Ocean Acidity

Identification

1. Indicator Description

This indicator shows recent trends in acidity levels in the ocean at four key locations. The indicator also presents changes in aragonite saturation by comparing historical data with the most recent decade. Ocean acidity and aragonite saturation levels are strongly affected by the amount of carbon dissolved in the water, which is directly related to the amount of carbon dioxide (CO_2) in the atmosphere. Acidity affects the ability of corals, some types of plankton, and other creatures to produce their hard skeletons and shells. This indicator provides important information about an ecologically relevant effect associated with climate change.

Components of this indicator include:

- Recent trends in ocean CO_2 and acidity levels (Figure 1)
- Historical changes in the aragonite saturation of the world's oceans (Figure 2)

2. Revision History

April 2010:   Indicator published.
May 2014:   Updated Figure 1 with data through 2012 for two sampling locations; updated Figure 2 with data through 2013.
August 2016:   Updated Figure 1 with data through 2014 for Hawaii and 2015 for Bermuda; updated Figure 2 with data through 2015.
April 2021:   Updated Figure 1 with data through 2018 for Hawaii and added Cariaco Basin as a site with data through 2017.
June 2024:   Updated Figure 1 with data through 2022 for Hawaii.

Data Sources

3. Data Sources

Figure 1 includes trend lines from four different ocean time series: the Bermuda Atlantic Time-Series Study (BATS); the European Station for Time-Series in the Ocean, Canary Islands (ESTOC); the Carbon Retention In a Colored Ocean (CARIACO) Program; and the Hawaii Ocean Time-Series (HOT). Data from these stations have been used in numerous peer-reviewed publications—for example, Bates et al. (2014).

Figure 2 contains aragonite saturation (Ω_{ar}) calculations derived from atmospheric CO_2 records from ice cores and observed atmospheric concentrations at Mauna Loa, Hawaii. These atmospheric CO_2 measurements are fed into the Community Earth Systems Model (CESM), maintained by the National Center for Atmospheric Research (NCAR). CESM is a dynamic ocean model that computes ocean CO_2 uptake and the resulting changes in seawater carbonate ion (CO_3^{2-}) concentration and Ω_{ar} over time.

4. Data Availability

Figure 1 compiles pCO₂ (the mean seawater CO₂ partial pressure in μatm) and pH data from four sampling programs in the Atlantic and Pacific Oceans and the Caribbean Sea. Raw data from the four ocean sampling programs are publicly available online. In the case of Bermuda and the Canary Islands, updated data were procured directly from the scientists leading those programs. BATS data and descriptions are available at: https://bats.bios.asu.edu/bats-data. CARIACO data can be found at: https://erddap.bco-dmo.org/erddap/tabledap/bcodmo_dataset_3093.htmlTable. ESTOC data can be downloaded from: https://plocan.eu/en/installations/ocean-observatory, although the ESTOC surface buoy stopped transmitting data after it was damaged in July 2010, and data access has been incomplete since then. HOT data were downloaded from the HOT Data Organization and Graphical System website at: https://hahana.soest.hawaii.edu/hot/hotco2/HOT_surface_CO2.txt. Additionally, annual HOT data reports are available at: https://hahana.soest.hawaii.edu/hot/reports/reports.html.

The map in Figure 2 comes from data that EPA obtained from Dr. Ivan Lima of the Woods Hole Oceanographic Institution (WHOI).

Methodology

5. Data Collection

Figure 1. Ocean Carbon Dioxide Levels and Acidity, 1983–2022

This indicator reports on the pH of the upper 5 meters of the ocean and the corresponding partial pressure of dissolved CO₂ (pCO₂). Each data set covers a different time period:

- BATS data used in this indicator are available from 1983 to 2015. Samples were collected from two locations in the Atlantic Ocean near Bermuda (BATS and Hydrostation S, at 31°43' N, 64°10' W and 32°10' N, 64°30' W, respectively). See: https://bats.bios.asu.edu/about.

- ESTOC data are available from 1995 to 2009. ESTOC is at 29°10' N, 15°30' W in the Atlantic Ocean.

- CARIACO data are available from 1995 to 2017. The CARIACO station is at 10.5° N, 64.67° W in the Caribbean Sea—specifically the Cariaco Basin off the coast of Venezuela.

- HOT data are available from 1988 to 2022. The HOT station is at 23° N, 158° W in the Pacific Ocean.

