

# Notes on Estimating Bias in Reconstructing Mean Ocean Temperature from Noble Gases

Perrin W. Davidson, Alan M. Seltzer, David P. Nicholson,  
Samar Khatiwala, and Sarah Shackleton

April 2, 2023

## Gas Exchange Parameterizations

We will consider three different parametrizations in this work. Specifically, we consider models that have fluxes that have the functional form:

$$\mathcal{F}_n = \mathcal{F}_d + \mathcal{F}_p + \mathcal{F}_c, \quad (1)$$

where we define the subscripts as follows:  $n$  as the net gas flux at the surface given initial conditions,  $d$  as the exchange due to passive diffusion,  $p$  as the partial dissolution of bubbles (i.e., bubble over a certain radius that burst at the surface), and  $c$  is complete dissolution of a bubble within the surface ocean. In our work, we additionally define a parameter  $b$  that separate the fluxes due to bubbles (i.e., subscripts  $p$  and  $d$ ) from exchange through passive diffusion. Therefore, we will be dealing with the functional form of fluxes:

$$\mathcal{F}_n = \mathcal{F}_d + b(\mathcal{F}_p + \mathcal{F}_c). \quad (2)$$

Additionally, we recognise the importance of sea ice in gas exchange. For this reason, we will use the sea ice fraction (sic or  $f_{ice}$ ) as the proportion of the open ocean grid cell through which passive diffusion can occur, leading to the updated general gas exchange functional form as:

$$\mathcal{F}_n = (1 - f_{ice}) \mathcal{F}_d + b(\mathcal{F}_p + \mathcal{F}_c). \quad (3)$$

Recent research has also considered the fraction of gas exchange that occurs between sea ice and seawater, which gives the final gas exchange functional form as:

$$\mathcal{F}_n = (1 + (k_{ice} - 1) f_{ice}) \mathcal{F}_d + b(\mathcal{F}_p + \mathcal{F}_c), \quad (4)$$

where  $k_{ice}$  is the diffusive percentage allowing gas exchange between sea ice and seawater. We contrast this to a set of models in which there is a single flux term:

$$\mathcal{F}_n = \mathcal{F}_d. \quad (5)$$

Modern gas exchange parametrizations use the magnitude of the wind speed at 10 [m] above sea level as the proxy for gas exchange. We define this wind speed as:

$$\overline{u_{10}} = \sqrt{u_{10}^2 + v_{10}^2}, \quad (6)$$

Parameterization	$\beta^{-1}$	$\gamma$	Flux Type
Wanninkhof (1992)	$3.7 \times 10^{-1}$	2	Eq. (5)
Sweeney <i>et al.</i> (2007)	$2.7 \times 10^{-1}$	2	Eq. (5)
Stanley <i>et al.</i> (2009)	$8.3 \times 10^{-7}$	2	Eq. (1)
Liang <i>et al.</i> (2013)	$\mathcal{O}(10^{-6})^1$	1	Eq. (1)

Table 1: Gas exchange coefficients for common diffusive gas exchange parametrizations considered in this work, from the function form presented in Eq. (7).

where  $(u, v)$  are the zonal and meridional winds at 10 [m], respectively. We note that (6) is simply the discrete l-2 norm. Specifically, these parametrizations for diffusion are normally of the form (modified from Eq. (1) from [1]):

$$\mathcal{F}_d = \beta^{-1} \overline{u_{10}}^\gamma Sc^{-n}, \quad (7)$$

for  $\beta^{-1}$  the coefficient modulating the magnitude of the flux,  $\gamma$  the power law relationship with wind,  $Sc$  the Schmidt number defined as the ratio between the kinematic viscosity and the gas diffusivity  $Sc = \nu/D$ , and  $n$  the power law relationship between gas exchange the Schmidt number (the molecular transport properties of the fluid). The  $n$  exponent ranges from 1/2 to 1 (from surface renewal to film models), is related to the shape of the turbulence decrease toward the interface, and is assumed to be  $n = 1/2$  [1]. A range of  $\beta^{-1}$  and  $\gamma$  are presented in Table 1 for common parametrizations of diffusive gas exchange. We note that it is common to relate diffusive fluxes of gases to  $\text{CO}_2$ , as many of the original gas exchange studies were interested in determining the role of the air-sea interface in the fluxes of  $p\text{CO}_2$ . In order to easily transform these, we note that, assuming a constant  $\beta$ ,  $\gamma$ , and  $n$  between two gases, we can relate gas  $a$  to gas  $b$  via:

$$\frac{k_a}{k_b} = \left( \frac{Sc_a}{Sc_b} \right)^{-n} \quad (8)$$

$$\Rightarrow k_a = k_b \left( \frac{Sc_a}{Sc_b} \right)^{-n}. \quad (9)$$

We discuss common parametrizations and our formulations of them below, which include the following variables:

$P_{slp}$ : pressure at the sea surface

$C_d$ : draft coefficient

$\rho_a$ : density of air

$\rho_w$ : density of seawater

660: Schmidt number of  $\text{CO}_2$

$P_w$ : water vapour pressure

$P_{wsat}$ : saturated water vapour pressure

$P_{ref}$ : standard reference atmospheric pressure (1 [atm])

