Air-Sea Gas Exchange

OCN 623 – Chemical Oceanography

17 March 2015

Readings:

Libes, Chapter 6 – pp. 158 -168

Overview

• Introduction

• Theory/models of gas exchange

• Mechanisms/lab studies 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., CO$_2$, DMS, CH$_4$, N$_2$O, CH$_3$Br)

- Regionally and locally
  - To understand indicators of water quality (e.g., dissolved O$_2$)
  - To predict evasion rates of volatile pollutants (e.g., VOCs, PAHs, PCBs)
Factors Influencing Air-water Transfer of Mass, Momentum, Heat

From SOLAS Science Plan and Implementation Strategy
Basic flux equation

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

- **Flux** (mol cm\(^{-2}\) s\(^{-1}\))
- **Gas transfer velocity** (cm s\(^{-1}\))
- **Concentration gradient** (mol cm\(^{-3}\))
  - "driving force"

- \( k \): Gas transfer velocity, piston velocity, gas exchange coefficient
- \( C_w \): Concentration in water near the surface
- \( C_a \): Concentration in air near the surface
- \( \alpha \): Ostwald solubility coefficient (temp-compensated Bunsen coeff)
Basic conceptual model

Atmosphere

Ocean

F = k(C_w - αC_a)

Laminar Stagnant Boundary Layer (transport by molecular diffusion)
Air/water side resistance

Magnitude of typical Ostwald solubility coefficients

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical Value</th>
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<tbody>
<tr>
<td>He</td>
<td>≈ 0.01</td>
</tr>
<tr>
<td>O₂</td>
<td>≈ 0.03</td>
</tr>
<tr>
<td>CO₂</td>
<td>≈ 0.7</td>
</tr>
<tr>
<td>DMS</td>
<td>≈ 10</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>≈ 10</td>
</tr>
<tr>
<td>PCB's</td>
<td>≈ 100-1000</td>
</tr>
<tr>
<td>H₂O</td>
<td>≈ ∞</td>
</tr>
</tbody>
</table>

Water-side resistance

Air- and water-side resistance

Air-side resistance
Gas transfer velocity $k$ of insoluble gases ($\alpha < 10$), function of:

- Environmental forcing of water boundary layer
- Thermodynamic property of gas and liquid

$$k = (\nu/D)^n f(q,L)$$

- $\nu$ = kinematic viscosity of water
- $D$ = Diffusion coefficient of gas in water
- $(\nu/D)$ = Schmidt number (Sc)
- $n$ = Schmidt number exponent
- $f(q,L)$ = function of turbulent velocity and length scale
Sc at 20 °C

Sc in seawater
Sc in freshwater

Schmidt Number (Sc)

Gas
He  Ne  Ar  O₂  CH₄  CO₂  N₂  Kr  NO₂  Rn  SF₆  CCl₂F₂ (F-12)  CCl₃F (F-11)
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**Stagnant Film Model** (Whitman, 1923; Lewis and Whitman, 1924)
- Film thickness is independent of gas
- $k$ only changes as a function of diffusion coefficient
- Commonly used in "historical work"
- Generally viewed as incorrect. Can introduce significant error in comparing $k$ of different gases (up to a factor of 2).
- **Implies that $k$ is proportional to $Sc^{-1}$**

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

\[
k = \frac{D}{z}
\]
Is the Stagnant Film Model realistic?
**Solid wall model** (Deacon, 1977)

- $k$ proportional to $Sc^{-2/3}$
- Relationship holds for exchange over smooth surfaces without waves
- Based on analogy between transfer of momentum and mass
- $k$ is related to Schmidt number ($Sc$) and friction velocity in air ($u_{*a}$):

\[
k = 0.082 \left( \frac{\rho_a}{\rho_w} \right)^{1/2} Sc^{-2/3} u_{*a}
\]

