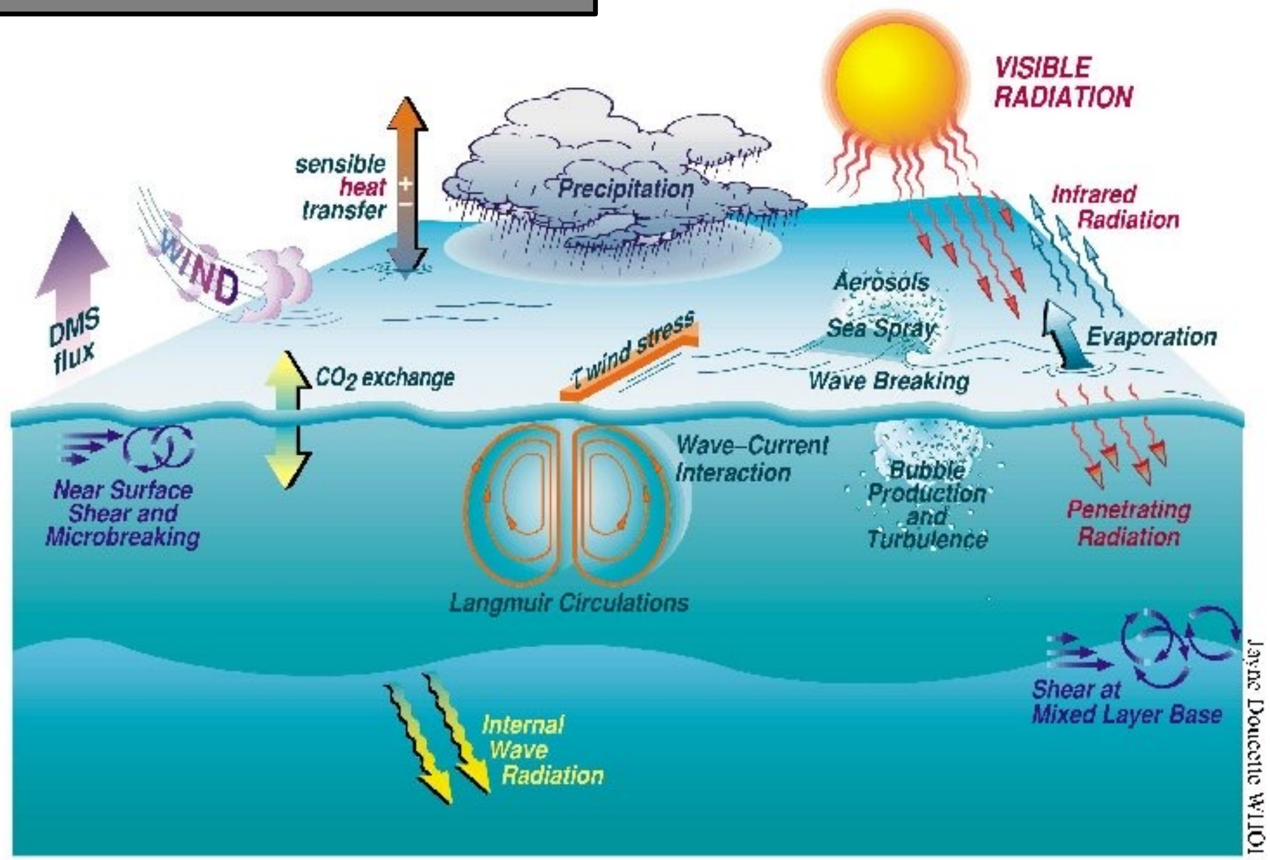
Why do we care about air-sea gas exchange?

- Globally –
  - understand cycling of important trace cases: CO_2, N_2O, DMS, CH_4
  - Predict / monitor oxygen loss

- Smaller scales:
  - Capturing rates of biological activity
  - Predict evasion of volatile pollutants

What affects gas exchange?

- ΔC (water concentration disequilibrium from saturation) determines driving force for air-sea exchange
- But how does gas actually move between the air and water?



Basic flux equation

- Solubility
  - How much gas water can hold at equilibrium
- Gas transfer coefficient
  - How quickly will a gas cross the air-sea boundary

$$F_c = G_C([C] - [C_{sat}])$$

$$\frac{mol}{m^2\ d} = \frac{m}{d}\left(\frac{\mu mol}{kg}\right)\left(\frac{kg}{m^3}\right)\left(\frac{mol}{\mu \text{mol}}\right)$$

$$F_c = G_C K_{H,c}(f_c^w - f_c^a)$$

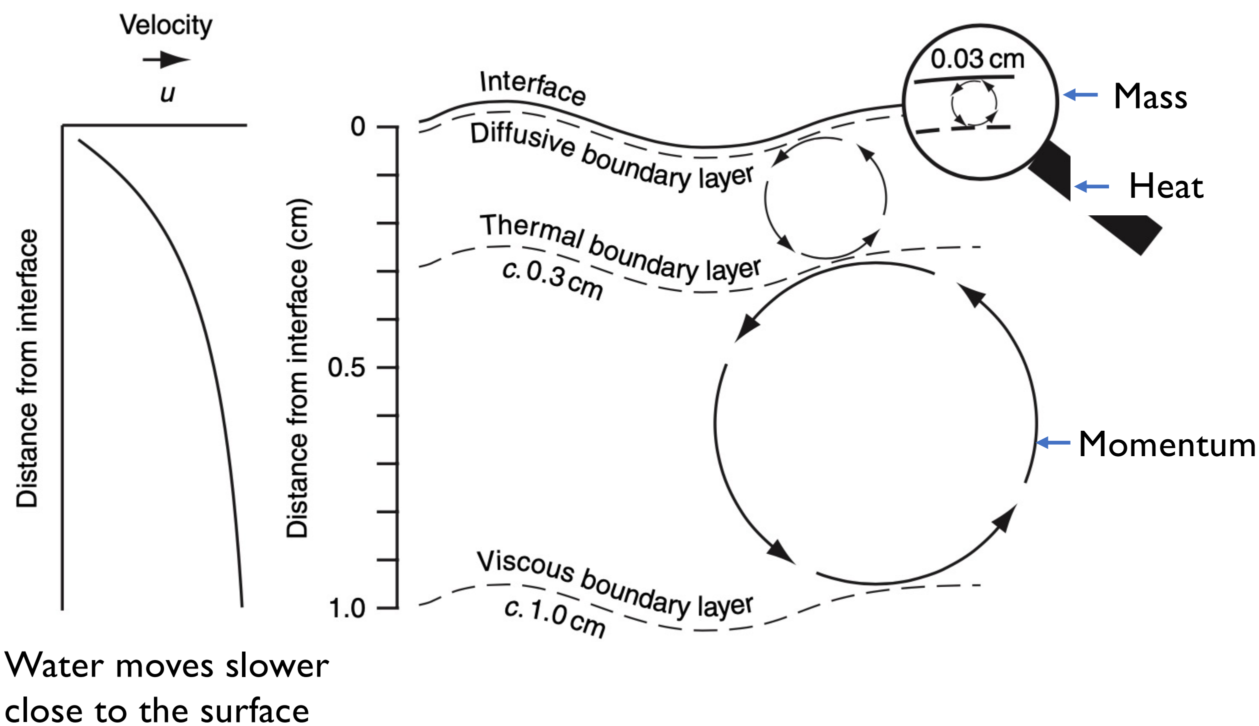
F_c = Flux (mol m^{-2} $time^{-1}$)
G_c = Gas transfer coefficient (m/time)*

