Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Liming the Ocean: Extreme chemical imbalance conjoins with negligible carbon-sequestration effect

Matthias Hofmann,*[a] Dirk Olonscheck[a], Olivia Serdeczny[a] and Anders Levermann[a,b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Anthropogenic climate change poses an unprecedented challenge to human society. Several strategies to counteract dangerous impacts of rising global mean temperatures and ocean acidification are currently being debated. Besides a rigorous reduction of anthropogenic carbon dioxide (CO_2) emissions – the most efficient way to stabilize the Earth's climate – climate engineering is sometimes regarded as an alternative way to counter the release of CO_2 into the atmosphere due to the combustion of fossil fuels and land use change[1]. Measures have been proposed to either reduce incoming solar radiation or actively remove CO_2 from the atmosphere[2]. By running numerical experiments until year 2200 using a coarse-resolution three-dimensional ocean general circulation model we investigate the sequestration efficiency of ocean liming as a climate engineering measure and its impacts on the state of the marine carbonate system and associated ecosystem. Assuming the IPCC "business-as-usual" CO_2 emission scenario A1F1[3] between years 2000 and 2100, our model ocean was exposed to continuous injection of limestone ($CaCO_3$) at different rates below the current carbonate compensation depth (CCD) between the years 2015 and 2115. In order to achieve an effective drawdown of atmospheric mixing ratios of CO_2 from 1200 ppmv to 1000 ppmv by the end of our simulation, an amount of 83.33×10^{15} gram $CaCO_3$ (corresponding to 10×10^{15} gram C) per year must be supplied to the oceans, more than three times exceeding the worldwide present-day output of limestone mining[4]. We find that ocean liming, in order to effectively counteract unabated CO_2 emissions, would lead to strongly increasing pH values by up to 2.5 units in the mesopelagic zone, entailing potentially harmful consequences for marine organisms. Due to the sluggishness of the vertical pH profile, we thus find ocean liming not to be a feasible technique to counteract a business-as-usual CO_2 emission scenario.

Introduction

Since the beginning of the industrial revolution humanity has been steadily emitting increasing amounts of greenhouse gases into the atmosphere. The cumulative CO_2 emissions between years 1850 and 2006 owing to burning of fossil fuels have been assessed to an amount of 330 Petagram Carbon (Pg C; 1 Pg = 10^{15} g) while changes in land use account for further 158 Pg C[5]. As a consequence, global mean temperatures have risen by about 0.8 °C since the beginning of the twentieth century due to the associated increased radiative greenhouse-gas forcing[6]. It has been projected, that unbridled future emissions of CO_2 and other greenhouse gases could lead to an increase of global mean temperatures by up to 6 °C by the end of the twenty-first century[7].

Sabine *et al.*[8] have shown that the present day ocean is a sink of atmospheric CO_2, which has already taken up approximately 118 ± 19 Pg C during 1800 and 1994. Currently the ocean absorbs about 2 Pg C per year[8], a process which might weaken in the future due to increasing sea surface temperatures (SSTs) and changes in ocean circulation[9]. Nonetheless, rising atmospheric pCO_2 will continue to effect changes in ocean chemistry, as the uptake of CO_2 by the oceans leads to the formation of bicarbonate ions according to:

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$$

A small part of the newly formed HCO_3^- decays into carbonate (CO_3^{2-}) and hydrogen (H^+) ions

$$HCO_3^- \rightarrow CO_3^{2-} + H^+$$

resulting in a lowering of the ocean`s pH value, a process referred to as ocean acidification[10]. In accordance with Sabine et al[8.] the surface oceans pH value has dropped from 8.2 to 8.1 corresponding to a 30% increase in H^+ ion concentration since preindustrial times[11]. A continuation of this process could have harmful consequences for marine biota[12].

Besides the concept of reducing anthropogenic CO_2 emissions as recommended by the Kyoto-protocol, a variety of climate engineering concepts has been proposed as methods to avoid dangerous climate change. Iron fertilization to stimulate the marine biological carbon pump of the ocean was one of the first concepts aiming at an increase of the ocean´s uptake of atmospheric CO_2[13]. However, field studies have shown that iron fertilization might be much less efficient than expected[14]. One of