**Friction velocity** (aka shear velocity) is the square-root of the kinematic stress. Close to the surface, friction velocity is not a function of height. A general rule is that the shear velocity is about 1/10 of the mean flow velocity. $\rho_a/\rho_w$ is the density ratio of air and water.
Film replacement model (Higbie, 1935; Danckwerts, 1970)
• $k$ proportional to $Sc^{-1/2}$

Eddy impingement model (Ledwell, 1984; Coantic, 1986; McCready, 1984; Kittagoroddski, 1984; Asher, 1989)
• $k$ proportional to $Sc^{-1/2}$ if all eddies reach surface

Stagnant fluid close to the interface is replaced periodically with material from the bulk
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Wind Wave Facility
Wind-wave tank results:
3 regimes
• Smooth surface
  \[ k = f(u^*) \, \text{Sc}^{-2/3} \]
• Wavy surface
  \[ k = f(u^*) \, \text{Sc}^{-1/2} \]
• Breaking waves
  \[ k = f(bubble, u^*) \, \text{Sc}^{-x} \]
  All bets are off

Issues:
• Scaling
• Tank (wall artifacts)

Fig. 8.2 Wind tunnel experiments of Broecker and Siems (1984) demonstrating the effect of bubbles on gas exchange. Reprinted by permission of Kluwer.
Gas Exchange and Environmental Forcing: Tanks

Example: tank artifact due to fetch

Wind-wave and other laboratory tanks are ideal systems to study processes, but absolute magnitudes generally cannot be applied to oceans.

Wanninkhof et al., 1991, Donelan and Drennan
Summary of laboratory studies

Variable affecting $k$:

- Wind
- Waves
- Bubbles/breaking waves
- Surfactants
- Temperature & humidity gradients
- Rain
- Tunnel shape?
- Tunnel dimensions??
Summary of laboratory studies

Good for studying mechanisms

Difficult to extrapolate results from wind/wave tanks to coastal seas and open oceans due to:

• Limited fetch
• Lack of gusting
• Boundary conditions
• Use of ‘clean’ freshwater
Surfactants

Two types
- **Insoluble** - an extra barrier (i.e., monolayer or additional liquid phase)
  - Impedes molecular diffusion across the surface
  - Effect only at very low wind speeds; easily dispersed by wind and waves

- **Soluble** - change surface tension
  - Modifies sea surface hydrodynamics
  - 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
Biological control on gas transfer?

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. Feltzer, pers. commun.

Laboratory versus field measurements
Skin-layer disruption by microbreaking events produces thermal signatures that can be detected and quantified using IR imagery.

**Hypothesis:** Microscale wave breaking is the underlying physical process that controls gas transfer at low to moderate wind speeds.
Gas Transfer by Bubbles

- Mechanisms by which breaking waves can enhance gas exchange
  - Bubble-mediated
    - Air in bubble exchanges directly with the bulk seawater
    - Bypasses the air-sea interface
    - Bubble approaches equilibrium more quickly for soluble gases
    - Bubble dissolves or rises
  - Surface disruption
  - Turbulent Patches
Mechanism 1: Bubble-Mediated Transfer

Schematic of Bubble Evolution

Gas Exchange

Atmosphere

Entrainment

Surfacing

Gas Exchange

Advection

Ocean

Solution

Woolf, 97
Mechanism 2: Surface Disruption

Gas transfer at the sea surface is usually limited by low diffusion across the ‘surface skin’. This can also lead to a “cool skin” measurable by a thermal camera (left). When a bubble plume surfaces (right), the skin is disrupted and - by implication - gas transfer enhanced.
Mechanism 3: Patches of Turbulence

- Time series of dispersion (size of a dyed patch, border labeled by curve) and turbulent intensity (size of crosses).
- Wave breaking introduces a patch of higher near-surface turbulence that gradually decays in intensity but expands in size.
- Gas transfer through the sea surface depends on near-surface turbulence intensity. Therefore, gas transfer is enhanced by the turbulence generated by breaking waves.

