At the completion of this module, students should be able to:

1. Explain how atmospheric CO₂ increases affect the CO₂/carbonate/pH system in the upper ocean
2. Identify the regions of the surface ocean that annually take-up and release CO₂
3. Explain the regional impacts of El Niño on air-sea CO₂ exchange
Current Status of Global CO\textsubscript{2}

- Anthropogenic CO\textsubscript{2} input to atmosphere is primarily from:
  - Oxidation of fossil organic matter (oil, coal and natural gas)
  - Cement production

- This CO\textsubscript{2} input...
  - Adds to the CO\textsubscript{2} inventory of the atmosphere and the oceans
  - Stimulates terrestrial biomass production

- CO\textsubscript{2} in the ocean is ~53x greater than in the atmosphere

- Uncertain at what rate anthropogenic CO\textsubscript{2} is being added to the ocean

Equations for CO\textsubscript{2} Speciation

The equilibrium of gaseous and aqueous CO\textsubscript{2}:

\[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \]

Subsequent hydration and dissociation reactions:

\[ \text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]

\[ \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]

When pH is between 7.5 and 8.5:

\[ \text{CO}_2(aq) + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- \]
Ocean CO₂ Tracks Atmospheric Increase

“Ocean Acidification”

CO₂ Partial Pressure  pH

Pre-industrial (1700s) pH = 8.18

Watch on YouTube:
www.youtube.com/watch?v=x1SgmFa0r04

Can you identify the globally important sources and sinks, and when they are most active?

Note how the arctic “traps” large amounts of N. Hemisphere CO₂ during winter.
• High values at equator (esp. in the Pacific) and along west coasts...from upwelling and subsequent gas evasion to atmosphere
• Low values where there is high bioproductivity
• Low values where cooling of ocean increases solubility of gas and causes CO$_2$ uptake from the atmosphere

Ocean Water-column Anthropogenic Carbon ($C_{ant}$)

Group Task

Ocean Water-column Anthropogenic Carbon ($C_{\text{ant}}$)

$C_{\text{ant}}$ is highest in the North Atlantic, and lowest along the equator and offshore of Antarctica. Why is this?? (Explain each of the three cases.)

- **High fluxes** of CO$_2$ *out of the ocean* at the **equator** (esp. in the Pacific) and **offshore of Antarctica** due to upwelling of CO$_2$-rich deep water....which prevents $C_{\text{ant}}$ transfer from the atmosphere

- **High fluxes** of CO$_2$ *into the ocean* in the **North Atlantic**, due to the high gas solubility of cold seawater, and local downwelling (deep water-mass formation)
El Niño-driven changes in CO$_2$ fluxes are primarily due to:
- Decreased upwelling of CO$_2$-enriched waters from the Equatorial Undercurrent
- Advection of CO$_2$-depleted waters from the western equatorial Pacific

Reading:
Libes, Chapter 6 – pp. 158 -168

© 2017 David Ho and Frank Sansone
At the completion of this module, students should be able to:

1. Explain the basic air-sea gas flux equation and its limitations
2. Describe the physical and biological factors affecting air-sea gas exchange
3. Explain how parameterizations relating air-sea gas exchange to wind speed are used

Why do we care about air-water gas exchange?

- Globally...
  - To understand cycling of biogeochemically important trace gases (e.g., CO₂, O₂, CH₄, N₂O)

- Regionally and locally...
  - To understand indicators of water quality (e.g., dissolved O₂, CH₄, N₂O)
  - To understand dynamics of volatile pollutants (e.g., CO₂, organics)
**Single-Film Gas Transfer Model**

![Diagram of gas transfer model](image)

- **Atmosphere**
- **Ocean**
- **C**
- **Ca**
- **Cw**
- **Film**
- **Laminar Stagnant Boundary Layer**
  (transport by molecular diffusion)
- **Turbulent atmosphere**
- **Turbulent bulk liquid**

**Basic Air-Sea Gas Flux Equation**

\[
F = k(C_w - \alpha C_a)
\]

- **Flux** (mol/cm\(^2\)/s)
  - positive = sea-to-air
- **Concentration gradient** (mol/cm\(^3\)) “Driving force”
- **Gas transfer velocity** (cm/s)
  - “Piston velocity”, “transfer velocity”, “resistance”, “gas exchange coefficient”
  - \( = D/z_{Film} \), molecular diffusivity/film-thickness

- **Cw** Concentration in water near the surface
- **Ca** Concentration in air near the surface
- **\(\alpha\)** Ostwald solubility coefficient *(temp-compensated Bunsen coeff)*
$F = k(C_w - \alpha C_a)$

**Group Task**

Why would the presence/absence of surface features like ripples and waves affect gas transfer in the surface ocean?
Complications: 1) Surfactants and other organics

Two types

- **Insoluble** – thin surface layer
  - Impedes molecular diffusion across the surface
  - Effect only at very low wind speeds; easily dispersed by wind and waves

- **Soluble** - change surface tension
  - Dampens capillary and gravity waves
  - Reduces microscale wave-breaking and subsurface turbulence

Ubiquitous in nature
Biological Control on Gas Transfer?

Complications: 2) Microscale Wave Breaking

Incipient breaking of small-scale waves that do not entrain air

May control gas transfer at low to moderate wind speeds
Complications: 3) Bubbles

- **Bubble injection** by breaking waves can enhance gas exchange:
  - Air in bubble exchanges directly with the bulk seawater
  - Bubble dissolution while rising
  - Bypasses the air-sea interface

- **Surface disruption** via turbulent patches

Bubble Production of Aerosols

Bubble bursting at the surface produces several jet drops (100 µm) and a large number of film drops (1-20 µm)

Lucinda Spokes, www.xplora.org

Determining Ocean Gas Transfer Velocity

1. Balance of decay and invasion/evasion rates:
   - $^{14}$C - Natural and bomb-produced
   - $^{222}$Rn - Radon deficiency

2. Deliberate tracers:
   - $^3$He/SF$_6$ water-column inventories

3. Directly measuring fluxes in the atmosphere:
   - Eddy covariance, eddy accumulation
   - Atmospheric gradient measurement

Parameterizations -- Motivation

- Why relate gas exchange to wind speed?
  - Wind generates near-surface turbulence and bubbles (the main drivers for gas exchange)
  - Wind speed is widely measured

- Relationships between gas transfer velocity ($k$) and 10-m wind speed ($u_{10}$) are used:
  - in global biogeochemical models
  - in combination with ocean pCO$_2$ climatologies to determine global ocean CO$_2$ exchange
Frequently Used Wind Speed/Gas Exchange Parameterizations

Climatology of global ocean pCO$_2$ (4° x 5° res)

Global annual mean air-sea flux - 2000

Global wind field

Relationship between wind speed and gas transfer velocity

Basic gas flux equation

$F = k(C_w - \alpha C_a)$