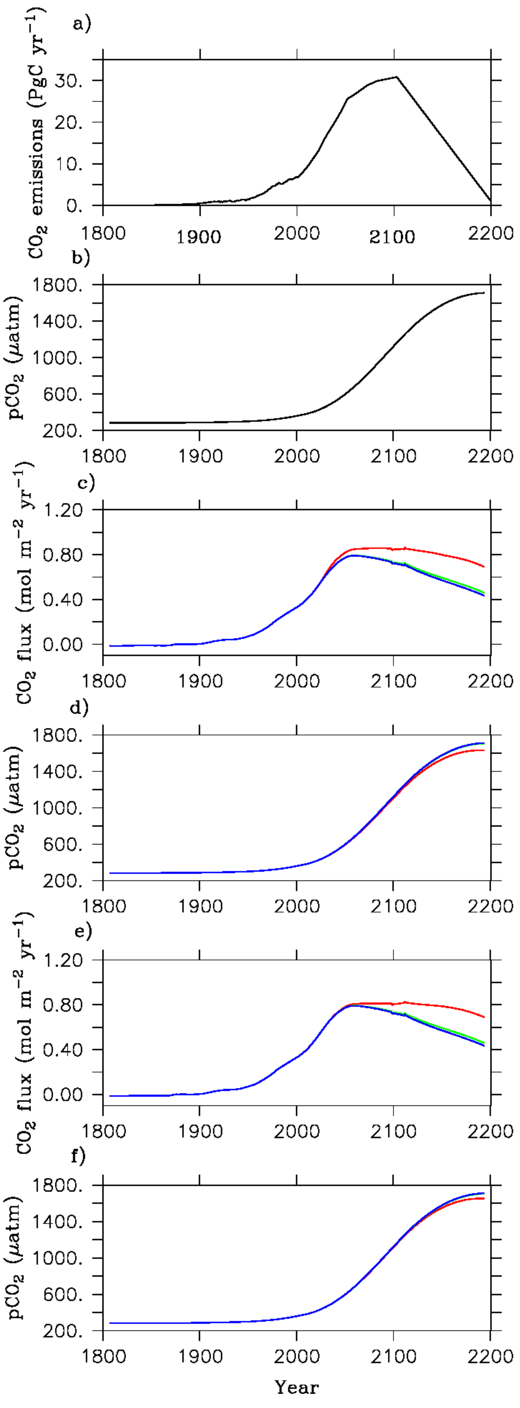

Figure 1: Time series of anthropogenic CO_2 emissions in Pg C year^{-1} (a), atmospheric partial pressure of CO_2 (pCO_2) in µatm for the no-liming control run (b), global mean CO_2 uptake by the ocean in mol C m^{-2} year^{-1} under different liming scenarios in the Bering Sea (blue: 0.01 Pg C year^{-1} equivalents of $CaCO_3$; green 1.0 Pg C year^{-1}; red 10.0 Pg C year^{-1}) (c), atmospheric pCO_2 under the different liming scenarios in the Bering Sea (blue: 0.01 Pg C year^{-1} equivalents of $CaCO_3$; green: 1.0 Pg C year^{-1}; red: 10.0 Pg C year^{-1}) (d), (e) the same as in (c) but for the upwelling area off Peru, (f) the same as in (d) but for the upwelling area off Peru

the most recent proposals for these so-called carbon-management technique is accelerated weathering via the dissolution of olivine[15] which attempts to enhance natural processes in the warm and humid tropical land area. In the meantime, a number of so-called solar-management techniques are being discussed. As an example, Crutzen *et al.*[16] proposed the injection of sulphuric acid into the stratosphere to increase the planetary albedo. Although a stabilization of global mean temperatures to preindustrial levels could be achieved, a number of serious problems such as the high dependency on continuous deployment[17] and ocean acidification[18] remain.

In order to find a climate engineering approach to solve both problems of anthropogenic climate change – global warming and ocean acidification – by altering the marine biogeochemistry, Rau and Caldeira (1999)[19], Caldeira and Rau (2000)[20] and Rau *et al.* (2007)[21] proposed to add limestone to the oceans. This concept could be regarded as an enhancement of the natural process of carbonate dissolution resulting in increased ocean alkalinity. As a result, this method would accelerate the oceans uptake of CO_2 under a concomitant relaxation of pH values towards preindustrial values.

Based on this concept, Harvey (2008)[22] suggests to sprinkle limestone powder at rates of 4 billion t of $CaCO_3$ per year over the ocean surface from where it sinks towards deep waters. Since the upper ocean is super-saturated with respect to carbonate, dissolution of $CaCO_3$ occurs only below the carbonate compensation depth (CCD). Harvey proposes to supply $CaCO_3$ only to upwelling regions exhibiting a shallow position of the calcite CCD (~500 m), guaranteeing resurfacing of carbonate enriched water masses, which has a stronger potential to take up atmospheric CO_2. Using an ensemble of one-dimensional water column advection-diffusion models distributed over the global ocean domain and utilizing vertical velocities derived from observations, the author concludes that the $CaCO_3$ supply of the proposed magnitude could help to reduce the atmospheric CO_2 content by up to 0.27 Gt C per year.

Here we address the feasibility of ocean liming with respect to changes in oceanic chemistry , with direct implications for marine ecosystems. More specifically, we investigate the amount of limestone required to reduce the atmospheric partial pressure of CO_2 (pCO_2) by at least 10 per cent in year 2200 compared to business-as-usual without liming and the effects this has on ocean pH.