[C] = Surface concentration (µmol/kg)
$[C]_{sat}$ = Saturation concentration

f_c^w = fugacity of the water
f_c^a = fugacity of the air

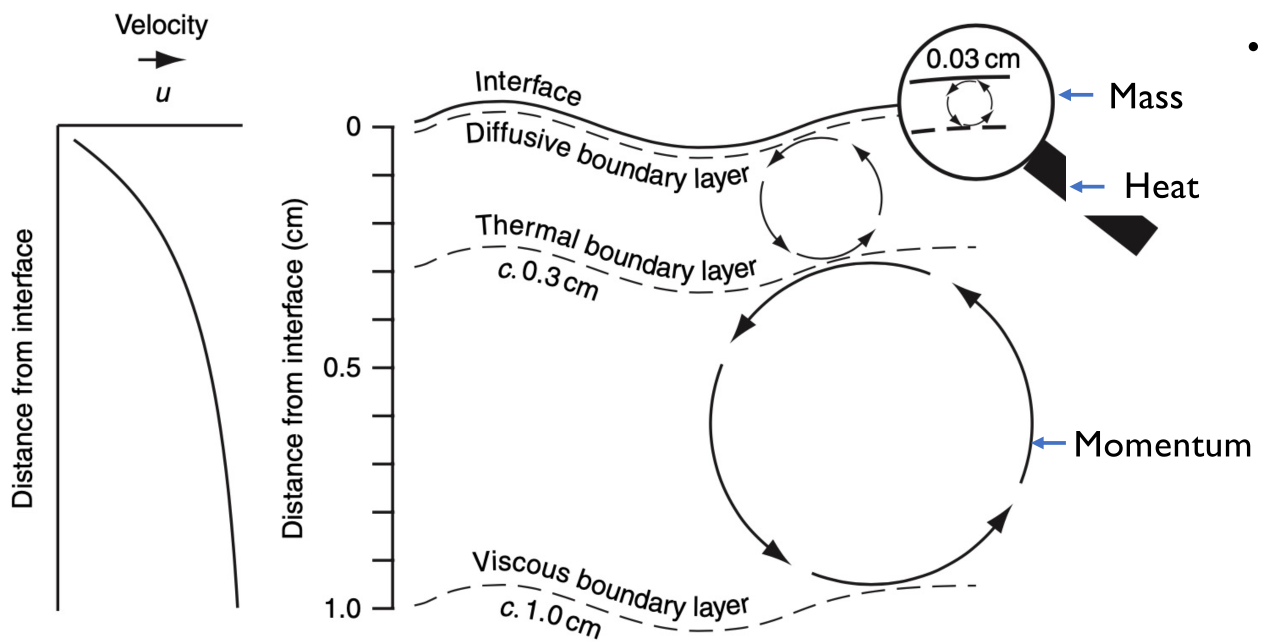
*Note that k is often used instead of G

Boundary layers: Schmidt number



Emerson and Hedges 2008

Boundary layers: Schmidt number



Water moves slower close to the surface

Emerson and Hedges 2008

- Gas exchange is partially a molecular diffusion process
- The layer over which molecular processes become important is dependent on the ratio of the molecular diffusion of a gas relative to the kinematic viscosity

$$G_C = G^* \times \left(\frac{D_C}{v}\right)^n$$

G^* = empirical constant (cm s^{-1})
D_C = molecular diffusivity of a gas c (cm^2 s^{-1})
v = kinematic viscosity (cm^2 s^{-1})

$$Sc_C = \frac{v}{D_c}$$

Sc_C= Schmidt number for gas C

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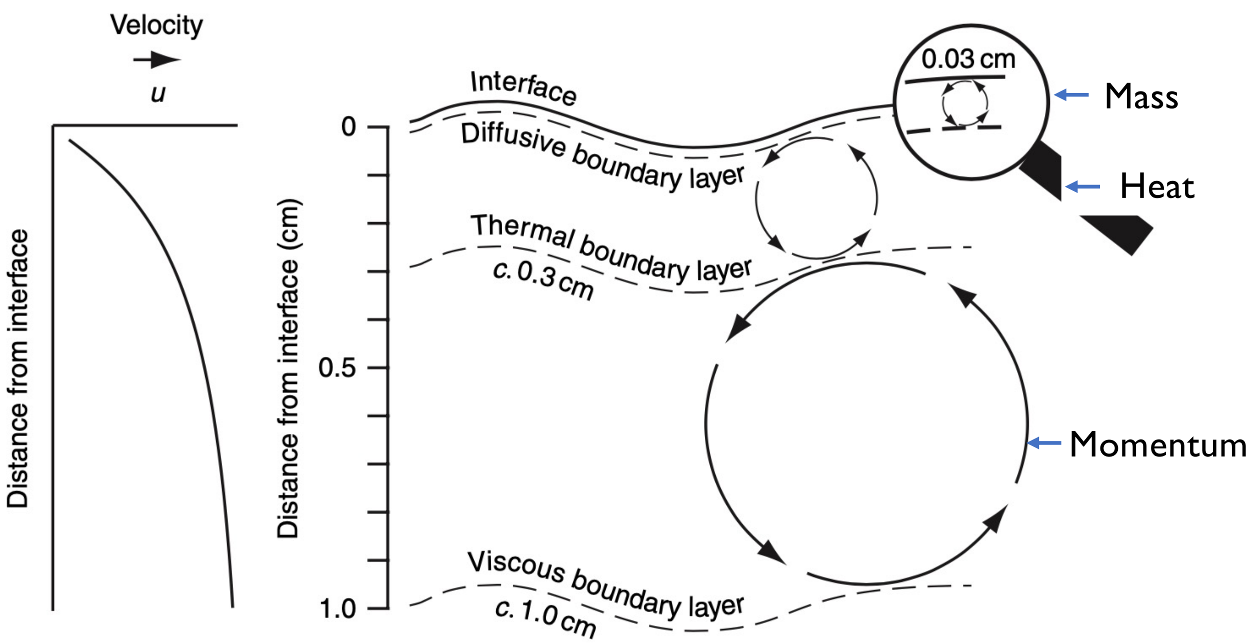
Boundary layers: Schmidt number



Water moves slower close to the surface

Emerson and Hedges 2008

Sc_C= Schmidt number for gas C

$$Sc_C = \left(\frac{v}{D_c}\right)^n$$

- v and D_C are strongly temperature dependent
- S_c can vary by a factor of 5-6 over oceanic temperature ranges, which makes gas transfer velocity a strong function of temperature
- n is somewhere between ½ and 1, depends on empirical model
- Sc lets us relate gas transfer coefficients for different gases

