovkin, V. (2020). Terrestrial methane emissions from the last glacial maximum to the preindustrial period. *Climate of the Past*, 16(2):575–595.
- Kohfeld, K. E. and Chase, Z. (2017). Temporal evolution of mechanisms controlling ocean carbon uptake during the last glacial cycle. *Earth and Planetary Science Letters*, 472:206–215.
- Köhler, P., Abrams, J. F., Völker, C., Hauck, J., and Wolf-Gladrow, D. A. (2013). Geoengineering impact of open ocean dissolution of olivine on atmospheric co₂, surface ocean ph and marine biology. *Environmental Research Letters*, 8(1):014009.
- Köhler, P., Nehrbaas-Ahles, C., Schmitt, J., Stocker, T. F., and Fischer, H. (2017). A 156 kyr smoothed history of the atmospheric greenhouse gases co₂, ch₄, and n₂o and their radiative forcing. *Earth System Science Data*, 9(1):363–387.

- Kwiatkowski, L., Torres, O., Bopp, L., Aumont, O., Chamberlain, M., Christian, J. R., Dunne, J. P., Gehlen, M., **Ilyina, T.**, John, J. G., et al. (2020). Twenty-first century ocean warming, acidification, deoxygenation, and upper-ocean nutrient and primary production decline from CMIP6 model projections. *Biogeosciences*, 17(13):3439–3470.
- Lacroix, F. (2020). *Riverine and coastal ocean contributions to global and regional oceanic cycling of carbon and nutrients*, volume 225 of *Reports on Earth System Science*. Max-Planck-Institut für Meteorologie, Hamburg. PhD Thesis, Université Libré de Bruxelles.
- Lacroix, F., **Ilyina, T.**, and Hartmann, J. (2020). Oceanic CO₂ outgassing and biological production hotspots induced by pre-industrial river loads of nutrients and carbon in a global modeling approach. *Biogeosciences*, 17:55–88.
- Lacroix, F., **Ilyina, T.**, Laruelle, G., and Pierre, R. (2021a). Reconstructing the pre-industrial coastal carbon cycle through a global ocean circulation model: Was the global continental shelf already both autotrophic and a CO₂ sink? *Global Biogeochemical Cycle*, 35:e2020GB00660.
- Lacroix, F., **Ilyina, T.**, Mathis, M., Laruelle, G. G., and Regnier, P. (2021b). Historical increases in land-derived nutrient inputs may alleviate effects of a changing physical climate on the oceanic carbon cycle. *Global change biology*, 27(21):5491–5513.
- Landschützer, P., Gruber, N., Haumann, F. A., Rödenbeck, C., Bakker, D. C., Van Heuven, S., Hoppema, M., Metzl, N., Sweeney, C., Takahashi, T., et al. (2015). The reinvigoration of the southern ocean carbon sink. *Science*, 349(6253):1221–1224.
- Landschützer, P., **Ilyina, T.**, and Lovenduski, N. S. (2019). Detecting regional modes of variability in observation-based surface ocean pCO₂. *Geophysical Research Letters*, 46(5):2670–2679.
- Landschützer, P., Keppler, L., and **Ilyina, T.** (2021). Ocean systems. In Poulter, B., Hayes, D., Canadell, J., and Thompson, R., editors, *Balancing Regional Greenhouse Gas Budgets: Accounting for Natural and Anthropogenic Flows of CO₂ and Other Trace Gases*, page xx. Elsevier, in press.
- Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., Korsbakken, J. I., Peters, G. P., Canadell, J. G., Jackson, R. B., Boden, T. A., Tans, P. P., Andrews, O. D., Arora, V. K., Bakker, D. C. E., Barbero, L., Becker, M., Betts, R. A., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P.,