The model

In this study we employ the Potsdam version of the Modular Ocean Model[23] which is based on GFDLs MOM-3[24]. This ocean general circulation model (OGCM) was coupled to a state-of-the-art sea-ice[25] and carbon cycle / marine ecosystem model[26]. The OGCM is driven by surface fluxes derived from an anomaly model of the atmospheric energy-moisture balance[23, 26] and utilizes the climatological NCEP/NCAR reanalysis database[27]. Its spatial resolution possesses a horizontal mesh size of 3.75°x3.75°. The vertical water column is divided into 24 unequally spaced levels with thickness increasing from 25 m at the top to about 500 m at the bottom. An empirical parameterization of bottom-enhanced vertical mixing using a

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

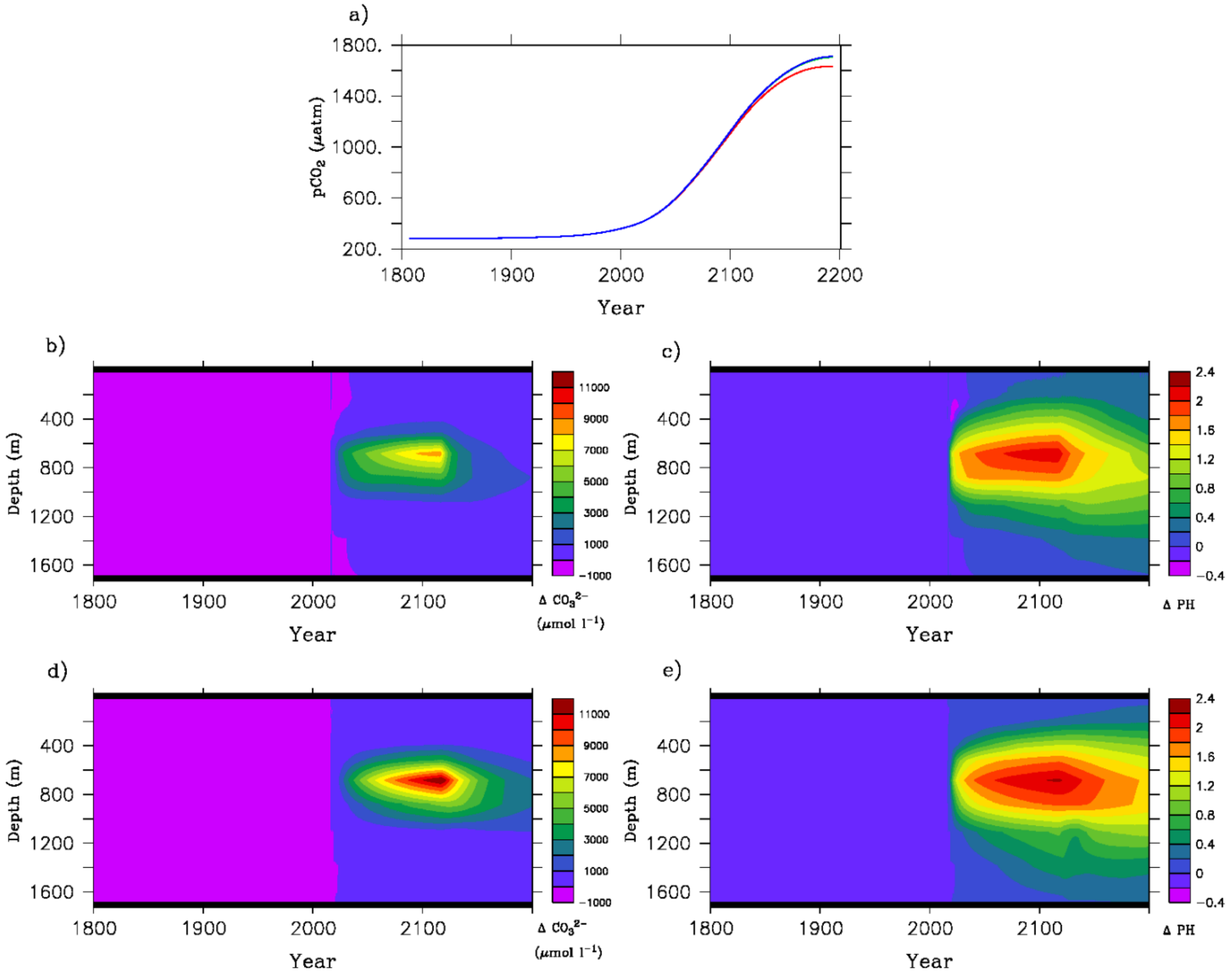

Figure 2: Evolution of atmospheric pCO_2 levels, oceanic CO_3^{2-} concentrations and pH values. (a) Time series of atmospheric pCO_2 levels in μatm under different liming scenarios (blue: 0.01 Pg C year^{-1} equivalents of $CaCO_3$; green: 1.0 Pg C year^{-1}; red: 10.0 Pg C year^{-1}). (b) Hovmoeller plot of the time evolution of the vertical profile of CO_3^{2-} concentrations in μmol/L in the water column of the Bering Sea under the maximum liming scenario. (c) The same as in (b) but for the pH value. (d) Hovmoeller plot of the time evolution of the vertical profile of CO_3^{2-} concentrations in μmol/L in the water column off Peru under the maximum liming scenario. (e) The same as in (d) but for the pH value.

vertical background diffusivity of 0.1 cm^2 s^{-1} was applied[28]. Isopycnic mixing was fixed to a number of 1.25x10^7 cm^2 s^{-1} whereas thickness diffusivity is allowed to vary between 0.275x10^7 and 0.55x10^7 cm^2 s^{-1}. The OGCM benefits from a tracer advection scheme which is nearly free of spurious diffusion and dispersion[23].