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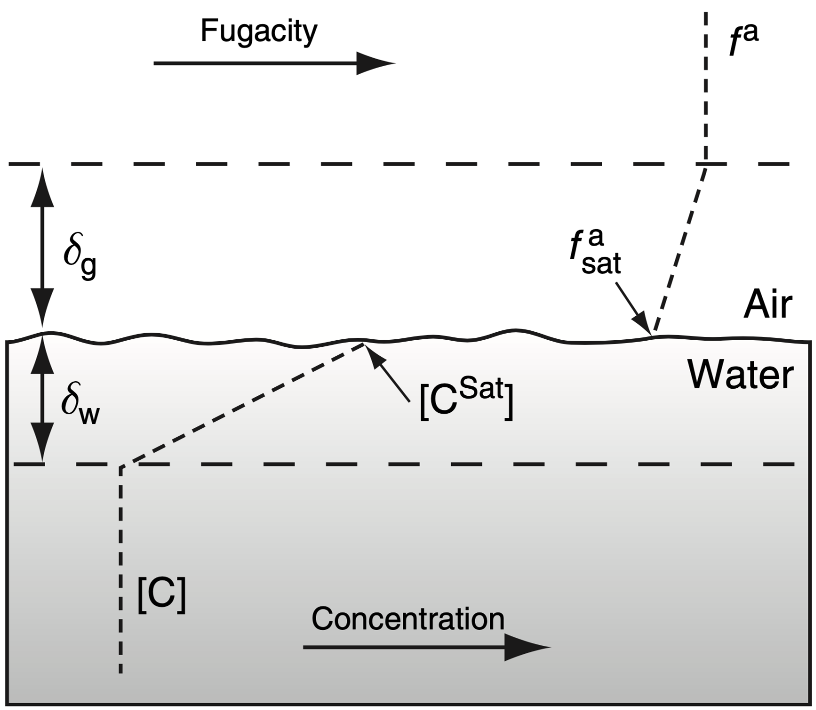
Gas exchange models: Stagnant Film



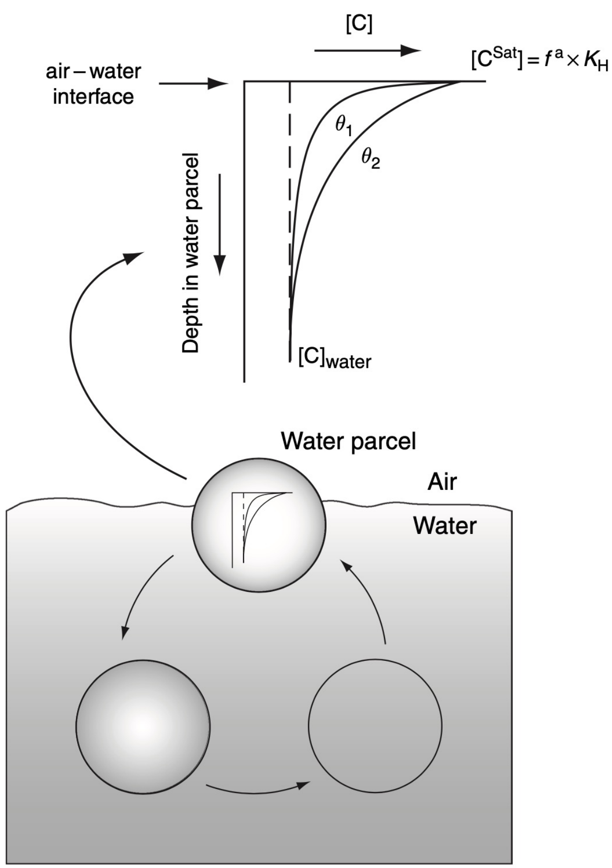
- Simple – gas exchange is purely due to supply of gas to the surface by molecular diffusion – both from the air and water sides

$$G_C = \frac{D_c}{\delta}$$

- Ignores wind speed, assumes there is always some stagnant layer of invariant thickness
- Gas exchange is dependent on molecular diffusion coefficient and therefor Schmidt number to the -1 (n=1)

Emerson and Hedges, Whitman, 1923

Gas exchange models: Surface renewal



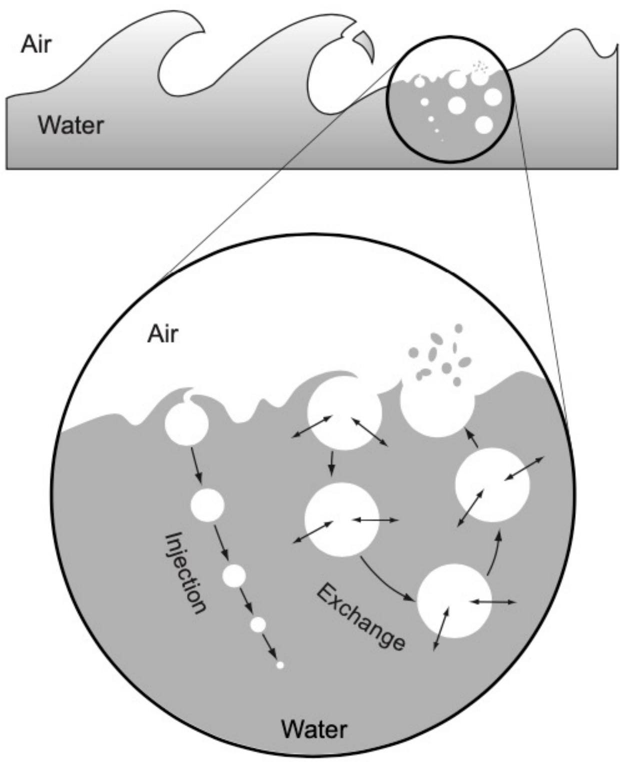
- Assumes gas exchange is primarily limited by supply of water parcels to the surface
- Yields an n=1/2 dependence on Schmidt number
- These are theories – in practice models have been tested empirically with n (and other coefficients/terms) fit to data

What actually happens in the ocean?

Mechanisms?

- wind speed
- wave height
- wave shape
- breaking vs. non-breaking (bubbles)
- spray
- relative direction of wind and waves

Bubble injection



Emerson and Hamme, 2021

Bubbles injected into the ocean can suffer two fates:

1. Forced into dissolution by increased pressure (completely dissolved/collapsed)
2. Sink down, exchanging gas with the surrounding water under higher pressure before returning to the surface (partially dissolved/collapsed)

Bubbles are a significant fraction of gas exchange at high winds for low solubility gases.

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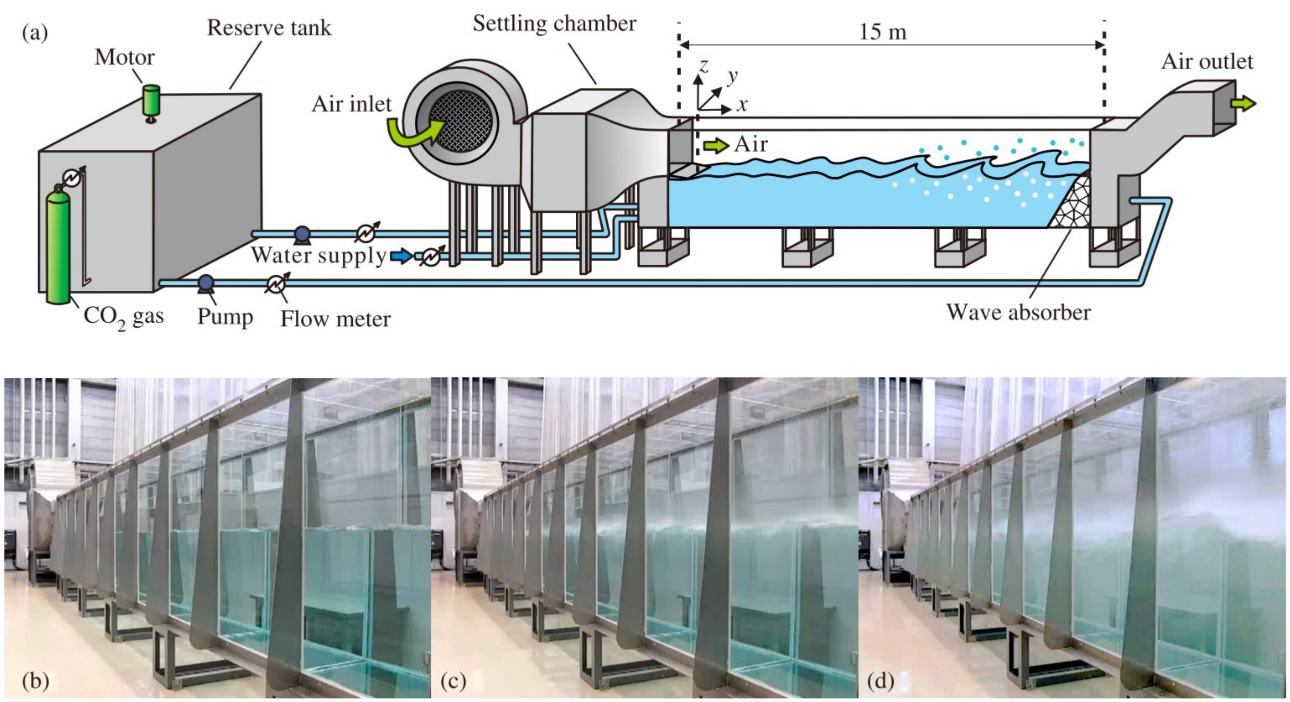
Empirical determinations (and uses) of G (k)