At the BATS and HOT stations, dissolved inorganic carbon (DIC) and total alkalinity (TA) were measured directly from water samples. DIC accounts for the carbonate and bicarbonate ions that occur when CO₂ dissolves to form carbonic acid, while total alkalinity measures the buffering capacity of the water, which affects the partitioning of DIC among carbonate and bicarbonate ions. At ESTOC and CARIACO, pH and alkalinity were measured directly—e.g., Bindoff et al. (2007).

Each station followed internally consistent sampling protocols over time. Bates et al. (2012) describe the sampling plan for BATS. Further information on BATS sampling methods is available at: https://bats.bios.asu.edu. ESTOC sampling procedures are described by González-Dávila et al. (2010). CARIACO procedures can be found at: www.st.nmfs.noaa.gov/copepod/time-series/ve-10101. HOT sampling procedures are described in documentation available at: https://hahana.soest.hawaii.edu/hot/hot_jgofs.html.

Figure 2. Changes in Aragonite Saturation of the World's Oceans, 1880–2015

The map in Figure 2 shows the estimated change in sea surface Ω_{ar} from 1880 to 2015. Aragonite saturation values are calculated in a multi-step process that originates from historical atmospheric CO_2 concentrations that are built into the model (the CESM). As documented in Orr et al. (2001), this model uses historical atmospheric CO_2 concentrations based on ice cores and atmospheric measurements (the latter collected at Mauna Loa, Hawaii).

6.   Indicator Derivation

Figure 1. Ocean Carbon Dioxide Levels and Acidity, 1983–2022

At BATS and HOT stations, pH and pCO_2 values were calculated based on DIC and TA measurements from water samples. BATS analytical procedures are described by Bates et al. (2012). HOT analytical procedures are described in documentation available at: https://hahana.soest.hawaii.edu/hot/hot_jgofs.html and: https://hahana.soest.hawaii.edu/hot/hotco2/HOT_surface_CO2_readme.pdf. At ESTOC, pCO_2 was calculated from direct measurements of pH and alkalinity. ESTOC analytical procedures are described by González-Dávila et al. (2010). CARIACO reported the fugacity of CO_2 (fCO_2), which EPA converted to pCO_2 using the seacarb package in R. The function to convert from fCO_2 to pCO_2 uses hydrostatic pressure, which EPA calculated by dividing the depth by 10.06 based on the pressure/depth relationship of 1 atmosphere to 10.06 meters. For all four locations, Figure 1 shows in situ measured or calculated values for pCO_2 and pH, as opposed to values adjusted to a standard temperature.

The lines in Figure 1 connect points that represent individual sampling events. No attempt was made to generalize data spatially or to portray data beyond the time period when measurements were made. Unlike some figures in the published source studies, the data shown in Figure 1 are not adjusted for seasonal variability. The time between sampling events is somewhat irregular at all four locations, so moving averages and monthly or annual averages based on these data could be misleading. Thus, EPA elected to show individual measurements in Figure 1.

Figure 2. Changes in Aragonite Saturation of the World's Oceans, 1880–2015

The map in Figure 2 was developed by WHOI using the CESM, which is available publicly at: www.cesm.ucar.edu/models. Atmospheric CO_2 concentrations were fed into the CESM, which is a dynamic ocean model that computes ocean CO_2 uptake and the resulting changes in seawater carbonate concentration over time. The CESM combines this information with monthly salinity and temperature data on an approximately 1° by 1° grid. Next, these monthly model outputs were used to approximate concentrations of the calcium ion (Ca^{2+}) as a function of salt (Millero, 1982), and to calculate aragonite solubility according to Mucci (1983). The resulting aragonite saturation state was calculated using a standard polynomial solver for MATLAB, which was developed by Dr. Richard Zeebe of the University of

Hawaii. This solver is available at:
www.soest.hawaii.edu/oceanography/faculty/zeebe_files/CO2_System_in_Seawater/csys.html.

Aragonite saturation state is represented as Ω_{ar}, which is defined as:

$$\Omega_{ar} = [Ca^{2+}][CO_3^{2-}] / K'_{sp}$$

The numerator represents the product of the observed concentrations of calcium and carbonate ions. K'_{sp} is the apparent solubility product, which is a constant that is equal to $[Ca^{2+}][CO_3^{2-}]$ at equilibrium for a given set of temperature, pressure, and salinity conditions. Thus, Ω_{ar} is a unitless ratio that compares the observed concentrations of calcium and carbonate ions dissolved in the water with the concentrations that would be observed under fully saturated conditions. An Ω_{ar} value of 1 represents full saturation, while a value of 0 indicates that no calcium carbonate is dissolved in the water. Ocean water at the surface can be supersaturated with aragonite, however, so it is possible to have an Ω_{ar} value greater than 1, and it is also possible to experience a decrease over time, yet still have water that is supersaturated.