The biogeochemistry sub-model is isogeochemical, i.e. weathering and exchange processes with the oceanic sediment are neglected. The model comprises the following prognostic ocean tracers: dissolved inorganic carbon (DIC), total Alkalinity (ALKA), phosphate (PO_4), oxygen (O_2), nitrate (NO_3), silicate ($SiOH_4$), phytoplankton (PHY), zooplankton (ZOO), dissolved organic carbon (DOC), particulate inorganic carbon (POC) and dissolved iron (Fe) supplied by the Aeolian dust input. According to Six and Maier-Reimer (1996)[29] a constant Redfield stoichiometry between organic carbon, nitrate, phosphate and oxygen was assumed. The growths rates of phytoplankton have been parameterized as a function of photosynthetically available radiation (PAR), temperature, mixed layer depth and the concentrations of micro (iron) and macro (phosphate, nitrate) nutrients, where only the scarcest nutrient available is regarded to be the limiting factor (Liebigs law).

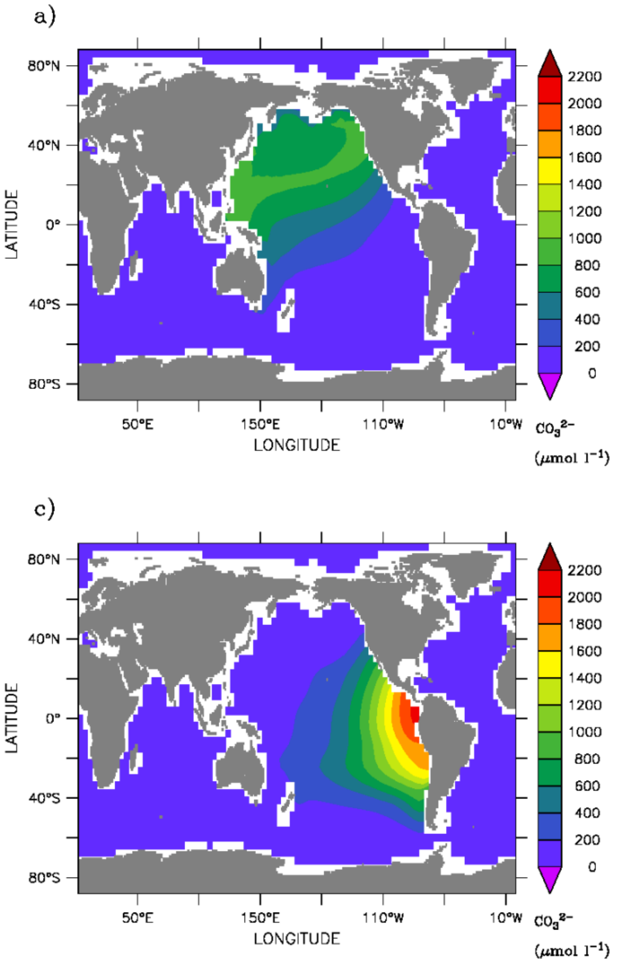

Figure 3: Distribution maps of CO$_3^{2-}$ and pH. (a) Distribution of CO$_3^{2-}$ concentrations at depth of about 700 m in μmol/L in year 2200 under the maximum liming of the Bering Sea region. (b) Distribution of pH values at depth of about 700 m in μmol/L in year 2200 under the maximum liming of the Bering Sea region. (c) The same as in (a) but for the region off Peru. (d) The same as in (b) but for the region off Peru.

Vertical sinking of POC and mineral ballast (biogenic calcite and opal) below the 100 m horizon in steady-state is prescribed by an exponential with depth declining function[26]. Across the sea surface the ocean can exchange CO$_2$ with a well-mixed atmospheric box. The air-sea gas-exchange of CO$_2$ is parameterized according to Wanninkhof *et al.* (1992)[30] while the CO$_2$ solubility and the carbonate system equilibrium constants were taken from Dickson *et al.* 1994[31]. A more detailed description of our model referred to as POTSMOM-C is given in Hofmann and Schellnhuber (2009)[26].

Experimental design

Our numerical experiments cover the time frame between years 1800 and 2200. Here we utilize the atmospheric anomalies of temperature, precipitation, relative humidity and sea level pressure resulting from an anthropogenically forced climate simulation as in Kuhlbrodt *et al.* (2009)[32] - based on the business-as-usual emission scenario A1FI - who employed a fully coupled Earth system model of intermediate complexity (CLIMBER-3α)[33]. The wind stresses were kept constant, i.e. we only used forcing data from NCEP/NCAR[27] even for the transient simulations.

