

Anthropogenic carbon and ocean pH

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Most fossil-fuel CO₂ released to the atmosphere will eventually be absorbed by the ocean¹ with potentially adverse consequences for marine biota²⁻⁴. We quantify pH changes that may result from continued release of fossil-fuel CO₂ to the atmosphere, and compare these with pH changes inferred from geological and historical records. We conclude that releasing fossil-fuel CO₂ to the atmosphere over several centuries may result in ocean pH changes greater than any inferred from the geologic record of the past 300 million years, with the possible exception of rare extreme events such as bolide impacts or catastrophic methane hydrate degassing.

When carbon dioxide dissolves in the ocean it increases the hydrogen-ion concentration, lowering ocean pH (i.e., negative common log of the hydrogen ion activity). Due to a paucity of relevant observations, we have a limited understanding of the effects of pH reductions on marine biota. Coral reefs², calcareous plankton³, and other organisms with calcium carbonate skeletal material or shells may be particularly impacted by decreased ocean pH. Most biota resides primarily near the surface where greatest pH change can be expected to occur, but deep ocean biota may be more sensitive to pH changes⁴.

To study effects of CO₂ emissions on ocean pH, we forced the LLNL ocean general circulation model⁵ with observed atmospheric pCO₂ from 1975 to 2000 and with CO₂ emissions from the IPCC IS92a scenario¹ from year 2000 to 2100. Beyond 2100, emissions from burning fossil fuel resources (F) are described with a logistic function (Fig. 1) implying fossil fuel resources⁶ of 5000 GtC in year 2000. Maximum simulated atmospheric CO₂ concentration exceeds 1900 ppm near year 2300. Maximum ocean pH decrease is 0.77 near the surface (Fig. 1), based on horizontally averaged ocean chemistry. We estimate, using the geochemical model^{7,8} described below, that consideration of changes in temperature, weathering, and sedimentation would reduce this maximum decrease by <10%.

A review⁹ of estimates of paleo-atmospheric CO₂ concentration from geochemical models, paleosols, algae and forams, plant stomata, and boron isotopes concluded that there is no evidence that concentrations exceeded 7,500 ppm or were less than 100 ppm over the past 300 myr. In addition, the highest concentrations inferred from the geologic record were thought to have developed over many millions of years as a result of slow processes involving tectonics and biological evolution. On these time scales, ocean chemistry is buffered by interaction with carbonate minerals¹⁰.

We estimated the effect of these past changes in atmospheric CO₂ on ocean pH with a simple three-box ocean model embedded in a model of the long term carbonate-silicate cycle^{7,8}. Modeled processes include weathering of carbonate and silicate minerals on land, production of shallow-water carbonate minerals, production and oxidation of biogenic organic carbon, production and dissolution of biogenic carbonate minerals in the ocean, air-sea gas exchange of carbon, and transport by advection, mixing, and biology.

In a series of simulations, atmospheric pCO₂ was increased linearly from the pre-industrial value (~280 ppm) to a stabilization value ranging from 100 ppm to 10,000 ppm

over time intervals ranging from 10 yr to 10^7 yr. For each model simulation, we recorded maximum predicted pH perturbation in for the surface ocean boxes (Fig. 2). If it occurs over several hundred thousand years or more, an increase in atmospheric CO₂ to 7,500 ppm decreases ocean pH by ~0.6 units.

Based on the record⁹ of atmospheric CO₂ over the past 300 myr and our geochemical model^{7,8}, we conclude that there is no evidence that ocean pH was more than 0.6 units lower than today. Our GCM results indicate that continued fossil-fuel burning with atmospheric CO₂ release could lead to pH decreases of ~0.7 units. Thus, we conclude that unabated CO₂ emissions over the next several hundred years may produce changes in ocean pH greater in magnitude than any experienced in the past 300 myr, with the possible exception of rare catastrophic events in Earth history^{7,11}.

