

Assessing the Importance of Asymmetries and Biases in the Air-Sea Flux of Carbon Dioxide

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Where did you go wrong?
It was travelling but 'twas
The Tilt Not The Pace

or

How biases creep into air-sea gas flux estimates due to omissions

Introduction

The ocean takes up approximately a quarter of the carbon dioxide emitted to the atmosphere by human activity. Estimating the exact amount absorbed by the ocean over the last years and decades is essential to understanding of the rise of carbon dioxide in the atmosphere and global heating, and the acidification of the ocean. Similarly, the ocean has a role in the cycling of other important gases. A powerful method of estimating oceanic uptake is through a 'bulk formula' that calculates the flux at the sea surface based on measurements of the gas in the lower atmosphere and upper ocean, and knowledge of physical processes at the sea surface. A correct calculation is dependent on careful use of the data and a clear understanding of processes that contribute to the final total.

The Bulk Formula and Near-Saturation Conditions

An air-sea gas flux is often expressed by a bulk formula, such as

$$F = K (C_w - C_a) = K \Delta C,$$

where K is the transfer velocity and ΔC is an *effective* concentration difference. Most recent studies of gas transfer velocity are convergent on its relationship to wind speed (Figure 1, below left). However, while there are many processes dictating upper ocean concentrations (Figure 2, below right), unless a gas is highly reactive in ocean or atmosphere, the air-sea exchange dictates that atmosphere and ocean will be close to equilibrium (near saturation). In this case, estimating the effective concentration difference sufficiently is challenging and arguably can be more important than further refinement of the transfer velocity. The next sections review subtleties of the bulk formula with respect to processes and effective concentration difference. A final section considers the implication of applying the bulk formula at a relatively low temporal resolution (monthly in most extant studies).