For Figure 2, monthly model outputs were averaged by decade before calculating Ω_{ar} for each grid cell. The resulting map is based on averages for two decades: 1880 to 1889 (a baseline) and 2006 to 2015 (the most recent complete 10-year period). Figure 2 shows the change in Ω_{ar} between the earliest (baseline) decade and the most recent decade. It is essentially an endpoint-to-endpoint comparison, but using decadal averages instead of individual years offers some protection against inherent year-to-year variability. The map has approximately 1° by 1° resolution.

7. Quality Assurance and Quality Control

Quality assurance and quality control (QA/QC) steps are followed during data collection and data analysis. These procedures are described in the documentation listed in Sections 5 and 6.

Analysis

8. Comparability Over Time and Space

Figure 1. Ocean Carbon Dioxide Levels and Acidity, 1983–2022

BATS, ESTOC, HOT, and CARIACO each use different methods to determine pH and pCO_2, though each individual sampling program uses well-established methods that are consistent over time.

Figure 2. Changes in Aragonite Saturation of the World's Oceans, 1880–2015

The CESM calculates data for all points in the Earth's oceans using comparable methods. Atmospheric CO_2 concentration values differ in origin depending on their age (i.e., older values from ice cores and more recent values from direct atmospheric measurement); however, all biogeochemical calculations performed by the CESM use the atmospheric CO_2 values in the same manner.

9. Data Limitations

Factors that may impact the confidence, application, or conclusions drawn from this indicator are as follows:

1. Carbon variability exists in the surface layers of the ocean as a result of biological differences, changing surface temperatures, mixing of layers as a result of ocean circulation, and other seasonal variations.

2. Changes in ocean pH and mineral saturation caused by the uptake of atmospheric CO_2 can take a long time to spread to deeper waters, so the full effect of atmospheric CO_2 concentrations on ocean pH may not be seen for many decades, if not centuries.

3. Ocean chemistry is not uniform throughout the world's oceans, so local conditions could cause a pH measurement to seem incorrect or abnormal in the context of the global data. Figure 1 is limited to four monitoring sites that represent different local influences. For example, the Cariaco Basin site is situated in a tectonic depression with restricted circulation and relatively high primary productivity compared with other areas.

4. Although closely tied to atmospheric concentrations of CO_2, aragonite saturation is not exclusively controlled by atmospheric CO_2, as salinity and temperature are also factored into the calculation.

10. Sources of Uncertainty

Figure 1. Ocean Carbon Dioxide Levels and Acidity, 1983–2022

Uncertainty measurements can be made for raw data as well as analyzed trends. Details on uncertainty measurements can be found in the following documents and references therein: Bindoff et al. (2007), Bates et al. (2012), Dore et al. (2009), and González-Dávila et al. (2010).

Figure 2. Changes in Aragonite Saturation of the World's Oceans, 1880–2015

Uncertainty and confidence for CESM calculations, as they compare with real-world observations, are measured and analyzed in Doney et al. (2009) and Long et al. (2013). Uncertainty for the approximation of Ca^{2+} and aragonite solubility are documented in Millero (1982) and Mucci (1983), respectively.

11. Sources of Variability

Aragonite saturation, pH, and pCO_2 are properties of seawater that vary with temperature and salinity. Therefore, these parameters naturally vary over space and time. Variability in ocean surface pH and pCO_2 data has been associated with regional changes in the natural carbon cycle influenced by changes in ocean circulation, climate variability (seasonal changes), and biological activity (Bindoff et al., 2007).

Figure 1. Ocean Carbon Dioxide Levels and Acidity, 1983–2022

Variability associated with seasonal signals is still present in the data presented in Figure 1. This seasonal variability can be identified by the oscillating line that connects sampling events for each site.

Figure 2. Changes in Aragonite Saturation of the World's Oceans, 1880–2015

Figure 2 shows how changes in Ω_{ar} vary geographically. Monthly and yearly variations in CO_2 concentrations, temperature, salinity, and other relevant parameters have been addressed by calculating decadal averages.

12. Statistical/Trend Analysis

This indicator does not report on the slope of the apparent trends in ocean acidity and pCO_2 in Figure 1. The long-term trends in Figure 2 are based on an endpoint-to-endpoint comparison between the first decade of widespread data (the 1880s) and the most recent complete 10-year period (2006–2015). The statistical significance of these trends has not been calculated.

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