Rapp and Melville, 1990
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Methods to determine gas transfer velocities in the ocean

1. Balance of (known) decay and invasion/evasion rates
   - $^{14}\text{C}$ - Both natural and bomb produced
   - $^{222}\text{Rn}$ - Radon deficiency method

2. Based on water column inventories:
   - $^{3}\text{He}/\text{SF}_6$ deliberate tracers

3. Measuring fluxes in the atmosphere (micrometeorological techniques)
   - Eddy covariance
   - Eddy accumulation
   - Atmospheric gradient
Figure 4-1. Chart showing the decay chain of the uranium and thorium series isotopes and the half-lives of each isotope. Alpha decays are shown by the vertical arrows and beta decays by the diagonal arrows.
Opportunistic tracers of air-sea gas exchange

\[ ^{14}\text{N} + n \rightarrow ^{14}\text{C} \]

Natural \(^{14}\text{CO}_2/^{12}\text{CO}_2\) invasion

\(^{14}\text{CO}_2/^{12}\text{CO}_2\) out gassing

Decay: \(^{14}\text{C} \rightarrow ^{14}\text{N} + \text{e}^-\)

Pre-industrial assumption:
\(^{14}\text{CO}_2\) in = \(^{14}\text{CO}_2\) out + Decay

\[ 0.061 \text{ mol m}^{-2} \text{ y}^{-1} \mu\text{atm}^{-1} = 21.4 \text{ cm h}^{-1} \]

Evasion of Radon

\[ ^{226}\text{Ra}_{\text{aq}} \rightarrow ^{222}\text{Rn}_{\text{gas}} + 4\text{He} \]

\[ ^{222}\text{Rn} \rightarrow ^{218}\text{Po} + 4\text{He} \]

\[ \left[ \text{Rn} \right]_{\text{mixed layer}} = \frac{\lambda_{\text{Rn}}}{\lambda_{\text{Rn}} + \lambda_{\text{gas exchange}}} \left[ \text{Rn} \right]_{\text{no loss}} \]

\[ 0.062 \text{ mol m}^{-2} \text{ y}^{-1} \mu\text{atm}^{-1} = 21.9 \text{ cm h}^{-1} \]
Tracer Infusion and Injection

\[ ^3\text{He} \] and \[ \text{SF}_6 \] dissolved in 4000 L of seawater in gas-tight tank through a headspace

The tracers are injected at the release site by pumping \[ ^3\text{He} \] and \[ \text{SF}_6 \]-infused seawater from the ship.
The tracers become diluted due to horizontal and vertical mixing and loss through air-water gas exchange.

Gas transfer velocities can be calculated from the change in ratio of the two tracers over time.

\[
k_{3\text{He}} = h \frac{d}{dt} \left( \ln \left( \frac{3\text{He}_{\text{exc}}}{\text{SF}_6} \right) / \left( 1 - \left( \frac{S_{\text{SF}_6}}{S_{3\text{He}}} \right)^{-1/2} \right) \right)
\]

\(^3\text{He} \) diffuses more rapidly than \( \text{SF}_6 \) across the air-water interface.

\( \text{SF}_6 \) and \(^3\text{He} \) mix horizontally & vertically.
$^3$He/SF$_6$ Deliberate Tracers

- Strong dependence on wind
- Similarities between coastal ocean and global ocean
Direct Flux Measurements

- Eddy covariance
- Eddy accumulation
- Atmospheric gradient

Work well over land
Very difficult over seas/oceans

Why?
  - Small fluxes (requirement for high precision/accuracy)
  - Ship Movement
  - Flow distortion
Eddy Covariance

$Flux = \overline{w'c'}$

- Covariance of vertical wind ($w$) and CO$_2$ or DMS ($c$)
- Downward air flows have higher CO$_2$ levels than upward air flow (due to CO$_2$ uptake by ocean)
- Requires very fast measurements of gas conc and vertical wind velocity
- Timescale $\sim$10-20 minutes
- Footprint $\sim$1 km$^2$
DMS Eddy Covariance Cruises