- Cosca, C. E., Cross, J., Currie, K., Gasser, T., Harris, I., Hauck, J., Haverd, V., Houghton, R. A., Hunt, C. W., Hurtt, G., **Ilyina, T.**, Jain, A. K., Kato, E., Kautz, M., Keeling, R. F., Klein Goldewijk, K., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lima, I., Lombardozzi, D., Metzl, N., Millero, F., Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S., Nojiri, Y., Padin, X. A., Pregon, A., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Reimer, J., Rödenbeck, C., , J., Séférian, R., Skjelvan, I., Stocker, B. D., Tian, H., Tilbrook, B., Tubiello, F. N., van der Laan-Luijkx, I. T., van der Werf, G. R., van Heuven, S., Viovy, N., Vuichard, N., Walker, A. P., Watson, A. J., Wiltshire, A. J., Zaehle, S., and Zhu, D. (2018). Global carbon budget 2017. *Earth System Science Data*, 10(1):405–448.
- Li, H. and **Ilyina, T.** (2018). Current and future decadal trends in the oceanic carbon uptake are dominated by internal variability. *Geophysical Research Letters*, 45(2):916–925.
- Li, H., **Ilyina, T.**, Müller, W. A., and Landschützer, P. (2019). Predicting the variable ocean carbon sink. *Science Advances*, 5(4):eaav6471.
- Li, H., **Ilyina, T.**, Müller, W. A., and Sienz, F. (2016). Decadal predictions of the north atlantic CO₂ uptake. *Nature Communications*, 7(1):1–7.
- Liu, B., Six, Katharina, D., and **Ilyina, T.** (2021). Incorporating the stable carbon isotope ¹³C in the ocean biogeochemical component of the max planck institute earth system model. *Biogeosciences*, accepted.
- Lovenduski, N. S., Bonan, G. B., Yeager, S. G., Lindsay, K., and Lombardozzi, D. L. (2019). High predictability of terrestrial carbon fluxes from an initialized decadal prediction system. *Environmental Research Letters*, 14(12):124074.
- Maerz, J., Six, K. D., Stemmler, I., Ahmerkamp, S., and **Ilyina, T.** (2020). Microstructure and composition of marine aggregates as co-determinants for vertical particulate organic carbon transfer in the global ocean. *Biogeosciences*, 17:1765–1803.
- Maher, N., Milinski, S., Suarez-Gutierrez, L., Botzet, M., Dobrynin, M., Kornbluh, L., Kröger, J., Takano, Y., Ghosh, R., Hedemann, C., Li, C., Li, H., Manzini, E., Notz, D., Putrasahan, D., Boysen, L., Claussen, M., **Ilyina, T.**, Olonscheck, D., Raddatz, T., Stevens, B., and Marotzke, J. (2019). The max planck institute grand ensemble: Enabling the exploration of climate system variability. *Journal of Advances in Modeling Earth Systems*, 11(7):2050–2069.
- Marotzke, J. (2019). Quantifying the irreducible uncertainty in near-term climate projections. *Wiley Interdisciplinary Reviews: Climate Change*, 10(1):e563.

