Surface pH, its mechanisms, and future projections in the global ocean

Li-Qing Jiang$^{1,2}$, Richard A. Feely$^3$, and Brendan Carter$^3$

Outline
* Background + Method
* pH distribution + mechanism
* Decadal change
* Projected pH in the 21st Century
Global Carbon Budget (2006-2015)

Global carbon dioxide budget (gigatones of carbon dioxide per year) 2006-2015

- **Fossil fuels & Industry**: 34.1 ± 1.7 GtCO₂/yr
- **Atmospheric growth**: 16.4 ± 0.4 GtCO₂/yr
- **Land-use change**: 3.5 ± 1.8 GtCO₂/yr
- **Land sink**: 11.5 ± 3.1 GtCO₂/yr
- **Ocean sink**: 9.7 ± 1.8 GtCO₂/yr

**Budget Breakdown**

- **34.1 GtCO₂/yr**: 91%
- **3.5 GtCO₂/yr**: 9%
- **16.4 GtCO₂/yr**: 44%
- **11.6 GtCO₂/yr**: 31%
- **9.7 GtCO₂/yr**: 26%

Source: CDIAC; NOAA-ESRL; Le Quéré et al 2016; Global Carbon Budget 2016

Data: CDIAC/NOAA-ESRL/GCP
Ocean acidification

Carbon dioxide ($\text{CO}_2$) combines with water ($\text{H}_2\text{O}$) to form carbonic acid ($\text{H}_2\text{CO}_3$), which dissociates into hydrogen ions ($\text{H}^+$) and bicarbonate ions ($\text{HCO}_3^-$). Hydrogen ions can also react with carbonate ions ($\text{CO}_3^{2-}$) to form bicarbonate ions ($\text{HCO}_3^-$).

Aragonite

Such as calcareous algae and coral reef.

Calcite

Such as Foraminifera and coccolithophorids.
Calcium carbonate saturation state

Global Biogeochemical Cycles
AN AGU JOURNAL

Research Article

Climatological distribution of aragonite saturation state in the global oceans

Li-Qing Jiang, Richard A. Feely, Brendan R. Carter, Dana J. Greeley, Dwight K. Gledhill, Krisa M. Arzayus

First published: 13 October 2015  Full publication history
DOI: 10.1002/2015GB005198  View/save citation
We extracted data that meet the below criteria from GLODAPv2:
- Depth <=20 m
- Contains both DIC and TA
- Salinity>=30

Further QC by removing clear outliers (e.g., data with DIC>TA).
pH calculation

- For stations with missing silicate and phosphate data, they were filled in by extracting from the nearest grid of the GLODAPv2 climatologies (Lauvset et al. 2016).

- pH is then calculated from in-situ temperature, salinity, pressure, DIC, TA, silicate and phosphate using a MATLAB version [van Heuven et al., 2009] of the CO2SYS program [Lewis and Wallace, 1998].
  - the dissociation constants for carbonic acid of Lueker et al. [2000]
  - potassium bisulfate (KHSO$_4^-$) of Dickson [1990a]
  - boric acid of Dickson [1990b]
  - total borate concentration equations of Uppstrom [1974]
**Seasonal pH correction**

**Issue:** Data are collected from different time of the year with a bias towards summer.

- SST in February and August 2000 are extracted from an SST atlas that is based on data collected from 1995 to 2004 (World Ocean Atlas 2013 version 2, Boyer et al. 2013)

- pH data was first corrected to the year of 2000, assuming constant TA and oceanic CO₂ increases at the same rate as the atmospheric CO₂.

- pH was then corrected to February and August based on this seasonal correction model.

A seasonal pH model was derived based on time-series OA monitoring from European Station for Time series in the ocean (ESTOC).
Aragonite and calcite in the surface ocean

Latitude
Longitude

Aragonite
Calcite
pH in the surface ocean

pH at Total Scale
Surface pH vs. SST

- Surface pH shows a weak negative relationship with SST, while saturation is positively correlated.

- Surface pH does not correlate with aragonite saturation state much.
SST effect I: Controls TA/DIC of surface water

- Temperature can change CO₂ solubility and influence exchange of carbon with the atmosphere or the surrounding water and changes the ratio of TA/DIC.

- For a body of water, colder temperature enables the water to absorb more CO₂, hence higher DIC, in order to maintain the same pCO₂ level.
The relative amounts of $\text{CO}_2(\text{g})$, $\text{H}_2\text{CO}_3$, $\text{HCO}_3^-$, $\text{CO}_3^{2-}$, and subsequently the pH in a body of water changes as temperature shifts.
Combined SST effect on surface pH

- pH does not show much latitudinal variations, although saturation state does.

- pH is NOT a good indicator for carbonate ion, and saturation state in the surface ocean.
**Decadal pH change**

- Not enough data to cover the globe in two decades. We plotted all data before 2000 and after 2000.

- pH shows clear decrease in the equatorial region, north Pacific, and Southern Ocean.
Assumption I: Total alkalinity remains constant.

Assumption II: Sea surface pCO$_2$ increases at the same rate as atmospheric CO$_2$ under the IPCC business as usual scenario (RCP 8.5).

Assumption III: SST increases at a rate of 0.15 °C per decade at the beginning of the 21$^{st}$ Century and linearly increased to 0.40 °C per decade at the end of the Century.
pH in 2010

pH at Total Scale

Latitude

Longitude

2010
pH in 2020

pH at Total Scale
pH in 2030

pH at Total Scale

February

August
pH in 2040

pH at Total Scale

February

August
pH in 2050

pH at Total Scale

[Map showing pH distribution in 2050 for February and August]
pH in 2060

pH at Total Scale
pH in 2070

pH at Total Scale

February

August
pH in 2090

pH at Total Scale

February 20 °E 60 °E 100 °E 140 °E 180 ° 140 °W 100 °W 60 °W 20 °W 20 °E

90 °S

60 °S

30 °S

0 °

30 °N

60 °N

90 °N

Longitude

September 20 °E 60 °E 100 °E 140 °E 180 ° 140 °W 100 °W 60 °W 20 °W 20 °E

90 °S

60 °S

30 °S

0 °

30 °N

60 °N

90 °N

Latitude

2090

2090
pH in 2100

pH at Total Scale

Latitude

Longitude

February

August
- pH change from 2000 to 2100

- On a percentage basis, hydrogen ion increases ~8.5% per decade, pH drops about ~0.45% per decade.

- pH change from 2000 to 2100 falls between -0.45 and -0.3.

- A mean pH drop of -0.36 (median:-0.36), which translates to an hydrogen ion increase of 130%.

- pH drop is smallest in the equatorial region and greatest towards the poles.
Spatial distribution of pH change from 2000 to 2100