- Lab experiments
  - Wave tanks
- Large-scale
  - Ocean inventory vs. atmospheric production
- Small-scale
  - Ocean inventory changes
  - Flux co-variance
  - Purposeful tracer release experiments
  - Upper ocean mass balances
- Modeling
  - Empirical or not?

Lab-based parameterizations: Wave tanks

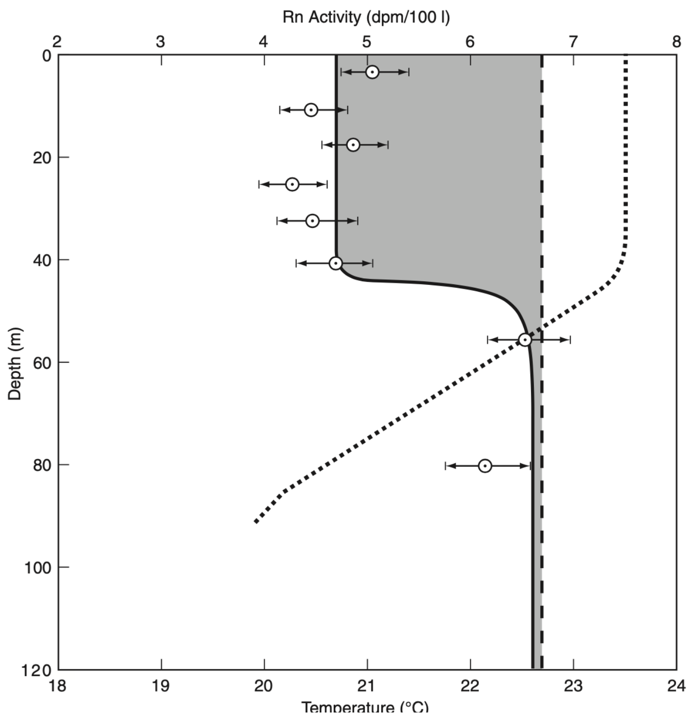


Wave tanks

- Controlled environment
- Repeatable
- Limited fetch, no gusts, no wind/wave mismatches, etc.
- Good for process understanding, but not for magnitude of mass transfer coefficient

Iwano et al. 2013

Experimental methods: Radon

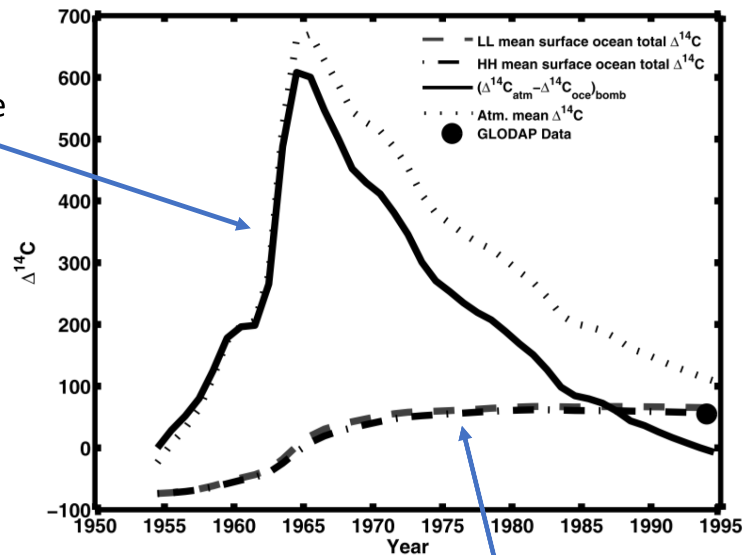


- Radon 226 is present in the ocean and readily measured (half-life of 1620 years)
- Decays to Radon 222 (half-life of 3.85 days)
- Radon 222 escapes to the atmosphere
- Deficit relative to expected can be used in a mass balance to determine the air-sea exchange term over a few days/weeks

Sarmiento and Gruber, 2006

Experimental methods: Radiocarbon

Nuclear bomb tests released ^{14}C into the atmosphere

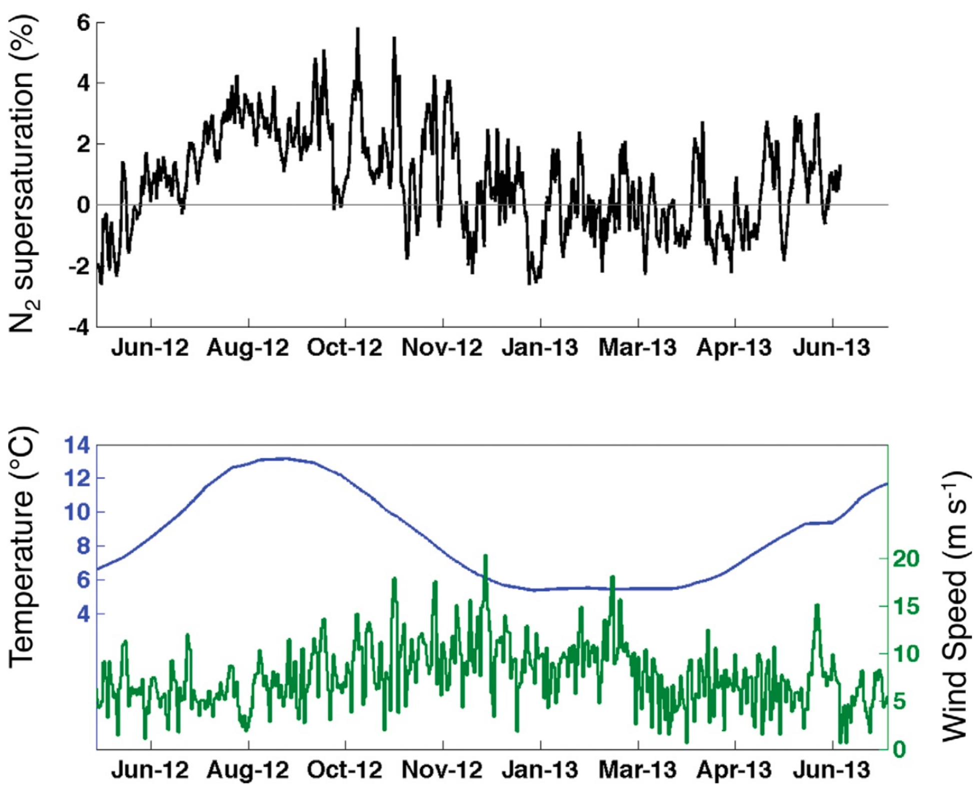


Sweeney et al. (2007)

Which then accumulated in the ocean.

