Parametrizations of Bubble-Mediated Gas Transfer; Fundamental Principles and a Laboratory Test

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Overview

• Properties of Bubble-Mediated Exchange
• Parametrizations of Transfer Velocity
• The LUMINY Experiment
• Test of the Original Model
• A “Dense Plume” Model
• Test of New Model
• Predictions for Different Plumes
Atmosphere

Entrainment

Bursting

Ocean

Exchange
What is Special About Bubble-Mediated Exchange?

- **Property 1**: Transfer from bubble under additional pressure
  - Flux = $K_b \left[(1+\delta)\frac{C_a}{H} - C_w\right] + K_o \left[\frac{C_a}{H} - C_w\right]$ 
- **Property 2**: Bubbles have a “finite capacity” and their contents change during their lifetime
  - Responsibility for solubility dependence
- Two properties can be dealt with separately
  - Can model a submerged bubble (extra pressure) changing with time but the extra pressure has no implications for Property 2
  - Much easier to forget about Property 1 while thinking about effects of Property 2
Two Reservoir Models

- Exchange between two reservoirs initially depends on the transfer velocity alone.
- In the course of equilibration, the reservoir with the smaller capacity takes control.
Asymptotic Limits Of Mediated Exchange

Individual bubbles governed by:

\[(4\pi r^3/3)\frac{dC_b}{dt} = 4\pi r^2 j(C_w - C_b)\]

This leads to asymptotes for population of bubbles:

(full equilibration, e.g., \(\beta >> 1\)) \(K_b = V_B/\beta\)

(no equilibration, e.g., \(\beta << 1\)) \(K_b = \int j \, dA_b\)

Boundary layer theories predict that for a mobilised bubble, \(j \propto D^{1/2}\) and for a immobilised bubble, \(j \propto D^{2/3}\).
A Semi-Empirical Parameterisation

\[ Kb = \frac{V_B}{\beta} \left[ 1 + (e^{\beta D n})^{-1/f} \right]^{-f} \]

Satisfies the asymptotes

Woolf ‘97

Estimates \( n=1/2; \ f=1.2, \)

\[ e=1.4 \times 10^4 \text{ s}^{1/2} \text{ m}^{-1} \]
What it looks like

- Woolf’97 model of bubble-mediated contribution to transfer.
- Note asymptote of Schmidt number control for insoluble gases.
- Solubility control for more soluble gases.
Physical Basis of Gas Transfer

Simplest arguments (and some data) suggest that $K$ should scale with $u_*$

e.g., $K_J = 1.57E-4 \ u_* (600/Sc)^{1/2}$  [Jähne et al. 1987]

But some mechanisms (bubbles, isolated patches of turbulence) should scale with whitecap coverage, $W$, or wave energy dissipation, $F_{ds}$

e.g., $K_b = 850 W$  CO$_2$ at 20$^\circ$C  [Woolf, 1997]

In total

Some recent models…

**NOAA/COARE**

\[ k = k_s + k_b \]

[Hare et al., (2004), JGR]

**Woolf & Ufermann**

\[ K = a/\sigma_{Ku}^o + c + b u^*H/\nu \]

where \( k_b \) and \( b \) derives from Woolf ‘97
Model Relationships of Transfer Velocity to Wind Speed (Sc=600)

"Hybrid RHW"

\[ K = K_j + 2 \times 10^{-5} R_{Hw} \]

\[ R_{Hw} = \frac{u_* H}{v_w} \]

Woolf, D.K. (2005),
Tellus, 57B, 87-94
LUMINY - The Cast List

Coordinator  Gerrit de Leeuw, TNO, NL
Experiments  Guillemette Caulliez, IRPHE, Fr

Gases

SF₆, He and CH₃Br          Phil Nightingale, Malcolm
                            Liddicoat and Jon Baker
                            PML/UEA, UK

N₂O                       Tae-Siek Rhee, MPIC, D
Air                        Peter Bowyer, NUIG, IE
Bubbles                   Ira Leifer, NUIG, IE

…and a cast of thousands
LUMINY - The Plumber’s Nightmare

Figure 2.
T-S Rhee
The Bubbles

- The aeration devices were arranged in mats, 0.6m beneath the water surface.
- Most “working” frits produced bubbles about 300µm in radius but some produced much larger bubbles.
Bubbles II

- The estimated total bubble distribution has a peak at very small radii and then a peak at ~ 300\(\mu\)m with a long tail including very large bubbles.
The Time Series - SF$_6$ and $^4$He

SF$_6$ and Helium: 20 March 97:
2.5 m/s wind + bubbles from outside tunnel then in