In order to be consistent with the climate simulation by Kuhlbrodt *et al.* (2009)[32] anthropogenic CO$_2$ was released between years 1800 and 2000 into the atmospheric box at rates inferred from reconstructions[34], while during 2001 and 2100 emission rates provided by the IPCC's SRES A1FI scenario[3] were utilized. During subsequent years we assume a linear

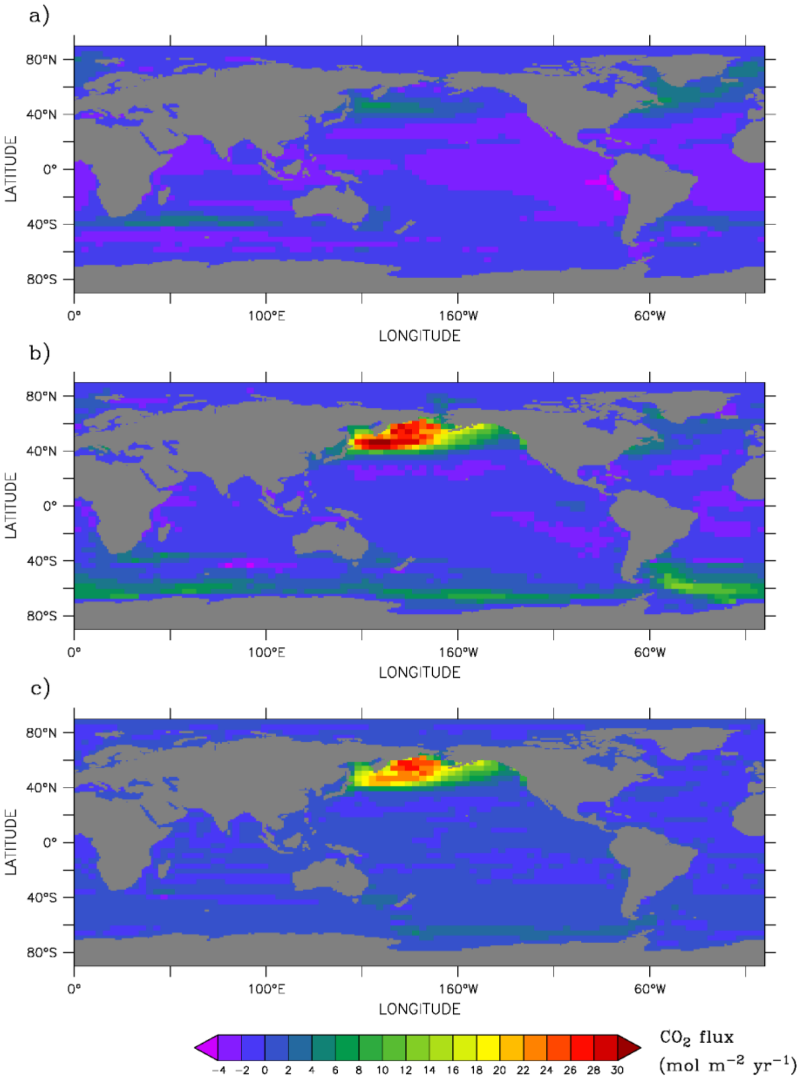

Figure 4: Air to sea flux of CO_2 in mol C m^{-2} $year^{-1}$ in year 2000 (a), and year 2200 (b) under maximum liming of the Bering Sea. (c) depicts the isolated contribution of liming to the air-sea CO_2 flux.

decline of emission rates to zero until year 2200. This corresponds to an emission of anthropogenic CO_2 of 4075 Pg C in total.

We have conducted two series of three model runs assuming an annual supply of 0.083, 8.333, and 83.333 Pg $CaCO_3$ corresponding to 0.01, 1.0, and 10.0 Pg C respectively during years 2015 until 2115 at two different upwelling regions in the Pacific Ocean located near coastal areas. Sites were chosen to mimic potential advantages to technical deployment which were associated with proximity to land and upwelling regions. The first location chosen was the Bering Sea (172.5° W, 56.25° N) and the second site the upwelling region in the Equatorial East Pacific off Peru (83.75° W, 0°). In our simulations we did not apply a sophisticated model of vertical particle sinking and dissolution as in the study by Harvey (2008)[22]. Although it must be regarded as a caveat, we mimic optimal supply of limestone by a corresponding input of DIC and total alkalinity at a fixed depth of 700 m, assuming immediate dissolution of limestone. Each mole of dissolving $CaCO_3$ increases the DIC content by one mole and the total alkalinity by two units[35], which results in a corresponding increase in the concentrations of CO_3^{2-} and an increase in the pH value. It is important to note that, in contrast to the model by Harvey (2008)[22] which only simulates vertical transport in the water column, POTSMOM-C allows to simulate the full three dimensional transport of any tracer.

Results and discussion

In steady-state, after a model spin-up over more than 6000 years, the atmospheric pCO_2 level equilibrates at about 282 μatm while net primary production of phytoplankton and export production of POC amounts to about 43.0 and 8.6 Pg C year^{-1} respectively, values comparable to observational estimates[36, 37, 38]. This initial state defines the models preindustrial climatological state in the year 1800.

Unbridled anthropogenic CO_2 emissions in the untreated case (without liming), following the scenario prescribed above (see Fig. 1a) lead to steadily increasing atmospheric pCO_2 levels which grow to a maximum of 1750 μatm in year 2200 (see Fig. 1 b). Global mean sea surface temperatures are projected to increase by 7.9 °C with a concomitant decline in the sea surface pH value by approximately 0.7 units until year 2200.