- We can calculate air-sea exchange by measuring ^{14}C in the ocean and calculating what the flux must have been to match ocean measurements to atmospheric measurements.
- Provides a long-term estimate

Experimental methods: Upper ocean mass balances



- N_2 supersaturation in the N. Pacific is purely due to physical processes
- If we can parameterize or ignore non-air-sea flux terms, we can solve for air-sea gas exchange

Emerson and Bushinsky, 2016

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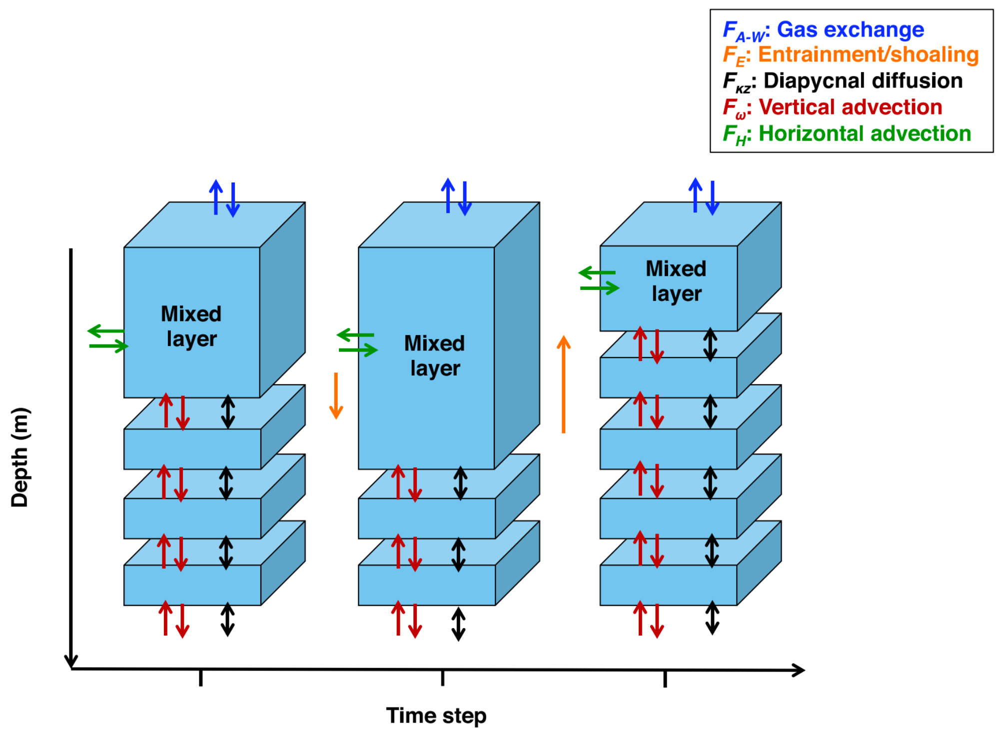
Experimental methods: Upper ocean mass balances



Bushinsky et al., 2016

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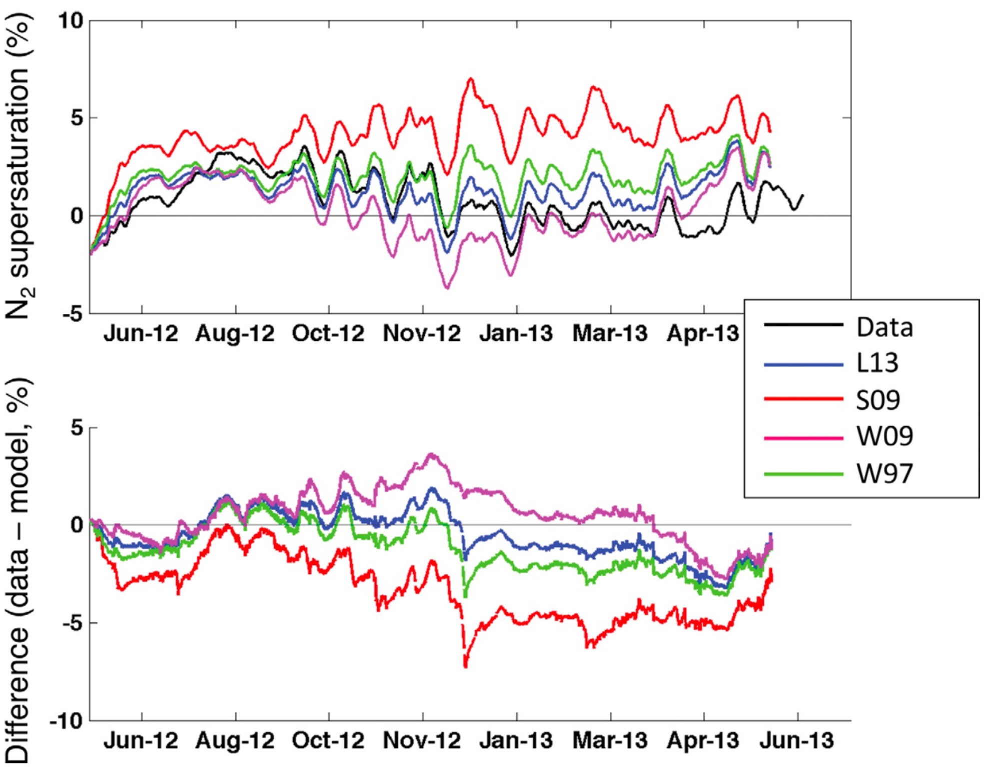
$$\frac{d(h[C])}{dt} = F_{A-W} + F_H + F_\omega + F_E + F_{\kappa z} \pm \cancel{J_C}^{\,0}$$