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Acknowledgements This research was supported by the DOE Office of Science Office of Biological and Environmental Research Ocean Carbon Sequestration Research Program. This work was performed under

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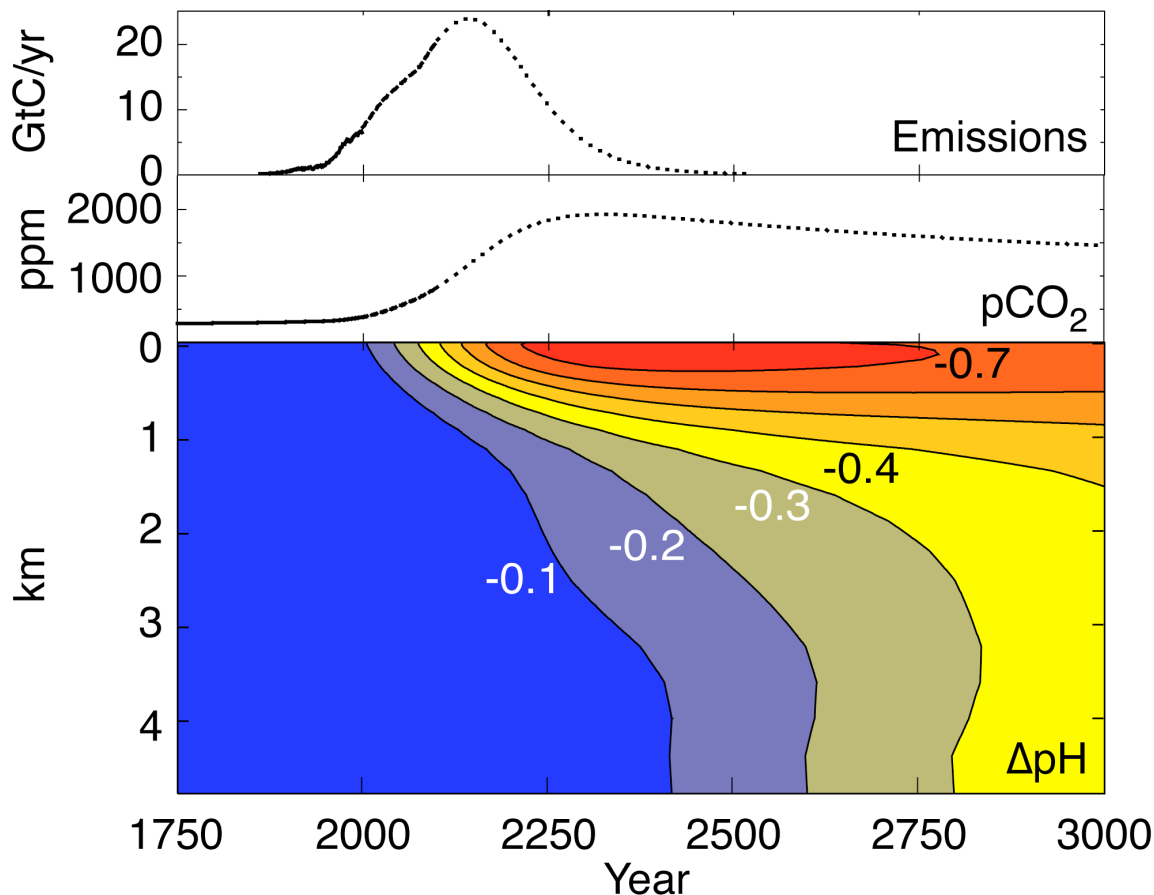


Figure 1. (top) Historical CO₂ emissions¹³ to year 2000, IS92a CO₂ emissions to year 2100, and emissions after 2100 burning remaining fossil fuels⁶ according to the logistic formula, $dF/dt = (-2.92 \times 10^5 \text{ GtC yr}^{-1} F(t) [(5270 \text{ GtC}) - F(t)])$. **(center)** Historical atmospheric CO₂ and CO₂ predicted from this emissions scenario. CO₂ levels rise from the pre-industrial value of 280 ppm to a maximum of >1900 ppm near year 2300. **(bottom)** Horizontally averaged ocean pH is predicted to decrease by more than 0.7 units near the surface. By the end of the millennium, deep-ocean pH is reduced more than 0.3 units.