### Liang 2013 (L13)

This parametrization is presented in [2]. The model equations are — for a single gas with concentration  $C$ , solubility  $S$ , Schmidt number  $Sc$ , and atmospheric mole fraction  $\chi_{atm}$  so as to make the

<sup>1</sup>We note that this is approximate as this parametrization is dependent on site-specific characteristics.

equations easier to read — as follows:

$$\mathcal{F}_d = \left( \frac{\sqrt{\rho_a C_d / \rho_w \bar{u}_{10}}}{r_{wt} + \alpha_{lc} r_a} \right) (S \chi_{atm} P_{atm}) \left( \frac{P_{slp}}{P_{atm}} - \frac{C}{S \chi_{atm} P_{atm}} \right), \quad (10)$$

$$\mathcal{F}_p = \left( 1.98 \times 10^6 \left( \sqrt{\rho_a C_d / \rho_w \bar{u}_{10}} \right)^{2.76} \left( \frac{Sc}{660} \right)^{2/3} \right) (S \chi_{atm} P_{atm}) \quad (11)$$

$$\times \left( \left( 1 + 152.44 \left( \sqrt{\rho_a C_d / \rho_w \bar{u}_{10}} \right)^{1.06} \right) \frac{P_{slp}}{P_{atm}} - \frac{C}{S \chi_{atm} P_{atm}} \right), \quad (12)$$

$$\mathcal{F}_c = \chi_{atm} 5.56 \left( \sqrt{\rho_a C_d / \rho_w \bar{u}_{10}} \right)^{3.86}. \quad (13)$$

We calculate the drag coefficient,  $C_d$ , as:

$$C_d = \begin{cases} 0.0012 & \text{if } \bar{u}_{10} \leq 11 \text{ [m s}^{-1}\text{]} \\ (0.49 + 0.0065 \bar{u}_{10}) \times 10^{-3} & \text{if } 11 < \bar{u}_{10} \leq 20 \text{ [m s}^{-1}\text{]} \\ 0.0018 & \text{if } 20 < \bar{u}_{10} \text{ [m s}^{-1}\text{]} \end{cases} \quad (14)$$

Furthermore, from [3], we define the following coefficients present in the parametrization above:

$$\text{(Water-side resistance to transfer)} \quad r_{wt} = \left( \frac{\rho_w}{\rho_a} \right)^{1/2} \left( \frac{13.3}{1.3} Sc_w^{1/2} + 0.4^{-1} \log \left[ \frac{0.5}{0.01} \right] \right), \quad (15)$$

$$\text{(Air-side resistance to transfer)} \quad r_{at} = \left( 13.3 Sc_a^{1/2} + C_d^{-1/2} - 5 \frac{\log [Sc_a]}{2 \cdot 0.4} \right), \quad (16)$$

$$\text{(Ideal gas Pressure at interface)} \quad \alpha_{lc} = S \chi_{atm} P_{atm} RT. \quad (17)$$

Here,  $Sc_a$  and  $Sc_w$  are the Schmidt numbers for air and water, respectively. We note that for  $b = 0$ , this is the COAREG3.1 [3], which has a linear relationship with  $\bar{u}_{10}$  winds.

## Stanley 2009 (S09)

This parametrization is presented in [4]. The model equations are — for a single gas with concentration  $C$ , solubility  $S$ , diffusivity  $D$ , Bunsen solubility coefficient  $\alpha$ , Schmidt number  $Sc$ , and atmospheric mole fraction  $\chi_{atm}$  so as to make the equations easier to read — as follows:

$$\mathcal{F}_d = (0.97 \pm 0.14) (8.6 \times 10^{-7}) \left( \frac{Sc}{660} \right)^{-0.5} \bar{u}_{10}^{-2} (S \chi_{atm} P_{atm} - C), \quad (18)$$

$$\mathcal{F}_p = ([2.3 \pm 1.5] \times 10^{-3}) (\bar{u}_{10} - 2.27)^3 \alpha D^{2/3} \frac{\chi_{atm} P_{atm}}{RT} \quad (19)$$

$$\times \left( 1 + \frac{\rho g (0.15 \bar{u}_{10} - 0.55)}{P_{atm}} - \frac{C}{S \chi_{atm} P_{atm}} \right), \quad (20)$$

$$\mathcal{F}_c = ([9.1 \pm 1.3] \times 10^{-11}) (\bar{u}_{10} - 2.27)^3 \frac{\chi_{atm} P_{atm}}{RT}, \quad (21)$$

where  $\pm \sigma$  is one standard deviation of the empirically determined constants. We note that for  $b = 0$ , we have a model that is similar to [5] or [6], which is a quadratic with  $\bar{u}_{10}$ .