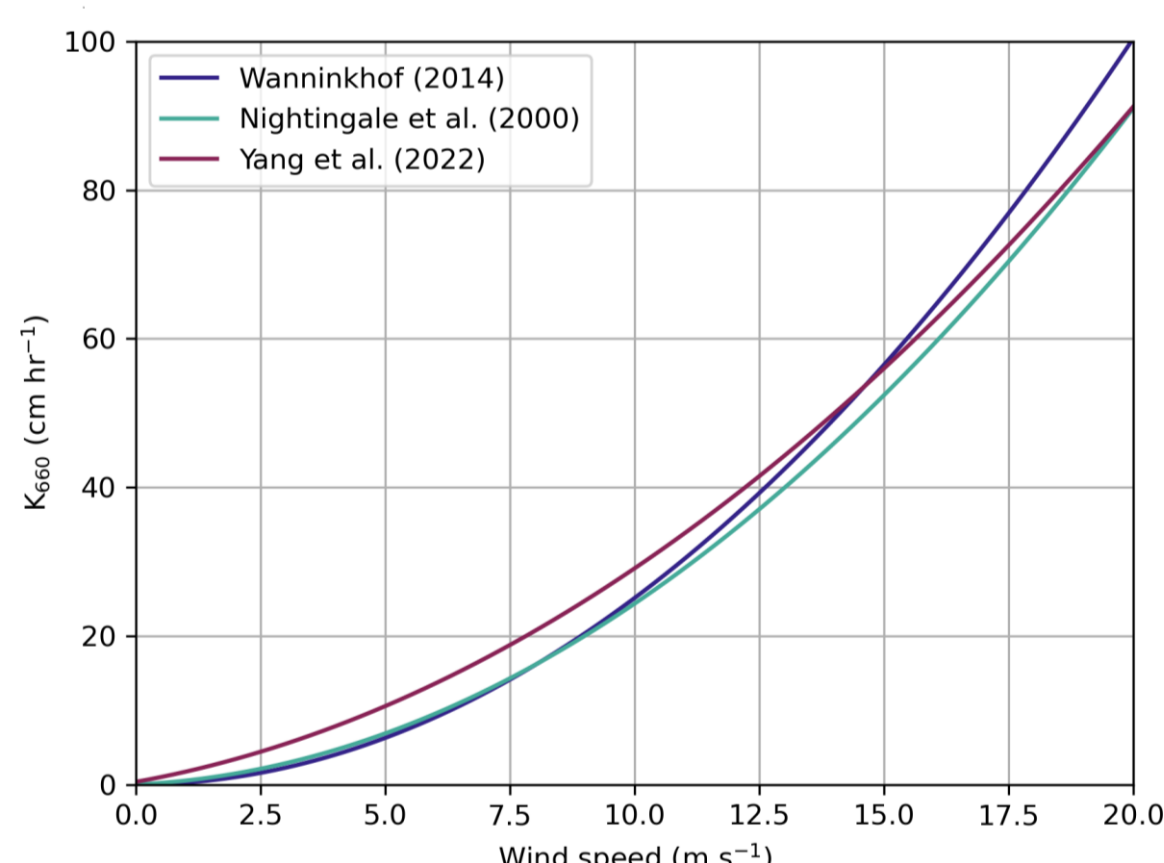


Figure 1. Gas transfer velocity vs wind speed

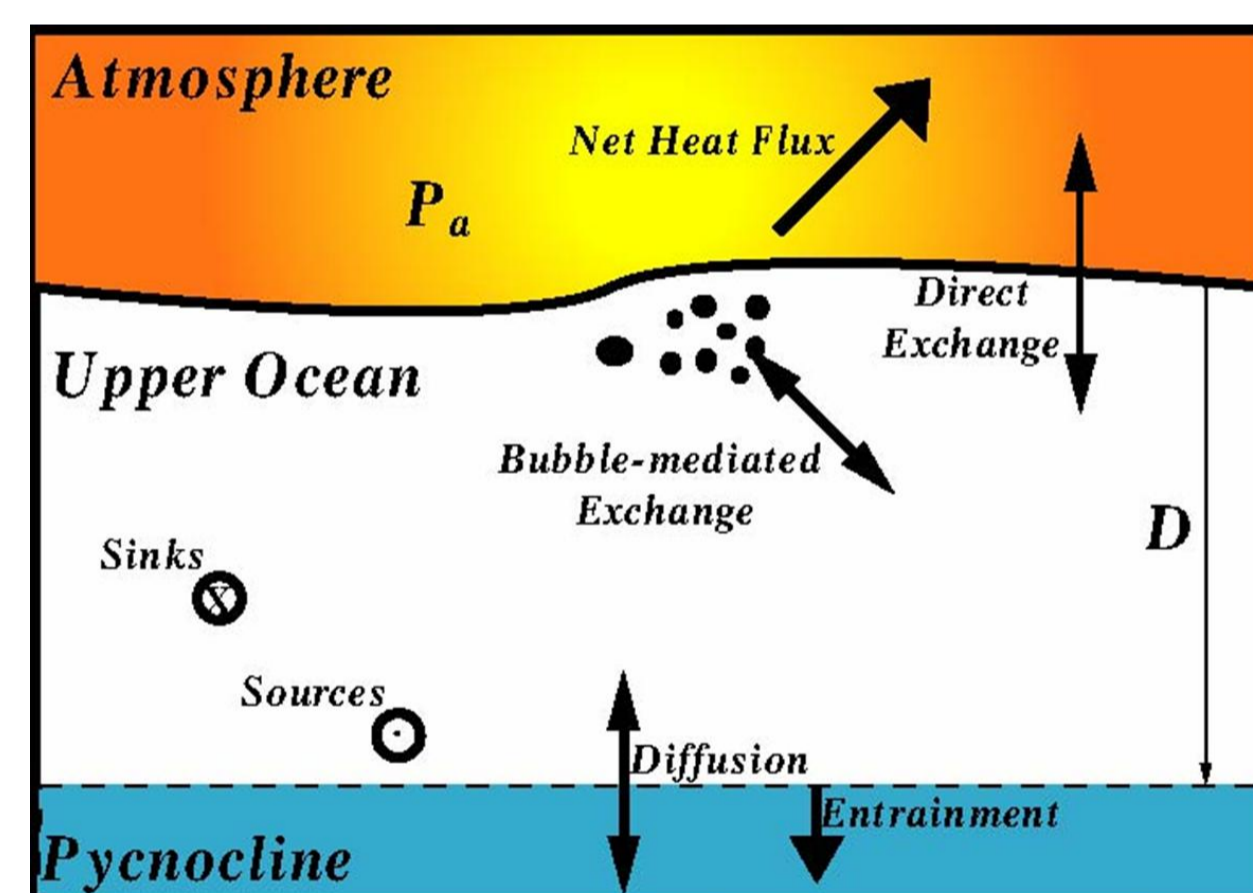


Figure 2. Schematic of gas flows in upper ocean

Bubbles and Spray

Bubbles and spray each introduce an asymmetry in air-sea gas fluxes, changing the effective concentration difference in the bulk formula. Transfer processes can be categorised according to their relevance to soluble or poorly soluble gases, and into those that increase exchange and transfer velocity (Categories 1, 3 and 6 in Figure 3 on right), and those that result in injection (Category 4) or ejection (Category 8). The shrinkage or complete dissolution of a bubble (Category 4) increases the oceanic sink [Woolf and Thorpe, 1991; Leighton et al., 2018]. Evaporation of spray droplets reduces the oceanic sink. An analysis of carbon dioxide fluxes [Dong et al., 2025] suggests that the net effect is an increase in the calculated oceanic sink of 0.3-0.4 PgC yr⁻¹.

Category	Glyph	Scaling 1	Scaling 2
1	↕	water	difference
Direct Waterside	↕		
3	♂	complex	difference
Exchange Bubble	♂		
4	⊕	air	absolute
Shrinking Bubble	⊕		
6	♂	complex	difference
Exchange Droplet + Bypass	♂		
8	⊕	water	absolute
Shrinking Droplet + Bypass	⊕		

Figure 3. Categories of air-sea gas transfer relevant to poorly soluble gases (Woolf, 2025)

Thermal Effects

Temperature and salinity gradients in the upper ocean theoretically complicate calculations of air-sea gas flux [Woolf et al., 2016] by various mechanisms (Figure 4 below). Estimates of effects vary [Woolf et al., 2019; Watson et al., 2020; Dong et al., 2022; Dong et al., 2025] but are substantial (tenths of PgC yr⁻¹ for CO₂). A field study [Ford et al., 2024] suggests that accounting for "cool skins" and "warm layers" is effective in reducing the difference between expected and measured CO₂ fluxes, while additional observational evidence for applying the temperature corrections is reported by Dong et al. [2024].