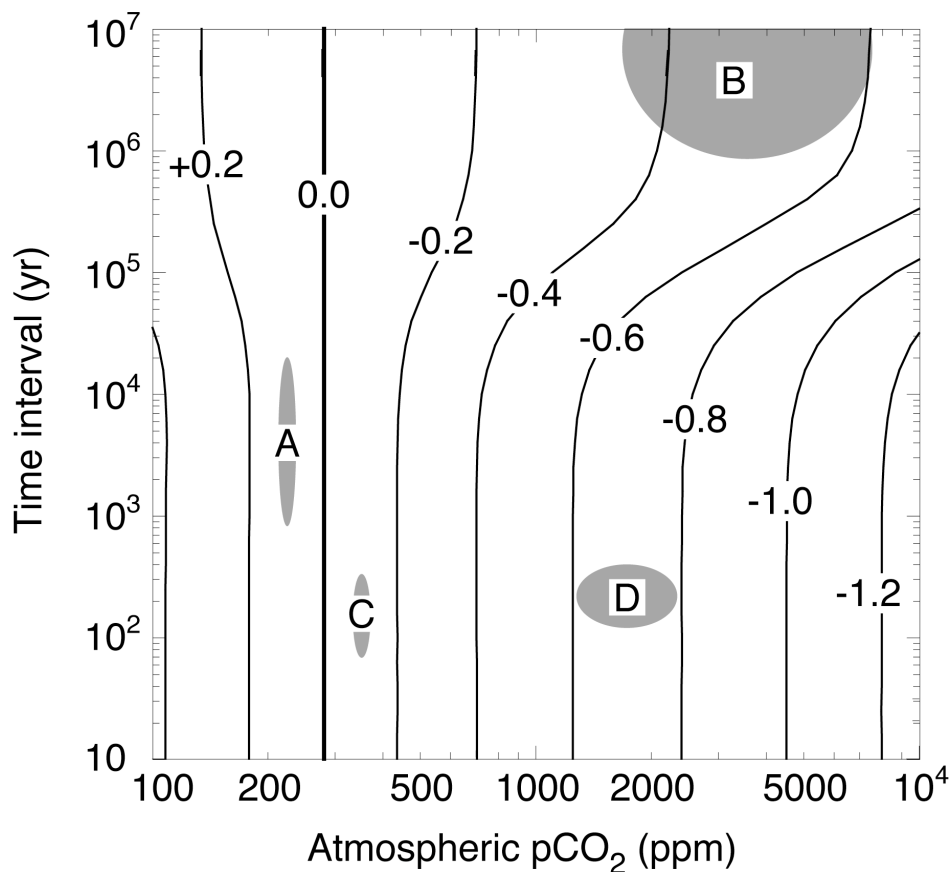


Figure 2. Estimated maximum surface ocean pH change as a function of final atmospheric pCO₂ and the transition time in which this pCO₂ is linearly approached from an initial "pre-industrial" condition of 280 ppm: (A) glacial-interglacial CO₂ changes¹², (B) long-term changes⁹ over the past 300 myr, (C) historical changes¹ in ocean surface waters, (D) unabated fossil-fuel burning over the next few centuries. When a CO₂ change occurs over a short time interval (i.e., < ~10⁴ yr), ocean pH is relatively sensitive to added CO₂. However, when a CO₂ change occurs over a long time interval (i.e., > ~10⁵ yr), ocean chemistry is buffered by interactions with carbonate minerals, lowering pH sensitivity⁷.