Liming of the Bering Sea and the upwelling region off Peru between years 2015 and 2115 with rates given above leads to measurable results in atmospheric pCO_2 drawdown only in case of the supply of an equivalent of 10 Gt C year^{-1}. As found in our numerical experiments, a lesser rate of limestone input would hardly offset unabated future anthropogenic CO_2 emissions (see Fig. 1d). For liming rates of equivalents of 0.01, and 1.0 Gt C year^{-1} the atmospheric pCO_2 drawdown reveals only values of less than 10 μatm at the end of our simulation. In case of a maximum liming, the atmospheric pCO_2 level would be reduced by approximately 100 μatm in year 2200 compared to the untreated case.

Since the extra CO_3^{2-} ions released by liming are added in the mesopelagic zone at depths of about 700 m, there is a time retardation between the moment of the first $CaCO_3$ supply and the beginning of the uptake of extra CO_2 by the ocean. In order to take effect the CO_3^{2-} enriched water masses need to be upwelled to the sea surface. As can be inferred from Figure 1 c, a recognizable CO_2 uptake by the ocean starts only several decades after year 2015.

From the Hovmoeller diagram (Figure 2 a and c) depicting the time evolution of the CO_3^{2-} concentrations within the water column at sites of limestone addition it becomes clear that an appreciable amount of CO_3^{2-} enriched water resurfaces not before year 2100. Our simulation also reveals that most of the extra CO_3^{2-} is transported laterally by advection and diffusion away from the input (and upwelling) location (Fig. 3 a and c), strongly weakening, the expected effect of atmospheric pCO_2 drawdown at the sea surface.

Figure 4 illustrates the impact of liming on the air to sea flux of atmospheric CO_2 in the Bering Sea. While the sea surface CO_3^{2-} concentration between years 2015 and 2115 increases the average carbon flux is enlarging from about zero to 20 mol C m^{-2} year^{-1} (Fig. 4a and b).

In order to crudely assess the efficiency of the method, the theoretical assumption could be made that one mole of $CaCO_3$ can take up one mole of CO_2 when diluting in water. However, because of the buffering properties of the ocean carbonate system this number must be multiplied by 0.6 under present day conditions[39]. From this, a cumulative limestone dissolution of an equivalent of 1000 Gt C could lead to a maximum carbon uptake from the atmosphere of about 600 Gt C, corresponding to approximately 280 μatm reduction in pCO_2. Since most of the extra CO_3^{2-} remains in the deep ocean, the efficiency of this method is even lower. Our model simulation results in only one third (about 100 μatm) of the expected atmospheric pCO_2 reduction.

The most important and presumably most dangerous side effect of reducing the atmospheric pCO_2 from 1750 to 1650 μatm is a tremendous increase in the oceans pH values at intermediate depth (see Fig. 2c and e). The accumulation of carbonate ions at the liming sites entails an increase of pH values from 7.8 in year 2000 to 10.0 in year 2115. Moreover, water masses carrying elevated pH values will spread across the whole basin of the Pacific Ocean (see Fig. 3 b and d) potentially threatening the health and life of all marine organisms. Responses of calcifying organisms to changes in ocean pH have been subject to investigation in recent years (e.g.[40, 41]) and proposals to sequester CO_2 in the deep ocean have motivated a broadening of the scope onto other marine organisms (e.g.[42,43,44]). Still, no data exists for gelatinous zooplankton[45]. Pörtner et al. (2004)[42] report acute sensitivity to decreases in pH in pelagic squid and higher tolerance in fish, due to species-specific capacity in extracellular acid-base regulation. Probably owing to the absence of such regulatory mechanisms, copepods exhibit increasing mortality rates with longer exposure period, although deep-living species appear to be more tolerant[46]. Thus, although little is still known about responses of many important taxa[45], extracellular acid-base regulation capacity has been suggested to determine species-specific sensitivities to changes in pH, and is further hypothesized to depend on the mode of life and habitat, with hypometabolic organisms (typically of the deep sea) exhibiting highest sensitivity[47]. Observations indicate that these compensatory mechanisms are associated with changes in energy use and allocation and thus imply potentially harmful long-term consequences for growth and reproduction on species, population and ecosystems levels[48].

To date, most experiments have focussed on physiological responses to increases in pCO_2 and decreases in pH values. While growth rates of various marine phytoplankton species have been shown to be limited by CO_2 availability under elevated pH values[49], to our knowledge virtually no information on sensitivities of mesopelagic taxa to increases in pH is available. It is however plausible to hypothesize similar responses as mentioned above, because acid-base regulation functions as a compensatory mechanism to changes in extracorporeal in relation to intracorporeal pH-levels.

However, this hypothesis represents as an optimistic best case. Increases in pH at rates associated with anthropogenically liming the ocean significantly exceed rates recorded in Earth history[50]. It is therefore unlikely that the evolutionarily developed adaptive processes of acid-base regulation will respond efficiently to a rapid rise of pH-values and enable marine organisms to adapt, even at high energy costs. Furthermore, differing sensitivities and mobility would further affect food availability, resulting in impacts on food-web interactions and ecosystem structure. Steadily increasing temperatures will continue to add another stressor to marine organisms, potentially further increasing sensitivity to pH changes[12].