DMS Eddy Covariance hourly average

- Equatorial East Pacific (TAO)
- Sargasso Sea (BIO)
- Northeast Atlantic (DOGEE)
- Southern Ocean (SO GasEx)
- Southeast Pacific (VOCALS)
- Southeast Pacific (Knorr06)
- Northeast Atlantic (Knorr07)
- Equ. & N. Pacific (PHASE I)

Map showing cruises and locations:
- Knorr_07
- Knorr_06
- TA O
- BIO
- VOCAL
- DOGE
- SO GASEX

Graph showing scatter plot with variables k_660 and U_{10n}.

During a storm transit in SO GasEx.
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Motivation

• Why relate gas exchange to wind speeds?
  – Wind generates near surface turbulence and bubbles (i.e., the main drivers for gas exchange in the ocean)
  – Wind speed is widely measured

• Relationships between gas transfer velocity ($k$) and 10-m wind speed ($u_{10}$) used:
  – in global biogeochemical models
  – in combination with ocean pCO$_2$ climatologies to determine ocean CO$_2$ uptake
Calculating Ocean CO₂ Uptake Using pCO₂ Disequilibrium

Climatology of global ocean pCO₂

Global wind field

Relationship between wind speed and gas transfer velocity

Mean Annual Air-Sea Total Flux for 2000 [Rev Oct 09] (NCEP II Wind, 3,040K, Γ=.26)

Basic flux equation

\[ F = k(C_w - αC_a) \]

http://www.ldeo.columbia.edu/res/pi/CO2/
Frequently used wind speed/gas exchange parameterizations

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

Total Citations as of Apr 13, 2014 from Google Scholar

- Liss & Merlivat [1986] 1516
- Wanninkhof [1992] 2433
- Wanninkhof & McGillis [1999] 547
- Nightingale et al. [2000] 691
- Ho et al. [2006] 187
- Wanninkhof et al. [2009] 186
Why are relationships different?
(Why do observations scatter?):

- Experimental uncertainty
- Variability in forcing
- Other parameters influence air-sea gas transfer
Global average of air-sea CO$_2$ transfer velocity from QuikSCAT scatterometer wind speeds

J. Boutin, Y. Quilfen, L. Merlivat, and J. F. Piolle

Table 3. Net Sea-Air CO$_2$ Flux$^a$ With k-U Relationships$^b$

<table>
<thead>
<tr>
<th>Latitude Band</th>
<th>Wind Speed</th>
<th>K</th>
<th>Pacific</th>
<th>Atlantic</th>
<th>Indian</th>
<th>Southern</th>
<th>All Basins</th>
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<td>QuikSCAT</td>
<td>$K_W$</td>
<td>-0.35</td>
<td>-0.29</td>
<td>-0.30</td>
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<td>-0.29</td>
<td>-0.29</td>
<td>-0.30</td>
<td>-0.24</td>
<td>-0.24</td>
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<tr>
<td>North of 50°N</td>
<td>NCEP</td>
<td>$K_W$</td>
<td>-0.31</td>
<td>-0.31</td>
<td>-0.30</td>
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<tr>
<td>14°N–50°N</td>
<td>QuikSCAT</td>
<td>$K_W$</td>
<td>-0.54</td>
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<td>0.05</td>
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<td>$K_H$</td>
<td>-0.44</td>
<td>-0.24</td>
<td>0.04</td>
<td>-0.63</td>
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<td>-0.44</td>
<td>-0.23</td>
<td>0.04</td>
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<td>-0.34</td>
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<td>-0.35</td>
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<td>-0.69</td>
<td>-0.33</td>
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<td>-1.64</td>
</tr>
</tbody>
</table>

$^a$In Pg (10$^{15}$ g) C a$^{-1}$. Deduced from Takahashi et al.’s [2002] $\Delta$pCO$_2$ fields and QuikSCAT wind speeds between 1999 and 2006 (this study).