- Marotzke, J., Müller, W. A., Vamborg, F. S., Becker, P., Cubasch, U., Feldmann, H., Kaspar, F., Kottmeier, C., Marini, C., Polkova, I., et al. (2016). MiKlip: A national research project on decadal climate prediction. *Bulletin of the American Meteorological Society*, 97(12):2379–2394.
- Masson-Delmotte, V., Zhai, P., Pirani, A., Connors, S. L., Péan, C., Berger, S., Caud, N., Chen, Y., Goldfarb, L., Gomis, M. I., Huang, M., Leitzell, K., Lonnoy, E., Matthews, J. B. R., Maycock, T. K., Waterfield, T., Yelekçi, O., R., Y., and Zhou, B. (2021). *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, in press.
- Mathis, M., Logemann, K., Maerz, J., Lacroix, F., Hagemann, S., Chegini, F., Ramme, L., **Ilyina, T.**, Korn, P., and Schrum, C. (submitted). Seamless integration of the coastal ocean in global marine carbon cycle modeling. *Journal of Advances in Modeling Earth Systems*.
- Matthews, H. D., Tokarska, K. B., Nicholls, Z. R., Rogelj, J., Canadell, J. G., Friedlingstein, P., Frölicher, T. L., Forster, P. M., Gillett, N. P., **Ilyina, T.**, et al. (2020). Opportunities and challenges in using remaining carbon budgets to guide climate policy. *Nature Geoscience*, 13(12):769–779.
- Mauritsen, T., Bader, J., Becker, T., Behrens, J., Bittner, M., Brokopf, R., Brovkin, V., Claussen, M., Crueger, T., Esch, M., Fast, I., Fiedler, S., Fläschner, D., Gayler, V., Giorgetta, M., Goll, D. S., Haak, H., Hagemann, S., Hedemann, C., Hohenegger, C., **Ilyina, T.**, Jahns, T., Jimenéz-de-la Cuesta, D., Jungclaus, J., Kleinen, T., Kloster, S., Kracher, D., Kinne, S., Kleberg, D., Lasslop, G., Kornbluh, L., Marotzke, J., Matei, D., Meraner, K., Mikolajewicz, U., Modali, K., Möbis, B., Müller, W. A., Nabel, J. E. M. S., Nam, C. C. W., Notz, D., Nyawira, S.-S., Paulsen, H., Peters, K., Pincus, R., Pohlmann, H., Pongratz, J., Popp, M., Raddatz, T. J., Rast, S., Redler, R., Reick, C. H., Rohrschneider, T., Schemann, V., Schmidt, H., Schnur, R., Schulzweida, U., Six, K. D., Stein, L., Stemmler, I., Stevens, B., von Storch, J.-S., Tian, F., Voigt, A., Vrese, P., Wieners, K.-H., Wilkenskjaeld, S., Winkler, A., and Roeckner, E. (2019). Developments in the MPI-M Earth System Model version 1.2 (MPI-ESM1.2) and its response to increasing CO₂. *Journal of Advances in Modeling Earth Systems*, 11(4):998–1038.
- Meccia, V. L. and Mikolajewicz, U. (2018). Interactive ocean bathymetry and coastlines for simulating the last deglaciation with the max planck institute earth system model (mpi-esm-v1.2). *Geosci. Model Dev.*, 11:4677–4692.

- Merryfield, W. J., Baehr, J., Batté, L., Becker, E. J., Butler, A. H., Coelho, C. A. S., Danabasoglu, G., Dirmeyer, P. A., Doblas-Reyes, F. J., Domeisen, D. I. V., Ferranti, L., **Ilyina, T.**, Kumar, A., Müller, W. A., Rixen, M., Robertson, A. W., Smith, D. M., Takaya, Y., Tuma, M., Vitart, F., White, C. J., Alvarez, M. S., Ardilouze, C., Attard, H., Baggett, C., Balmaseda, M. A., Beraki, A. F., Bhattacharjee, P. S., Bilbao, R., de Andrade, F. M., DeFlorio, M. J., Díaz, L. B., Ehsan, M. A., Fragkoulidis, G., Grainger, S., Green, B. W., Hell, M. C., Infanti, J. M., Isensee, K., Kataoka, T., Kirtman, B. P., Klingaman, N. P., Lee, J.-Y., Mayer, K., McKay, R., Mecking, J. V., Miller, D. E., Neddermann, N., Justin Ng, C. H., Ossó, A., Pankatz, K., Peatman, S., Pegion, K., Perlwitz, J., Recalde-Coronel, G. C., Reintges, A., Renkl, C., Solaraju-Murali, B., Spring, A., Stan, C., Sun, Y. Q., Tozer, C. R., Vigaud, N., Woolnough, S., and Yeager, S. (2020). Current and emerging developments in subseasonal to decadal prediction. *Bulletin of the American Meteorological Society*, 101(6):E869–E896.
- Müller, W. A., Jungclaus, J. H., Mauritsen, T., Baehr, J., Bittner, M., Budich, R., Bunzel, F., Esch, M., Ghosh, R., Haak, H., **Ilyina, T.**, Kleine, T., Kornblueh, L., Li, H., Modali, K., Notz, D., Pohlmann, H., Roeckner, E., Stemmler, I., Tian, F., and Marotzke, J. (2018). A higher-resolution version of the Max Planck Institute Earth System Model (MPI-ESM1. 2-HR). *Journal of Advances in Modeling Earth Systems*, 10(7):1383–1413.
- O’Driscoll, K., Mayer, B., **Ilyina, T.**, and Pohlmann, T. (2013). Modelling the cycling of persistent organic pollutants (pops) in the north sea system: fluxes, loading, seasonality, trends. *Journal of Marine Systems*, 111:69–82.
- O’Neill, B. C., Tebaldi, C., van Vuuren, D. P., Eyring, V., Friedlingstein, P., Hurtt, G., Knutti, R., Kriegler, E., Lamarque, J.-F., Lowe, J., Meehl, G. A., Moss, R., Riahi, K., and Sanderson, B. M. (2016). The scenario model intercomparison project (scenariomip) for cmip6. *Geoscientific Model Development*, 9(9):3461–3482.
- Paulsen, H. (2018). *The effects of marine nitrogen-fixing cyanobacteria on ocean biogeochemistry and climate – an Earth system model perspective*, volume 205 of *Reports on Earth System Science*. Max-Planck-Institut für Meteorologie, Hamburg. PhD Thesis, Universität Hamburg.
- Paulsen, H., **Ilyina, T.**, Jungclaus, J. H., Six, K. D., and Stemmler, I. (2018). Light absorption by marine cyanobacteria affects tropical climate mean state and variability. *Earth System Dynamics*, 9(4):1283–1300.
- Paulsen, H., **Ilyina, T.**, Six, K. D., and Stemmler, I. (2017). Incorporating a prognostic representation of marine nitrogen fixers into the global ocean bio-