Conclusions

Our study reveals that an input to the oceans localized in the Bering Sea and the upwelling area off Peru of 83.33 Pg $CaCO_3$ (10 Pg C) per year between 2015 and 2115 would be necessary to reduce the atmospheric pCO_2 level from 1750 to 1650 μatm by year 2200. This amount exceeds the worldwide production of lime stone in year 2006 by more than a factor of 3. In contrast to the study by Harvey (2008)[17], in our model lateral advection and isopycnal diffusion transports the extra carbonate ions rapidly away from the injection site, greatly diminishing the efficiency of CO_2 drawdown. As a result, carbonate enriched intermediate waters resurface approximately 50 to 100 years after injection.

Furthermore, addition of carbonate ions via dissolving limestone that would result in drawdown of pCO_2 of 100 μatm would increase the pH value at the injection site by up to 2.5 units. Environmental impacts thereof are unknown. However, as marine organisms are not evolutionary adapted to rates of changes similar to rates associated with anthropologically liming the ocean, impacts are likely to be severe and potentially outweigh avoided impacts of climate change. Liming the ocean is thus not a feasible climate engineering option.

Acknowlwdgements

M. Hofmann was supported by the Deutsche Forschungsgemeinschaft (DFG), reference number RA 977/5-2.

Notes and references

[a] *Potsdam Institute for Climate Impact research, Telegraphenberg A62, D-14473 Potsdam, Germany. Fax: ++49 331 288 2570; Tel: ++49 331 288 2567; E-mail: hofmann@pik-potsdam.de*

[b] *Physics Institute, Potsdam University, Potsdam, Germany*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1 J.J. Blackstock and J.C.S. Long, *Science* 2010 **327**, 527;

2 Royal Society (2009) *Geoengineering the climate: science, government and uncertainty*. The Royal Society, London

3 N. Nakicenovic and R. Swart, 2000, IPCC *Special Report on Emissions Scenarios*, Cambridge Univ. Press, UK

4 EU Commission, Mining, metals and minerals.
Lime, 2011, available for download at
http://ec.europa.eu/enterprise/sectors/metals-minerals/non-metallic-mineral-products/lime/index_en.htm

5 J. G. Canadell, C. LeQuere, M. R. Raupach, C. B. Field, E. T. Buitenhuis, P. Ciais, T. J. Conway, N. P. Gillett, R. A. Houghton and G. Marland, *Proc. Natl. Acad. Sci.U. S. A.*, 2007, **104**, 18866-18870

6 *IPCC climate change 2007: The phisical science basis. Contribution of working group I to the fourth assessment report of the Intergovernmental Panel on Climate Change*, ed. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor and H. L. Miller, Cambridge University Press, 2007

7 J. Schewe, A. Levermann, M. Meinshausen, *Earth System Dynamics* 2011, **2**,25

8 C. L. Sabine, R. A. Feely, N. Gruber, R. M. Key, K. Lee, J. L. Bullister, R. Wanninkhof, C. Wong, D. W. R. Wallace, B. Tilbrook, F. J. Millero, T.-H. Peng, A. Kozyr, T. Ono and A. F. Rios, *Science*, 2004, **305**, 367-371

9 C. LeQuere, C. Rödenbeck, E. T. Buitenhuis, T. J. Conway, R. Langenfelds, A. Gomez, C. Labuschagne, M. Ramonet, T. Nakazawa, N. Metzl, N. Gillett, and M. Heimann, *Science*, 2007, **316**, 1735-1738

10 C. Caldeira and M. E. Wickett, *Nature*, 2003, **425**, 365

11 J. C. Orr, V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfray, A. Mouchet, R. G. Najjar, G.-K. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M.-F. Weirig, Y. Yamanaka, and A. Yool, *Nature*, 2005, **437**, 681-686

12 M. Hofmann and H. J. Schellnhuber, *Energy Environ. Sci*., 2010, **3**, 1883-1896

13 J. H. Martin, R. M. Gordon, and S. E. Fitzwater, *Nature*, 1990, **345**, 156-158

14 S. W. A. Naqvi and V. Smetacek, In « Oceans : The new frontier, eds. By : Jacquet, P. ; Pachauri, R. K. ; Tubina, L. » TERI Press ; New Delhi ; India ; 2011 ; 197-206