## Nicholson 2016 (N16)

This parametrization is presented in [7]. The model equations are — for a single gas with concentration  $C$ , solubility  $S$ , diffusivity  $D$ , and atmospheric mole fraction  $\chi_{atm}$  so as to make the equations easier to read — as follows:

$$\mathcal{F}_d = k \left( S \chi_{atm} P_{atm} \left( \frac{P_{slp} - P_w}{P_{ref} - P_{wsat}} \right) - C \right), \quad (22)$$

$$\mathcal{F}_p = (\overline{u_{10}} - 2.27)^3 \chi_{atm} \frac{P_{slp}}{P_{ref}} (1.06 \times 10^{-9}), \quad (23)$$

$$\mathcal{F}_c = (\overline{u_{10}} - 2.27)^3 \chi_{atm} \frac{P_{slp}}{P_{ref}} (2.19 \times 10^{-6}) D^{1/2} S. \quad (24)$$

Here,  $k$  is defined as in [6], or of the form:

$$k = 0.27 \overline{u_{10}}^2. \quad (25)$$

## Interglacial Gas Exchange Metric

In our work, we defined two terms,  $\Delta R_{i,j}^k$  and  $\Sigma_{i,j}$ , which allowed us to explore saturation anomalies between the Last Glacial Maximum (LGM) and the Pre-Industrial Control (PIC) and were predicted on the following proposition:

**Proposition** (Pressure-Independent Interglacial Change Parameter,  $\Sigma$ ). *The interglacial change parameter:*

$$\Sigma_{i,j} = \Delta R_{i,j}^{LGM} - \Delta R_{i,j}^{PIC},$$

where:

$$\Delta R_{i,j}^k = \frac{C_i^k C_{j,eq}^k}{C_j^k C_{i,eq}^k} - 1,$$

with  $i, j$  denoting noble gases at an age  $k$ , is pressure independent.

*Proof.* We know from the Ideal Gas Law that:

$$P = N \left( \frac{RT}{V} \right) = N \cdot \text{const},$$

and thus pressure is an *extensive* property of the gases. We get from this *Dalton's Law of Partial Pressures* for gases  $i$  in a volume  $V$  with pressure total  $P$ :

$$P = \sum_i p_i.$$

Now, we note that we can apply for a single gas  $i$  Dalton's Law and the Ideal Gas Law to get:

$$\frac{p_i}{P} = \frac{n_i}{N} = \chi_i,$$

where we have noted that this ratio is simply the mole fraction of the gas  $i$  in the volume  $V$ . Thus, we get that:

$$p_i = \chi_i P.$$

Next, we recall *Henry's Law*, which states a concentration of a gas  $C_i$  at equilibrium is given by:

$$C_{i,eq} = K_H^i p_i = K_H^i \chi_i P.$$

From this, we note, for two gases  $i, j$ :

$$\frac{C_{i,eq}}{C_{j,eq}} = \frac{K_H^i \chi_i}{K_H^j \chi_j}.$$

Therefore, we can write:

$$\Delta R_{i,j}^k = \frac{C_i^k K_H^j \chi_j^k}{C_j^k K_H^i \chi_i^k} - 1,$$

which implies that both  $\Delta R_{i,j}^k$  and  $\Sigma_{i,j}$  are independent on total pressure,  $P$ . Taking the definition of these parameters as in the proposition, we can see then that we do not need to make any assumptions of atmospheric pressure changes between the LGM and the PIC as they do not come into our definitions of these parameters.  $\square$

Now, we will be using this parameter to determine the change in saturation states in the ocean between the LGM and the PIC

## References

- [1] Bernd Jähne, Gerhard Heinz, and Wolfgang Dietrich. Measurement of the diffusion coefficients of sparingly soluble gases in water. *Journal of Geophysical Research: Oceans*, 92:10767–10776, 9 1987.
- [2] Jun Hong Liang, Curtis Deutsch, James C. McWilliams, Burkard Baschek, Peter P. Sullivan, and David Chiba. Parameterizing bubble-mediated air-sea gas exchange and its effect on ocean ventilation. *Global Biogeochemical Cycles*, 27:894–905, 9 2013.
- [3] C. W. Fairall, Mingxi Yang, Ludovic Bariteau, J. B. Edson, D. Helmig, W. McGillis, S. Pezoa, J. E. Hare, B. Huebert, and B. Blomquist. Implementation of the coupled ocean-atmosphere response experiment flux algorithm with co2, dimethyl sulfide, and o3. *Journal of Geophysical Research: Oceans*, 116, 2011.
- [4] Rachel H.R. Stanley, William J. Jenkins, Dempsey E. Lott, and Scott C. Doney. Noble gas constraints on air-sea gas exchange and bubble fluxes. *Journal of Geophysical Research: Oceans*, 114:11020, 11 2009.
- [5] Rik Wanninkhof. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research*, 97, 1992.
- [6] Colm Sweeney, Emanuel Gloor, Andrew R. Jacobson, Robert M. Key, Galen McKinley, Jorge L. Sarmiento, and Rik Wanninkhof. Constraining global air-sea gas exchange for co2 with recent bomb 14c measurements. *Global Biogeochemical Cycles*, 21, 6 2007.
- [7] D. P. Nicholson, S. Khatiwala, and P. Heimbach. Noble gas tracers of ventilation during deep-water formation in the weddell sea. *IOP Conference Series: Earth and Environmental Science*, 35, 5 2016.