Experimental methods: Upper ocean mass balances



Emerson and Bushinsky, 2016

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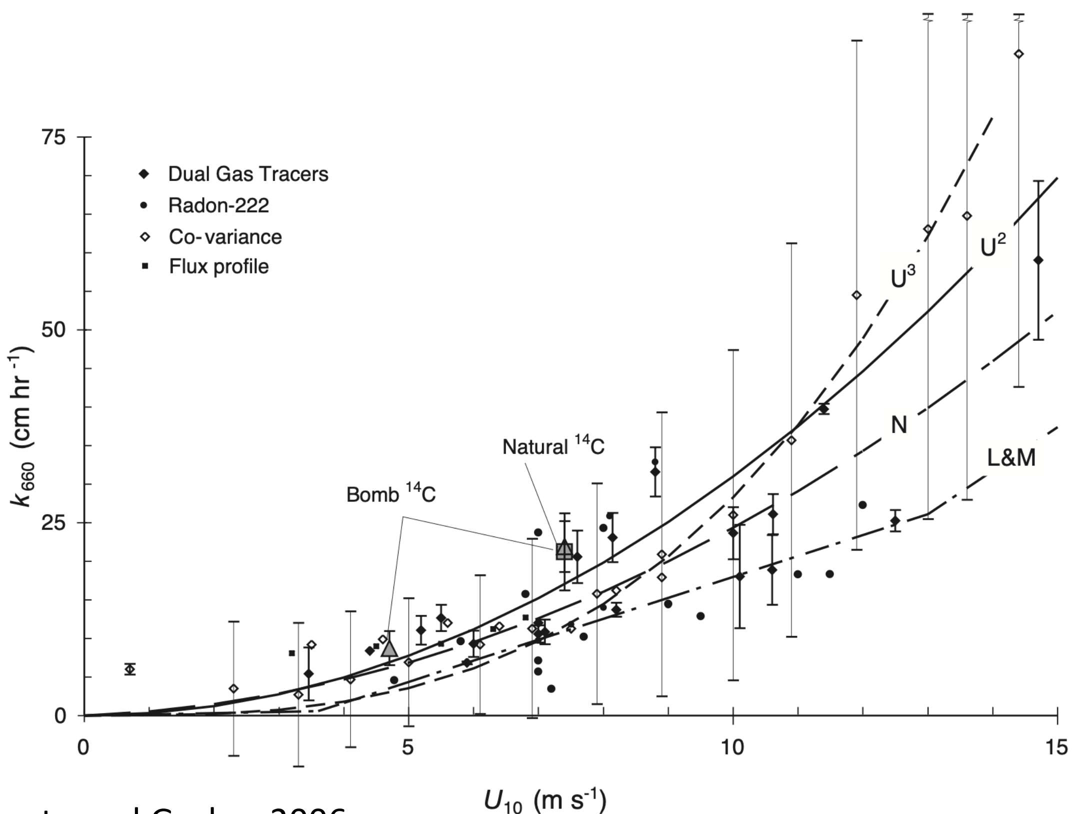
$$\frac{d(h[C])}{dt} = F_{A-W} + F_H + F_\omega + F_E + F_{\kappa z} \pm \cancelto{0}{J_C}$$

- By testing different air-sea flux parameterizations we can find the one that minimizes differences from obs.
- Additional work then used this approach to tune the bubble injection terms

Ocean observation derived gas transfer coeff.

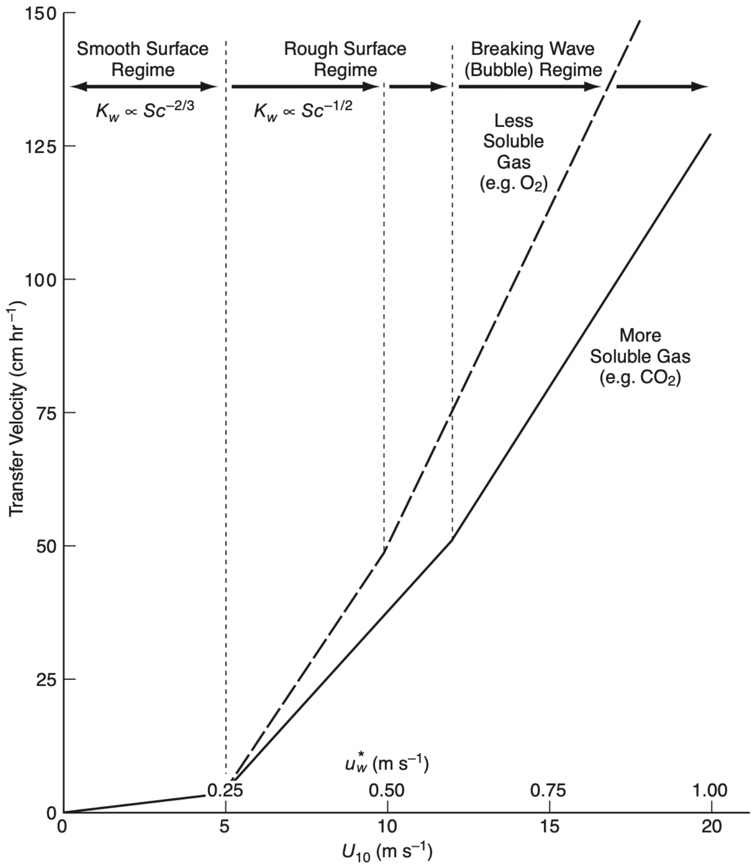


Sarmiento and Gruber 2006

- Wide range in experimental observations
  - Does k vary according to U^2? U^3?

- Some of this reflects uncertainty in observations
- Some of this is the fact that wind speed alone cannot fully capture the wind-wave dynamics

Ocean observation derived gas transfer coeff.

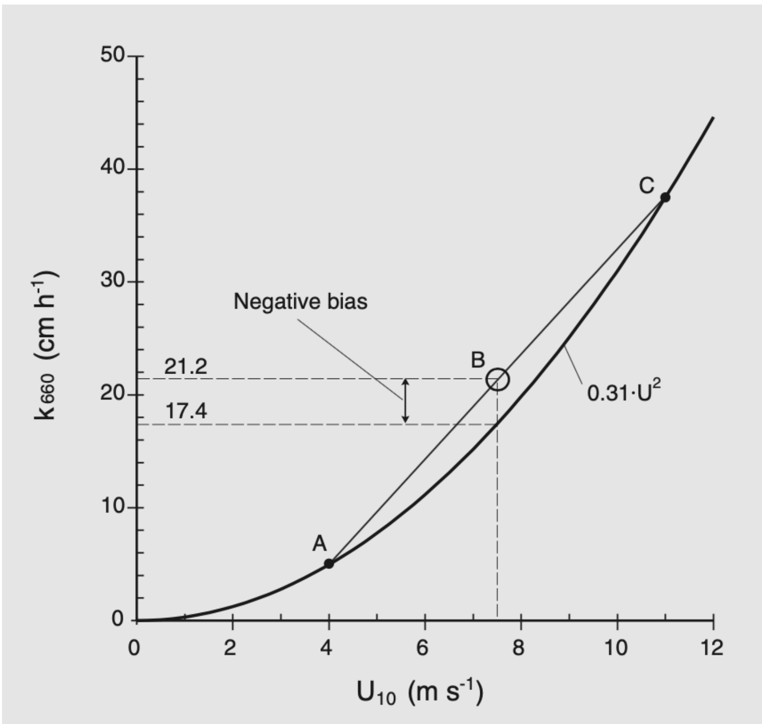


- Idealized relationship between the mass transfer velocity and wind speed at 10 m

$$F_{A-W} = F_S + F_C + F_P \qquad \text{mol m}^{-2}\text{ s}^{-1}$$

Total air-water flux ($F_{A\text{-}W}$) is a combination of diffusive flux, completely dissolved bubbles (F_C) and partially dissolved bubbles (F_P)