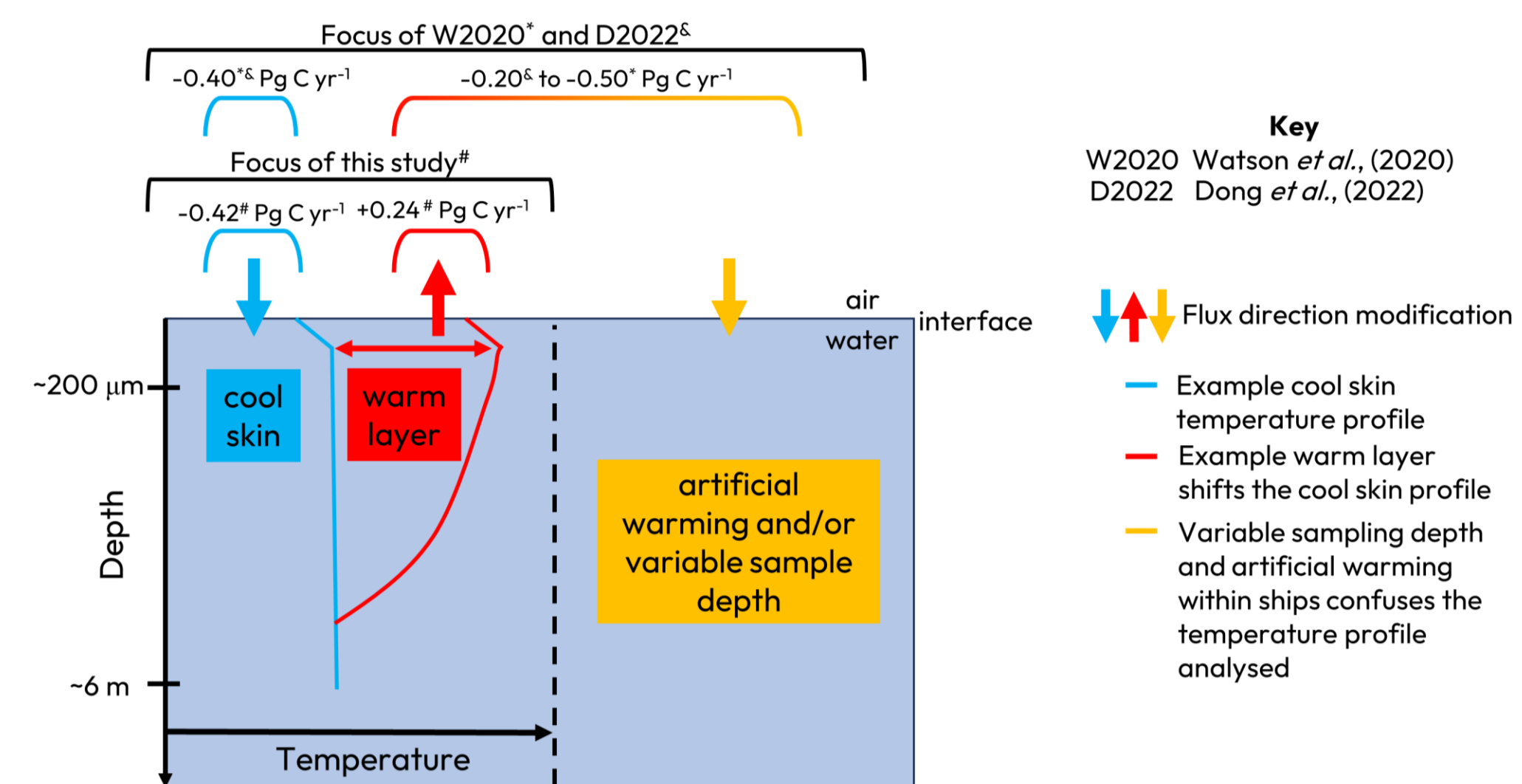


Figure 4. Schematic of thermal effects on gas fluxes (Ford et al., 2024).

Covariances

Construction of climatologies requires the adoption of discrete and practical increments of space and time. In the case of global air-sea gas climatologies, typically monthly values of key variables are used, though the non-linear dependence of transfer velocity on wind speed is accounted for. The danger in this discretisation is that the effect of covariances of key factors *within* each averaging period are omitted. A true average of the product of two factors can be expressed in terms of products of the averages and covariance, and we can define a "Z score" from the ratio of the two terms:

$$\overline{a \cdot b} = \overline{a} \overline{b} + \overline{a' b'}$$

$$Z = \frac{\overline{a' b'}}{\overline{a} \overline{b}} = CV_a \cdot CV_b \cdot r_{ab}$$

The covariance can be substantial if all three of the variance of the two factors and their correlation are high. Therefore, key covariances can be identified by exploring the Coefficient of Variation (standard deviation/mean) of factors and correlations between pairs. There are interesting correlations between wind speed and barometric pressure associated with weather systems that translate to transfer velocity and pressure (Figure 5). The correction reduces the calculated oceanic sink by ~0.1 PgC yr⁻¹.

Figure 5. (top) Coefficient of Variation (CV) for the transfer velocity. (middle top) CV of atmospheric pressure. (middle bottom) Correlation coefficient. (bottom) Z score. All for January 2015 from ERA5. No ice masks.

Summary

Progress on air-sea gas fluxes is sufficient that we should concern ourselves with a few neglected processes and subtleties of calculation. If we target an uncertainty in the oceanic CO₂ sink of O(0.1) PgC yr⁻¹, then alterations in either the downward or upward flux (each ~80 PgC yr⁻¹) of only ~0.1% are within scope. Several contributions of this type and scale have been identified and are the subject of ongoing research to reduce the total uncertainty in total fluxes.

<https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2022GB007360> [Dong et al., 2022]
<https://www.science.org/doi/full/10.1126/sciadv.adh5781> [Dong et al., 2024]
<https://www.nature.com/articles/s41467-025-66652-5> [Dong et al., 2025]
<https://www.nature.com/articles/s41561-024-01570-7> [Ford et al., 2024]
<https://www.nature.com/articles/s41598-018-25818-6> [Leighton et al., 2018]
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<https://www.mdpi.com/2673-1924/6/2/27> [Woolf, 2025]
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<https://www.frontiersin.org/journals/marine-science/articles/10.3389/fmars.2022.826421/full> [Yang et al., 2022]

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