- geochemical model hamocc. *Journal of Advances in Modeling Earth Systems*, 9(1):438–464.
- Peters, G. P., Le Quéré, C., Andrew, R. M., Canadell, J. G., Friedlingstein, P., **Ilyina, T.**, Jackson, R. B., Joos, F., Korsbakken, J. I., McKinley, G. A., et al. (2017). Towards real-time verification of CO₂ emissions. *Nature Climate Change*, 7(12):848–850.
- Pihl, E., Alfredsson, E., Bengtsson, M., Bowen, K. J., Cástan Broto, V., Chou, K. T., Cleugh, H., Ebi, K., Edwards, C. M., Fisher, E., and et al. incl. **Ilyina, T.** (2021). Ten new insights in climate science 2020 – a horizon scan. *Global Sustainability*, 4:e5.
- Popp, B. N., Takigiku, R., Hayes, J., Louda, J. W., and Baker, E. W. (1989). The post-paleozoic chronology and mechanism of ¹³C depletion in primary marine organic matter. *American Journal of Science*, 289(4):436–454.
- Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., Laruelle, G. G., Lauerwald, R., Luyssaert, S., Andersson, A. J., Arndt, S., Arnosti, C., Borges, A. V., Dale, A. W., Gallego-Sala, A., Godderis, Y., Goossens, N., Hartmann, J., Heinze, C., **Ilyina, T.**, Joos, F., LaRowe, D. E., Leifeld, J., Meysman, F. J. R., Munhoven, G., Raymond, P. A., Spahni, R., Suntharalingam, P., and Thullner, M. (2013). Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature Geosci*, 6(8):597–607.
- Rickaby, R. E., Elderfield, H., Roberts, N., Hillenbrand, C.-D., and Mackensen, A. (2010). Evidence for elevated alkalinity in the glacial southern ocean. *Paleoceanography*, 25(1).
- Riddick, T., Brovkin, V., Hagemann, S., and Mikolajewicz, U. (2018). Dynamic hydrological discharge modelling for coupled climate model simulations of the last glacial cycle: the mpi-dynamichd model version 3.0. *Geosci. Model Dev.*, 11:4291–4316.
- Ropelewski, C. F. and Halpert, M. S. (1987). Global and regional scale precipitation patterns associated with the El Niño/Southern Oscillation. *Monthly weather review*, 115(8):1606–1626.
- Schlunegger, S., Rodgers, K. B., Sarmiento, J. L., **Ilyina, T.**, Dunne, J. P., Takano, Y., Christian, J. R., Long, M. C., Frölicher, T. L., Slater, R., and Lehner, F. (2020). Time of emergence and large ensemble intercomparison for ocean biogeochemical trends. *Global Biogeochemical Cycles*, 34(8):e2019GB006453. e2019GB006453 2019GB006453.