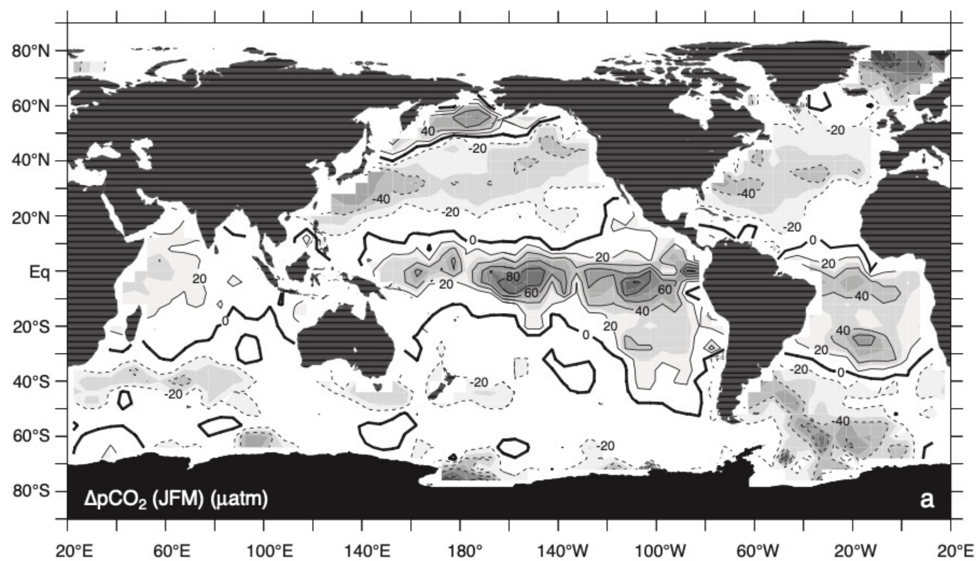
Be careful with average winds…

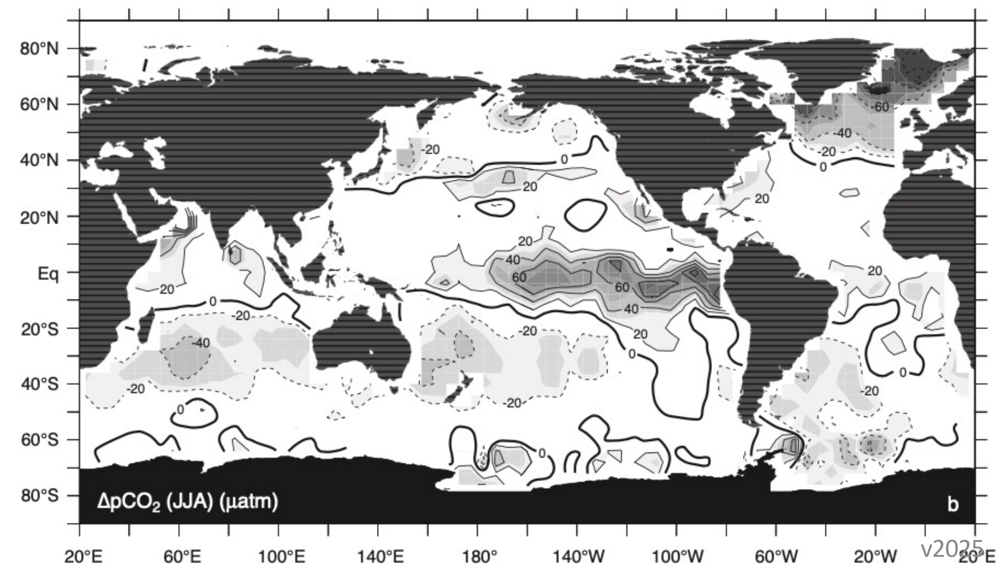


- Calculating the mean gas transfer velocity based on mean wind speeds can lead to bias
- Make sure you use a parameterization that uses a similar wind averaging to your observations

