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

1. Explain the Laminar Stagnant Boundary Layer model for air-sea gas exchange
2. Describe the physical and biological factors affecting air-sea gas exchange
3. Explain why current parameterizations relate air-sea gas exchange to wind speed, and how the parameterizations are used
Outline

- Introduction
- Models of gas exchange
- Mechanisms of gas exchange
- Field measurements
- Parameterizations

Why do we care about air-water gas exchange?

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

- Regionally and locally...
  - To understand indicators of water quality (e.g., dissolved O₂)
  - To predict evasion rates of volatile pollutants (e.g., CO₂, organics)
Single-Film Gas Transfer Model

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

**Basic Flux Equation**

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

- **Flux** (mol/cm\(^2\)/s)
- **Concentration gradient** (mol/cm\(^3\))
- **Gas transfer velocity** (cm/s)
- “Piston velocity”, “transfer velocity”, “resistance”, “gas exchange coefficient”
  \[ = \frac{D}{z_{film}} \text{ molecular diffusivity/film-thickness} \]

- **\( C_w \)**: Concentration in water near the surface
- **\( C_a \)**: Concentration in air near the surface
- **\( \alpha \)**: Ostwald solubility coefficient (*temp-compensated Bunsen coeff*)
Air/water side resistance

Magnitude of typical Ostwald solubility coefficients, $\alpha$

<table>
<thead>
<tr>
<th>Gas</th>
<th>Water-side resistance (soluble gas)</th>
<th>Air- and water-side resistance</th>
<th>Air-side resistance (insoluble gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He $\approx 0.01$</td>
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<tr>
<td>$O_2 \approx 0.03$</td>
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<tr>
<td>$CO_2 \approx 0.7$</td>
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<td>DMS $\approx 10$</td>
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<td>CH$_3$Br $\approx 10$</td>
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<td>PCB’s $\approx 100-1000$</td>
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<tr>
<td>$H_2O \approx \infty$</td>
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</tbody>
</table>

Group Task

What real-world factors or conditions might cause this idealized model of air-sea exchange be incorrect?

Make a list and be prepared to present it.
Factors Influencing Air-water Transfer of Mass, Momentum, Heat

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

Libes Fig. 6.6b

(b) Smooth surface regime Rough-surface regime Breaking-wave (bubble) regime

Transfer velocity (cm/s)

Wind speed (m/s)

From SOLAS Science Plan and Implementation Strategy
Complications: 1) Surfactants

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

Dependence of $k$ on wind speed is a function of surfactants

Ubiquitous in nature

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**Biological control on gas transfer?**

![Graphs showing correlations](image)

Figure 5.4. Correlations of $k_w$ with (A) surfactant concentration, (B) in situ chlorophyll fluorescence, (C) dissolved organic carbon (DOC) and (D) coloured dissolved organic matter (CDOM) fluorescence at 450 nm, for seawater samples collected in Monterey Bay (●) and along a Gulf Stream transect from Narragansett to Bermuda (■). Experimental conditions as in Figure 5.3. Transfer velocities vary with surface film conditions, which are time-dependent due to diffusion and adsorption of surfactants at the interface; therefore, for comparative purposes, these correlation plots utilize initial $k_w$ values obtained for freshly formed surfaces. From unpublished data of Frew, Goldman and Bock; DOC data from E. T. Peltzer, pers. commun.
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)

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
**Group Task**

Why is there interest in measuring the gas-transfer velocity over varying spatial scales?

What is a gas-flux-related marine issue for each of these spatial scales:

1) 10 km$^2$ - Effects of oil slicks, wind shadows on gas fluxes, studies of phytoplankton patchiness

2) 500 km$^2$ - Effects of meso-scale eddies, localized storms on gas fluxes

3) 10,000 km$^2$ – Calculation of global fluxes at 1° x 1° resolution

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**Parameterizations -- Motivation**

- Why relate gas exchange to wind speeds?
  - 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
Calculating Ocean CO₂ Uptake Using pCO₂ Disequilibrium

Climatology of global ocean pCO₂ (4° x 5° res)

Global wind field

 Relationship between wind speed and gas transfer velocity

Global annual mean air-sea flux - 2000

Basic flux equation

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

Frequently Used Wind Speed/Gas Exchange Parameterizations

- Wanninkhof & McGillis [1999]
- Wanninkhof [1992]
- Wanninkhof et al. [2009]
- Ho et al. [2006]
- Nightingale et al. [2000]
- Liss & Merlivat [1986]