- Schmittner, A., Oschlies, A., Matthews, H. D., and Galbraith, E. D. (2008). Future changes in climate, ocean circulation, ecosystems, and biogeochemical cycling simulated for a business-as-usual CO₂ emission scenario until year 4000 AD. *Global Biogeochem. Cycles*, 22(1):GB1013–.
- Schuster, U. and Watson, A. J. (2007). A variable and decreasing sink for atmospheric CO₂ in the north atlantic. *Journal of Geophysical Research: Oceans*, 112(C11).
- Schwinger, J., Tjiputra, J., Goris, N., Six, K. D., Kirkevåg, A., Seland, Ø., Heinze, C., and **Ilyina, T.** (2017). Amplification of global warming through pH dependence of dms production simulated with a fully coupled earth system model. *Biogeosciences*, 14(15):3633.
- Séférian, R., Berthet, S., Yool, A., Palmieri, J., Bopp, L., Tagliabue, A., Kwiatkowski, L., Aumont, O., Christian, J., and Dunne, John et al. incl. **Ilyina, T.** (2020). Tracking improvement in simulated marine biogeochemistry between cmip5 and cmip6. *Current Climate Change Reports*, pages 1–25.
- Séférian, R., Gehlen, M., Bopp, L., Resplandy, L., Orr, J. C., Marti, O., Dunne, J. P., Christian, J. R., Doney, S. C., **Ilyina, T.**, Lindsay, K., Halloran, P. R., Heinze, C., Segschneider, J., Tjiputra, J., Aumont, O., and Romanou, A. (2016). Inconsistent strategies to spin up models in cmip5: implications for ocean biogeochemical model performance assessment. *Geoscientific Model Development*, 9(5):1827–1851.
- Shepherd, J. G. (2009). *Geoengineering the climate: science, governance and uncertainty*. Royal Society.
- Six, K. D., Kloster, S., **Ilyina, T.**, Archer, S. D., Zhang, K., and Maier-Reimer, E. (2013). Global warming amplified by reduced sulphur fluxes as a result of ocean acidification. *Nature Climate Change*, 3(11):975–978.
- Sonntag, S., Ferrer González, M., **Ilyina, T.**, Kracher, D., Nabel, J. E. M. S., Niemeier, U., Pongratz, J., Reick, C. H., and Schmidt, H. (2018). Quantifying and comparing effects of climate engineering methods on the earth system. *Earth's Future*, 6(2):149–168.
- Spring, A. (2021). *Variability and potential predictability of the global carbon cycle in a perfect-model framework*, volume xx of *Reports on Earth System Science*. Max-Planck-Institut für Meteorologie, Hamburg. PhD Thesis, Universität Hamburg.