15 P. Köhler, J. Hartmann, and D. A. Wolf-Gladrow, 2010, *Proc. Natl. Acad. Sci.U. S. A.*, **107**, 20228-20233

16 P. J. Crutzen, *Climatic Change*, 2006, **77**, 211-220

17 V. Brovkin, V. Petoukhov, M. Claussen, E. Bauer, D. Archer, C. Jaeger, *Climatic Change*, 2009, **92**, 243

18 H. D. Matthews, L. Cao, and K. Caldeira, *Geophys. Res. Lett.*, 2009, **36**, L10706, doi :10.1029/2009GL037488

19 G. H. Rau, K. G. Knauss, W. H. Langer, and K. Caldeira, *Energy*, 2007, **32**, 1471-1477

20 K. Caldeira and G. H. Rau, *Geophys. Res. Lett*., 2000, **27**, 225-228

21 G. H. Rau and K. Caldeira, *Energy Conversion and Management*, 1999, **40**, 1803-1813

22 L. D. D. Harvey, 2008, *J. Geophys. Res.*, **113**, C04028, doi :10.1029/2007jc004373

23 M. Hofmann and M. A. M. Maqueda, 2006, *J. Geophys. Res.*, **111**, C05006, doi :10.1029/2005JC003279

24 R. C. Pacanowski and M. S. Griffies, 2000, MOM 3.0 Manual

25 T. Fichefet and M. A. M. Maqueda, 1997, *J. Geophys. Res.*, **102**, 12609-12646

26 M. Hofmann and H. J. Schellnhuber, 2009, *Proc. Natl. Acad. Sci.U. S. A.*, **106**, 3017-3022

27 E. Kalnay, M. Kanamitsu, R. Kistler, W. Collins, D. Deaven, L. Gandin, M. Iredell, S. Saha, G. White, J. Woollen, Y. Zhu, M. Chelliah, W. Ebisuzaki, W. Higgins, J. Janowiak, K. C. Mo, C. Ropelewski, J. Wang, A. Leetmaa, R. Reynolds, R. Jenne, and D. Joseph, 1996, *Bull. Amer. Meteorol. Soc.*, **77**, 437-471

28 H. Hasumi and N. Suginohara, 1999, *J. Geophys. Res.*, **104**, 23367-23374

29 K. Six and E. Maier-Reimer, 1996, *Global Biogeochem. Cycles*, **10,** 559-583

30 R. Wanninkhof, 1992, *J. Geophys. Res.*, **97**, 7373-7382

31 DOE, 1994, eds., A. Dickson and C. Goyet (ORNL/CDIAC-74)

32 T. Kuhlbrodt, S. Rahmstorf, K. Zickfeld, F. Vikerbo, S. Sundby, M. Hofmann, P. M. Link, A. Bondeau, W. Cramer, and C. Jaeger, 2009, Clim. Change, 96, 489-537

33 M. Montoya, A. Griesel, A. Levermann, J. Mignot, M. Hofmann, A. Ganopolski, and S. Rahmstorf, 2005, *Clim. Dyn.*, **25**, 237-263

34 G. Marland , T. A. Boden , R. J. Andres , 2007, *Global, regional, and national fossil fuel CO2 emissions in trends: A compendium of data on global change* (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy Oak Ridge, Tenn., U.S.A., Oak Ridge, Tenn., U.S.A.), Technical Report

35 R. Zeebe and D. A. Wolf-Gladrow, 2001, *CO_2 in seawater: Equilibrium, kinetics, isotopes*, Elsevier, Amsterdam

36 B. Schneider, L. Bopp, M. Gehlen, J. Segschneider, T. L. Frölicher, P. Cadule, P. Friedlingstein, S. C. Doney, M. J. Behrenfeld, and F. Joos, 2008, *Biogeosciences*, **5**, 597-614

37 R. G. Najjar, X. Jin, F. Louanchi, O. Aumont, K. Caldeira, S. C. Doney, J. C. Dutay, M. Follows, N. Gruber, F. Joos, K. Lindsay, E. Maier-Reimer, R. J. Matear, K. Matsumoto, P. Monfray, A. Mouchet, J. C. Orr, G.-K Plattner, J. L. Sarmiento, R. Schlitzer, R. D. Slater, M. F. Weirig, Y. Yamanaka, and A. Yool, 2007, Global Biogeochem. Cycles, 21, doi :10.1029/2006GB002857

38 K. Matsumoto et al., 2004, Geophys. Res. Lett., 31, L07303, doi:/10.1029/2003GL018970

39 M. Frankignoulle, C. Canon, and J. P. Gattuso, 1994, *Limnol. Oceanogr.*, **39**, 458-462

40 U. Riebesell, I. Zondervan*, B. Rost*, P. D. Tortell, R. E. Zeebe, F. M. M. Morel, 2002 *Nature*, **407**, 364

41 M.D. Iglesias-Rodriguez et al. 2008, *Science*, **320**, 336

42 H. O. Pörtner, M. Langenbuch and A. Reipschläger, *Journal of Oceanography*, 2004, **60**, 705

43 A. Ishimatsu, T. Kikkawa, M. Hayashi, K.-S. Lee and J. Kita, *Journal of Oceangprahy*, 2004, **60**¸731

44 T. Kikkawa, J. Kita, A. Ishimatsu, *Marine Pollution Bulletin*, 2004, **48**, 108

45 V. J. Fabry, B. A. Seibel, R. A. Feely and J. C. Orr, *ICES Journal of Marine Science*, 2008, **65**, 414

46 Y. Watanabe, A. Yamaguchi, H. Ishida, T. Harimoto, S. Suzuki, Y. Sekido, T. Ikeda, Y. Shirayama, M. Mac Takahashi, T. Ohsumi, J. Ishizaka, *Journal of* Oceanography, 2006, **62**, 196

47 H.-O. Pörtner, *Marine Ecology Progress Series*, 2008, **373**, 203

48 H.-O. Pörtner, M. Langenbuch, B. Michaelidis, *J. Geophys. Res*, 2005 **110**, C09S10

49 L. T. Bach, U. Riebesell and K. G. Schulz, *Limnol. Oceanogr.*, 2011, **56**, 2040

50 P. N. Pearson and M. R. Palmer, *Nature*,2000, **406**, 695