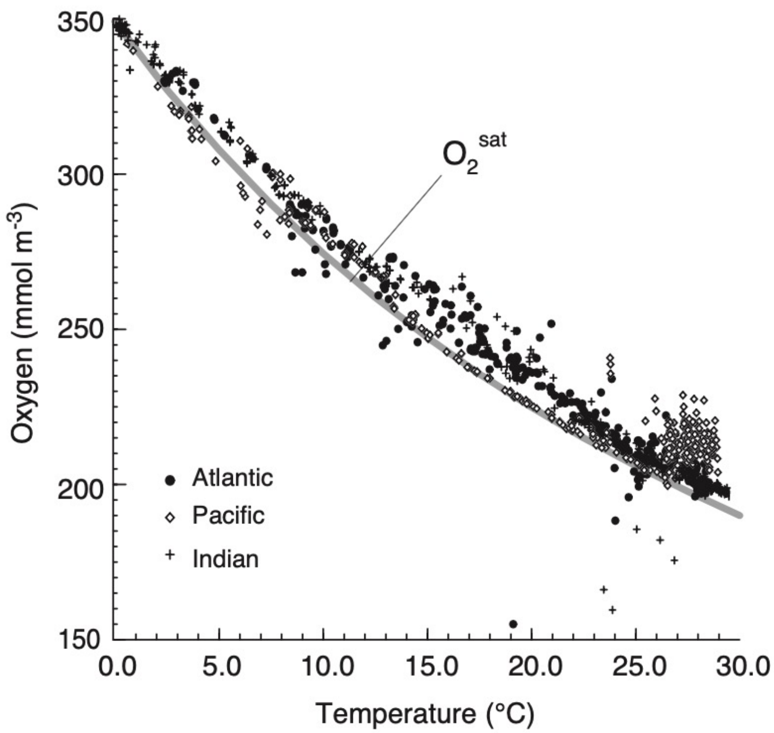
Sarmiento and Gruber, 2006

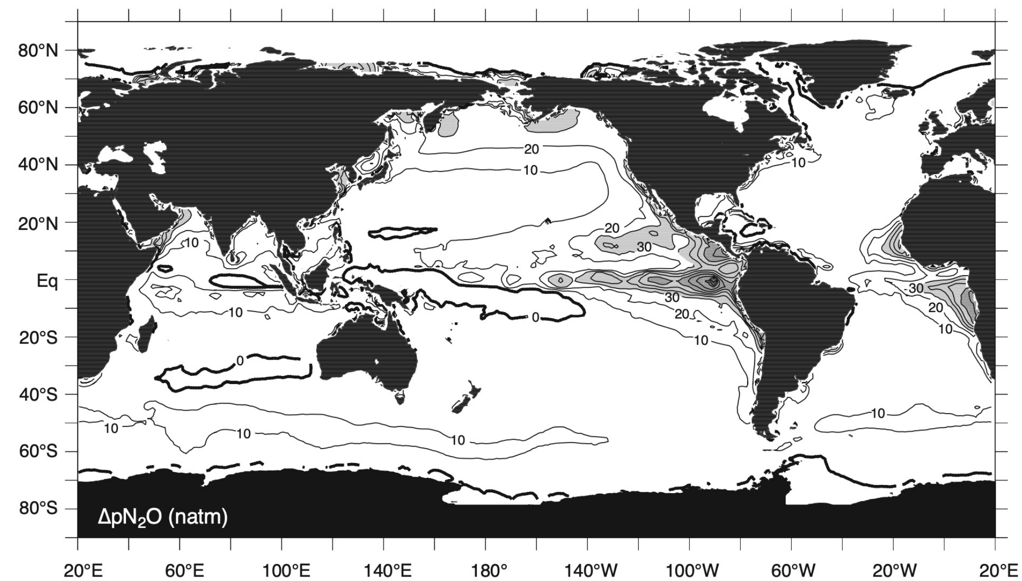
pCO_2 anomalies



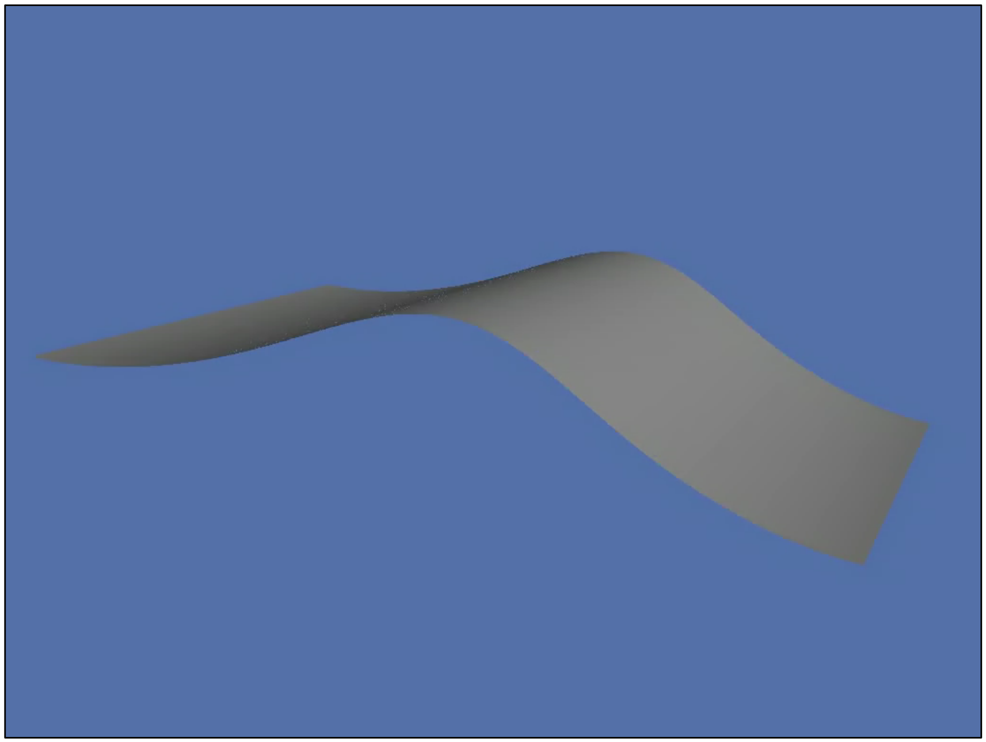


Oxygen and N_2O anomalies





Numerical model of breaking waves



Deike et al. (2017)

- Physical model of breaking wave dynamics
- Goal is to understand breaking wave behavior beyond more wind = more waves
- As wave models become available, this may add another possible parameterization term that can reduce the spread in current estimates.

Currently in review:

A universal wind-wave-bubble formulation for air-sea gas exchange and its impact on oxygen fluxes

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This manuscript was compiled on September 20, 2024

Bubble mediated gas exchange associated with wave breaking is a critical pathway for ocean-atmosphere exchange of low solubility gases such as oxygen and noble gases. Yet, ocean and climate models, as well as observation-based products, usually rely on wind-only air-sea flux formulations derived from carbon constraints that ignore the asymmetric nature of the bubble flux, contributing to discrepancies between estimates of oxygen inventories and their response to climate change. Without bubbles, gas exchange is controlled by a symmetric wind-driven exchange, with the sign of the ocean-atmosphere gas partial pressure difference controlling whether outgassing or uptake occurs. Bubbles entrained by wave breaking can i) enhance this symmetric turbulent exchange, and ii) contribute an additional asymmetric flux, always leading to an uptake, as they get squeezed by hydrostatic pressure (large bubbles) or even collapse and fully dissolve (small bubbles). We present an observation-constrained theoretical framework of the air-sea flux accounting for air entrainment due to wave breaking and bubble symmetric and asymmetric exchange. The combined evidence from theory, laboratory and field measurements of carbon dioxide fluxes and noble gas supersaturation yields a universal formulation of gas exchange which we implement into a global ocean-biogeochemical model. We discuss the resulting oxygen fluxes and demonstrate that our wind-wave-bubble formulation better reproduces observed in-situ oxygen concentrations in water mass formation regions – where air-sea exchange is high - than a commonly used wind-only formulation. We show that the asymmetric bubble flux is essential for evaluating oxygen air-sea fluxes and estimating the magnitude of the ocean oxygen loss associated with global warming.

air sea gas exchange | bubbles | wave breaking | supersaturation | oxygen

Gas exchange at the ocean-atmosphere interface is essential for understanding ocean biogeochemical cycles, and fluxes, critical for the Earth's climate, including the magnitude of the ocean carbon sink (1, 2) and the warming-driven ocean oxygen loss (e.g., 3) associated with anthropogenic activities. Processes controlling ocean-atmosphere gas exchange involve a wide range of scales from micrometer scale bubbles, to meter scale waves, and ocean basin wide variations in wind and atmospheric pressure (4–6). Ocean and climate models (e.g., 7–9), as well as observation based products (10, 11, e.g.,) usually represent the ocean-atmosphere gas flux F, as a function of the gas partial pressure difference between air and water ($P_a - P_w$, a measure of the disequilibrium across the interface), the gas solubility (S, the amount of gas that can dissolve for given thermodynamical conditions), and a gas transfer velocity k_w, often expressed as a function of wind speed and gas diffusivity (the ability of a gas to diffuse through the interface) (12–18):

$$F = k_w S(P_a - P_w). \quad [1]$$

Such wind-only turbulent diffusive gas transfer velocity formulations of k_w are relatively easy to implement and were successful at evaluating global scale ocean fluxes of the medium solubility gases such as CO_2 for which they were originally designed (13, 14). However, these formulations only implicitly account for bubbles, and lack the effect of squeezed and fully dissolving bubbles entrained into the water column (4–6). These omitted bubble effects are first order processes in the exchange of low solubility gases such as O_2, N_2 (19–23), gases used as tracer to understand ocean ventilation (noble gases, SF_6 (24, 25)), and contribute to current biases and uncertainties in air-sea oxygen fluxes and global ocean oxygen loss estimates (3, 7, 26–28). Finally, these wind-only formulations also exclude the direct control of wave breaking at a particular ocean location on the entrainment of bubbles. Local wave breaking is influenced by waves travelling far distances, which leads to multiple possible values of the gas transfer velocity k_w at any given wind speed and introduces high-frequency and

Significance Statement

Bubble mediated gas exchange is a critical pathway for ocean-atmosphere exchange of low solubility gases such as oxygen, with profound implications for biogeochemical cycles. Bubbles are entrained by breaking waves and get squeezed due to hydrostatic pressure in the water column leading to an increased uptake through an asymmetric contribution. Ocean and climate models, as well as observation-based products, usually ignore this contribution. We present an observation-constrained theory for bubble gas exchange leveraging noble gas supersaturation and float oxygen concentrations in wintertime in the Southern Ocean. We implement the wind-wave-bubble formulation in a global ocean circulation model and demonstrate the improved representation of oxygen fluxes and concentrations, with significant implications for our ability to predict changes in ocean oxygen content.

Conceptualization: L.D., L.R.; Data Curation: X.Z., P.R., B.R., R.S.; Formal Analysis: L.D., L.R., X.Z., S.B., R.S.; Funding Acquisition: L.D., L.R.; Methodology: L.D., L.R., S.B., B.R., R.S.; Software: L.D., L.R., S.B., B.R., X.Z., P.R.; Visualization: P.R., X.Z., L.D., L.R., S.B.; Writing – Original Draft: L.D.; Writing – Review & Editing: L.D., L.R., P.R., B.R., R.S., S.B.

The authors declare no conflict of interest.

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