- Spring, A., Dunkl, I., Li, H., Brovkin, V., and **Ilyina, T.** (2021). Trivial improvements of predictive skill due to direct reconstruction of global carbon cycle. *Earth System Dynamics*, 12(4):1139–1167.
- Spring, A. and **Ilyina, T.** (2020). Predictability horizons in the global carbon cycle inferred from a perfect-model framework. *Geophysical Research Letters*, 47(9):e2019GL085311.
- Spring, A., **Ilyina, T.**, and Marotzke, J. (2020). Inherent uncertainty disguises attribution of reduced atmospheric CO₂ growth to CO₂ emission reductions for up to a decade. *Environmental Research Letters*.
- Stocker, T. F. (2000). Past and future reorganizations in the climate system. *Quaternary Science Reviews*, 19(1):301–319.
- Sun, Y., Zulla, M., Joachimski, M., Bond, D., Wignall, P., Zhang, Z., and Zhang, M. (2019). Ammonium ocean following the end-permian mass extinction. *Earth and Planetary Science Letters*, 518:211–222.
- Takano, Y. and **Ilyina, T.** (submitted). Uncertain current and near future ocean deoxygenation due to internal climate variability and observational gaps.
- Tanhua, T., Orr, J. C., Lorenzoni, L., and Hansson, L. (2015). Monitoring ocean carbon and ocean acidification. *WMO Bulletin*, 64(1).
- Vancoppenolle, M., Bopp, L., Madec, G., Dunne, J., **Ilyina, T.**, Halloran, P. R., and Steiner, N. (2013). Future arctic ocean primary productivity from cmip5 simulations: Uncertain outcome, but consistent mechanisms. *Global Biogeochemical Cycles*, 27(3):605–619.
- Zeebe, Richard, E. and Wolf-Gladrow, D. (2001). *CO₂ in seawater: Equilibrium, kinetics, isotopes*, volume 65 of *Elsevier Oceanography Series*. Elsevier.
- Zeebe, R. E. and Zachos, J. C. (2007). Reversed deep-sea carbonate ion basin gradient during Paleocene-Eocene thermal maximum. *Paleoceanography*, 22(3):PA3201.
- Zeng, N., Yoon, J.-H., Vintzileos, A., Collatz, G. J., Kalnay, E., Mariotti, A., Kumar, A., Busalacchi, A., and Lord, S. (2008). Dynamical prediction of terrestrial ecosystems and the global carbon cycle: A 25-year hindcast experiment. *Global Biogeochemical Cycles*, 22(4).
- Ziemen, F. A., Kapsch, M.-L., Klockmann, M., and Mikolajewicz, U. (2019). Heinrich events show two-stage climate response in transient glacial simulations. *Climate of the Past*, 15(1):153–168.

Acronyms

Ω calcite saturation state.

^{230}Th radionuclide thorium.

AMOC Atlantic Meridional Overturning Circulation.

AOA Artificial Ocean Alkalinization.

BMBF the Federal Ministry of Education and Research.

CaCO₃ calcium carbonate.

CDR Carbon Dioxide Removal.

CMIP Coupled Model Intercomparison Project.

CO₃²⁻ carbonate ion.

DFG Deutsche Forschungsgemeinschaft.

DIC Dissolved Inorganic Carbon.

DMS dimethylsulfide.

ESM Earth System Model.

FANTOM Fate and Transport Ocean Model.

GC-Carbon Grand Challenge on Carbon Feedbacks in the Climate System.

GCB Global Carbon Budget.

HAMOCC Hamburg Ocean Carbon Cycle model.

ICON Icosahedral Nonhydrostatic model.

ICV Internal Climate Variability.

IPCC Intergovernmental Panel on Climate Change.

LGM Last Glacial Maximum.

MPI-ESM Max Planck Institute's Earth System Model.

MPI-GE Max Planck Institute Grand Ensemble.

MPI-M Max Planck Institute for Meteorology.

pCO₂ partial pressure of CO₂.

PETM Paleocene-Eocene Thermal Maximum.

POC Particulate Organic Carbon.

PTB Permian-Triassic Boundary.

SAI Stratospheric Aerosol Injection.

TA Total Alkalinity.

UNFCCC United Nations Framework Convention on Climate Change.

WCRP World Climate Research Program.

Hinweis / Reference

Die gesamten Veröffentlichungen in der Publikationsreihe des MPI-M
„Berichte zur Erdsystemforschung / Reports on Earth System Science“,
ISSN 1614-1199

sind über die Internetseiten des Max-Planck-Instituts für Meteorologie erhältlich:
<http://www.mpimet.mpg.de/wissenschaft/publikationen.html>

*All the publications in the series of the MPI -M
„Berichte zur Erdsystemforschung / Reports on Earth System Science“,
ISSN 1614-1199*

*are available on the website of the Max Planck Institute for Meteorology:
<http://www.mpimet.mpg.de/wissenschaft/publikationen.html>*