- Headspace
- Bubbles from outside
- Bubbles from headspace
- Water

Symbols:
- SF6 Cw
- SF6 Ca/H
- Helium Ca/H
- Helium Cw

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.
The Equations

Where the aeration devices are fed with air from outside of the laboratory, the time series should be described by

\[ \frac{V}{A} \frac{dC_w}{dt} = K_b \left[ (1+\delta)\frac{C_{atm}}{H} - C_w \right] + K_o \left[ \frac{C_a}{H} - C_w \right] \]

Where the aeration devices are fed with air from the headspace

\[ \frac{V}{A} \frac{dC_w}{dt} = K_b \left[ (1+\delta)\frac{C_a}{H} - C_w \right] + K_o \left[ \frac{C_a}{H} - C_w \right] \]

By finding values of \( K_b \) and \( K_o \) which describe the time series for the former case or both cases (the errors are smaller for the latter) these two components of gas transfer are separated.
## The Results

<table>
<thead>
<tr>
<th>Gas</th>
<th>$K_T$ (cm/h)</th>
<th>$K_b$ (cm/h)</th>
<th>$K_o$ (cm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₆</td>
<td>53</td>
<td>44</td>
<td>9</td>
</tr>
<tr>
<td>He</td>
<td>74</td>
<td>60</td>
<td>14</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>8.5</td>
<td>2.0</td>
<td>6.5</td>
</tr>
<tr>
<td>N₂O</td>
<td>15.5</td>
<td>5.5</td>
<td>10.0</td>
</tr>
<tr>
<td>Air</td>
<td>64</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Components of Transfer Velocity

- Blue: Total
- Green: Bubble-mediated
- Brown: Surface

He | Air | N₂O | CH₃Br | SF₆
---|-----|-----|-------|-----
0  | 0   | 0   | 0     | 0   
0  | 0   | 0   | 0     | 0   
10 | 10  | 10  | 10    | 10  
30 | 30  | 30  | 20    | 30  
50 | 50  | 50  | 40    | 50  
70 | 70  | 70  | 60    | 70  

cm/h
Model Fit - 1st Try

The Original Woolf’97 Model but with the measured volume flux of bubbles
Predictably underestimates exchange of poorly soluble gases
No Surprise - designed for large bubbles rising only 10 cm
Model Fit - 2nd Try

- Adjust “e”
- Just use a sensible value given the known bubble distribution and fitted on measured transfer velocity of air
Model Fit - 3rd Try

- Adjust “f”
- Essentially assumes a broader bubble size distribution. Improves He and N$_2$O at the expense of SF$_6$
- NOT SATISFACTORY
Model Fit - 4th Try

- Ignore Air
- This allows us to fit the other gases.
- BUT NOT REALLY SATISFACTORY
Model Fit - 5th Try

- Fiddle with n
- $n=1/4$
- This works but involves abandoning the physics!
A New Model

Atmosphere

Plume

Ocean

Bubble
Two Reservoir Models

- Exchange between two reservoirs initially depends on the transfer velocity alone.
- In the course of equilibration, the reservoir with the smaller capacity takes control.
Asymptotic Limits Of Mediated Exchange

Original asymptotes for population of bubbles:

(full equilibriation, e.g., $\beta >> 1$) $K_b = V_b/\beta$
(no equilibriation, e.g., $\beta << 1$) $K_b = \int j \, dA_b$

Are joined by $K_b = V_P$

A limit for low solubility and high diffusivity
A Semi-Empirical Parameterisation

Simply change

\[ Kb = \frac{V_B}{\beta} \left[ 1 + \left( e^{\beta D^n} \right)^{-1/f} \right]^{-f} \]

To

\[ Kb = X \cdot \frac{V_B}{\beta} \left[ 1 + \left( e^{\beta D^n/X} \right)^{-1/f} \right]^{-f} \]

where

\[ X = \frac{\beta V_P}{(V_B + \beta V_P)} \]

Gives the extra asymptote
Revision of Woolf ‘97 - Dense Plume Model

- Simple model is modified to include finite plume size. Here void fraction is assumed to be 25%.
Model Fit - Dense Plume, n=0.5

Dense plume model (here $V_P/V_B = 13$; void fraction of $\sim 7\%$) allows low He, high SF$_6$ values to be explained

N.B. Theoretical difficulties for air
Model Fit - Dense Plume, n=2/3

- Dense plume model works equally well if bubbles are immobile (here $V_P/V_B = 12$; void fraction of $\sim 7.5\%$)
More models …(1) a very shallow plume (25%, n=1/2)
More models …(2) an "average" plume (5%, n=1/2)
More models ...(3) a deeper plume (1%, n=2/3)
Summary

• Bubble-mediated Transfer
  – Supersaturation
  – Two Reservoir Models of Exchange
  – Solubility matters
  – Size [of plume] matters

• Validation
  – Seems to work
  – Need more cal/val